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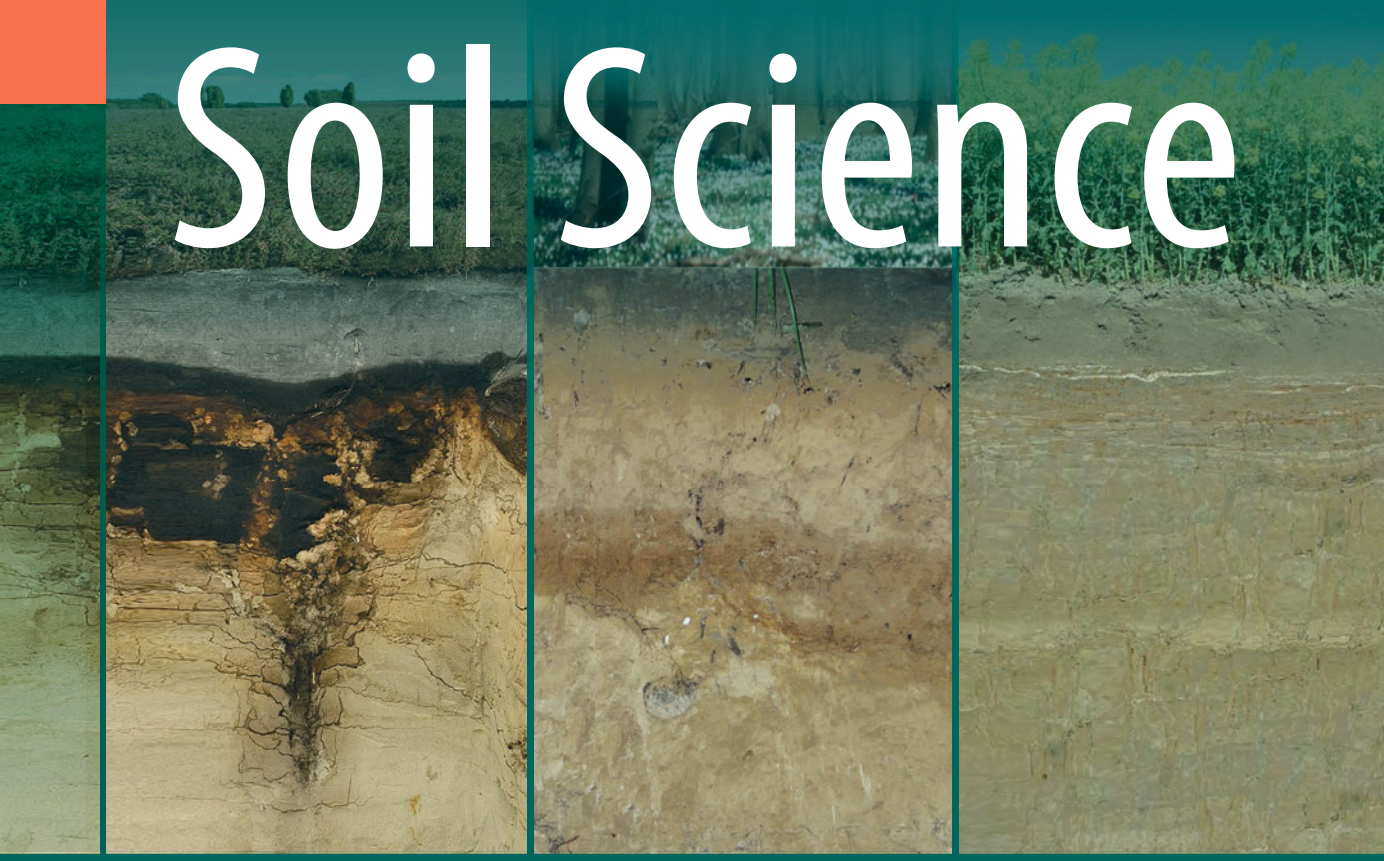
Scheffer/Schachtschabel

Soil Science



Springer

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Preface for the First English Edition

Soils provide us with food, feed, fiber, and fuel. Furthermore, they support many different forms of life on Earth. This book aims to promote the understanding of soils, their development, their functions and their distribution, and enable closer contact with this important natural resource.

For most of the chapters, the first English edition of this soil science textbook represents a translation of the German 16th edition published in 2010, originating from the first edition in German in 1937. In keeping with the organization and contents that made the German editions bestsellers, the textbook covers all major aspects of soil science. However, the chapters on soil development and classification and soil geography were completely revised and adapted to international classification systems. A number of figures have also been redrawn and revised for the first English edition. This textbook aims to provide an up-to-date account of the current state of knowledge in soil science. This textbook is designed as a basic textbook for use in soil science courses and other courses that explore current developments in this field and is an invaluable resource for students in agriculture, forestry, ecology, and environmental sciences. It will also be very useful as a basic work that provides scientists and professionals with a profound introduction to specific topics as well as the most relevant literature. It will guide students through soil physical, chemical, and biological processes and introduce them to soil geography, soil classification, and threats to soil functions. This book represents a joint effort by German authors who have diverse complementary backgrounds in soil science and who developed this book over the past decades. The group of authors has worked closely together, creating a textbook that has continuity in depth and style and that is state of the art at the time of publishing. The authors wish to thank the publisher for their excellent cooperation. We hope that the present and future generations will use the knowledge in this book for a better understanding of soils. We welcome any comments from all those who use this text.

The authors acknowledge the eminent help by Jacinda Richman, Annett Büttner, and the publisher along the way to realizing this edition.

Spring 2015 The authors

Preface and Brief Historical Outline for the 16th Edition

Scheffer/Schachtschabel is renowned as the standard textbook on soil science both for students in the fields of agriculture, forestry, and natural sciences in German-speaking countries, and for scientists and users concerned with soils.

Written by the agricultural chemist Friedrich (Wilhelm) Scheffer, the first edition was published in 1937 under the title "Agrikulturchemie, Teil A: Boden" (Agricultural Chemistry, Part A: Soil). Its 112 pages contained an evaluation of soils according to their capacity for producing plants, whereby the focus was on the properties lending fertile soils their high productivity.

This first edition therefore only dealt with a portion of what was considered "soil science" at the time, since in "Teil B: Pflanzenernährung" (Part B: Plant Nutrition), Scheffer provided a detailed explanation of the air, heat, and nutrient balance of soils as the basis for plant production. The second edition of "Teil A: Boden" (Part A: Soil) (1944) included a more detailed description of humic substances as a product of microbial transformation of organic matter, clay minerals based on X-ray diffraction, and of the soil types including their genesis.

The third edition, published in 1952 and expanded to 240 pages, was called "Lehrbuch der Agrikulturchemie und Bodenkunde, 1. Teil Bodenkunde" (Agricultural Chemistry and Soil Science, Part 1 Soil Science). From now on, it was written by Fritz Scheffer in collaboration with Paul Schachtschabel (Fig. 1) and was revised at regular intervals of 4–6 years.

With the ninth edition (1976), the textbook was finally given its present name "Scheffer/Schachtschabel: Lehrbuch der Bodenkunde" (Scheffer/Schachtschabel: Textbook of Soil Science), which remained as a "trademark" for all later editions. From this time on, new information was compiled by a team of authors, which was expanded or developed according to the specialized requirements. In the last three decades, this was mainly ensured by the authors Blume, Brümmer, Hartge, Schachtschabel, and Schwertmann. A more extensive description of the evolution of "Scheffer/Schachtschabel" can be found in Blume et al. (2007).

With the continuously increasing number of pages in the last editions (the 15th edition comprised 593 pages), the contents of "Scheffer/

Fig. 1 Prof. Dr. Dr. h.c. F. Scheffer (left) and Prof. Dr. Dr. h.c. P. Schachtschabel (right) at the International Soil Science Conference in 1960 in Madison, USA

Schachtschabel" had also become differentiated to such an extent that a new concept became necessary for the 16th edition. This involved focusing on the condensation of the knowledge to the essentials, to do better justice to the textbook character, and still maintain the integrity of the respective subject matter. The contents of the 16th edition represent the basis for this English translation.

In the 16th edition, Chap. 4 "Soil Organisms and Their Habitat" was completely revised by Prof. Dr. E. Kandeler, and Chap. 5 "Chemical Properties and Processes" by Prof. Dr. R. Kretzschmar, while all of the other chapters were updated by including the current state of research. Chapter 6 presents more recent insights into soil structural development, soil mechanics, and the water balance, and the section on soil color was also revised. Parts of Chap. 7 were rewritten for the English edition. The names for the soil horizons (Sect. 7.3) and the soil classifications (Sect. 7.4) were mainly presented according to the World Reference Base for Soil Resources (WRB) and the US Soil Taxonomy, and the chapter on German classification was reduced. Section 7.5 now discusses the properties, genesis, ecology, and use of all significant soils on Earth, primarily according to the WRB. Similar to the WRB and the US Soil Taxonomy, the Reductosols were also treated as oxygen-poor soils without water surplus and were supplemented with the

Asphaltic Reductosols. New additions included soils characterized by a yermic horizon in continental hot and cold deserts. The same applies for Zoosols, i.e., soils with profound conditioning by animals (in addition to earthworms and steppe mammals in Chernozems, also termites in subtropical regions and penguins in Antarctica). Section 7.6 is now dedicated to Paleosols on Earth, Mars, and Titan. More than thirty representative soil profiles are shown on three color pages, as well as a deep colored soil section on the planet Mars compared to a soil from India.

Chapter 8 Soil Geography was restructured accordingly, while Chap. 9 Soils–Plant Relations was completely restructured and expanded with the physical properties of soils (Sects. 9.1–9.4). The sections on nutrient supply (9.5) and on plant macronutrients (9.6) were also largely rewritten; Sects. 9.7 (micronutrients) and 9.8 (beneficial elements) were revised. Chapter 10 deals with the threat to soil functions by chemical and nonchemical degradation, possible remediation measures, and methods for the assessment of chemical soil contaminations. The significance of soil protection is discussed in detail in Chap. 11, including the fundamental laws and chemical issues involved in soil protection.

Methodical details are not discussed in any of the chapters, since there are enough other textbooks and practical manuals for this purpose; furthermore, the literature was reduced, since modern specialized literature today is easily accessible to those interested in soil science.

The chapters were divided among the authors as follows:

1. Brümmer † (Blume, Stahr)
2. Stahr
3. Kögel-Knabner
4. Kandeler
5. Kretzschmar
6. Horn
7. Blume, Fleige
8. Stahr
9. Brümmer † (Amelung, Horn)
10. Wilke (Horn, Thiele-Bruhn, Welp)
11. Stahr

Numerous staff members and colleagues have contributed in many ways to the production of the 16th German edition; without their collaboration, the completion of the German textbook as a basis for the English translation in the present form would not have been possible. We would like to thank you all sincerely. In particular, we would like to mention Prof. Dr. J. Bachmann, Dr. R. Baritz, Dr. Iso Christl, Prof. Dr. W. Foissner, Prof. T. Friedel, Dr. T. Gaiser, Dr. J. Gauer, Dr. S. Haase, B. Heilbronner, Dr. A Kölbl, Prof. Dr. B. Ludwig, Dr. M. von Lützow, Dr. S. Marhan, Dr. W. Markgraf, Dr. S. Peth, Dr. L. Philippot, Dr. C. Poll, Prof. Dr. L. Ruess, Dr. D. Stasch, Prof. Dr. R. Tippkötter, Dr. A. Voegelin, Dr. J. Wiederhold, and Dr. M. Zarei.

We thank the lector Dr. J. Lorenzen-Peth for didactical correction and critical review, and the publisher, particularly Dr. C. Iven, for his trustworthy and patient collaboration.

Not only are soil scientists interested in soils, but also farmers, foresters, gardeners, landscapers and landscape planners, ecologists, crop technicians, hydrologists, geographers, geologists, mineralogists, chemists, biologists, and archeologists. This is equally true for all those who deal with problems associated with nature conservation, environmental protection, and legislation, as well as with soil remediation in the political, administrative, standardization, and business sectors. In all of these sectors, Scheffer/Schachtschabel has become an indispensable source of information on soils. This is particularly true for students and for the next generation of scientists. May the new edition find like-minded readers and serve them as a useful companion. We also hope that the translation of the German version will spread the knowledge contained in Scheffer/Schachtschabel around the world, and contribute to a better and more comprehensive understanding of the processes taking place in soils as a vulnerable and especially nonrenewable resource.

The book cover shows a Podzol, an Albeluvisol/Retisol, and a Fluvic Gleysol.

Spring 2015 The authors

Reference

Blume H-P, Hartge KH, Schwertmann U (2007) Die Bedeutung des Ferdinand Enke Verlages für die Verbreitung bodenkundlichen Wissens. In: Blume H-P, Stahr K (Hg) Zur Geschichte der Bodenkunde (Chapter 4). Hohenheimer Bodenkundliche Berichte Nr. 83

Contents

1 Introduction: Soils—The Earth's Skin

Soils are the biologically active part of the outermost layer of the Earth's crust, ranging in thickness from a few centimeters to several decameters. The Earth's crust, in turn, generally has a thickness of 5–40 km and is part of the lithosphere, which has an average thickness of approx. 100 km and consists of the tectonic plates with the continents. The total distance between the ground surface to the Earth's center is of 6370 km. These orders of magnitude illustrate how soils form a thin and fragile skin on the Earth's surface, requiring special care.

Soil science is the science of the properties and functions, as well as the development and distribution of soils. It deals with the possibilities for soil use and the risks associated with misuse by humans, as well as the prevention and remediation of soil contamination and damage.

1.1 Soils as Natural Bodies in Ecosystems

Soils evolve on land (terrestrial soils), in transition zones between water and land (semiterrestrial soils), and under water (subhydric soils). Terrestrial and semi-terrestrial soils are delimited at the bottom by solid or unconsolidated rocks, and at the top by vegetation cover and the interface with the atmosphere, with gradual transitions to neighboring soils. They consist of **minerals** of various types and sizes (Chap. 2), and of **organic substances**, the humus (Chap. 3). Minerals and humus are spatially arranged in a specific way, forming together the **soil structure** with a characteristic void system. The void system consists of pores of various shapes and sizes, which are filled with **soil solution**, i.e. with water and dissolved substances, and **soil air**. Here, numerous chemical and physical interactions take place between the solid, liquid and gaseous phases (Chaps. 5 and 6).

Soils are always biologically active. Their voids contain a multitude of **soil organisms** that may include more than 10 million microorganisms per gram of fertile soil, some of which have yet to be discovered, and together with other organisms, transform the soil into a highly active biogeochemical reactor. Parallel to this, the larger soil fauna loosens, mixes and aggregates the soil and thereby shapes its habitat (Chap. 4).

Soils are natural bodies of various ages that evolve through soil-forming processes, depending on the type of parent rock and relief under a specific climate, and thus specific vegetation and litter with characteristic biotic communities (biocoenoses). Therefore, the evolution of soils is connected with the development of life on Earth. This was already stated by the soil scientist W.L. Kubiena in 1948. In the Precambrian, as the first bacteria and algae developed in the ocean, there were only subhydric soils. With the development of the first terrestrial plants 430 million years ago in the Silurian, semiterrestrial and finally also terrestrial soils were formed. At the end of the 19th century, the Russian soil scientist W.W. Dokučaev recognized soils as independent

H.-P. Blume et al., *Scheffer/Schachtschabel Soil Science*, DOI 10.1007/978-3-642-30942-7_1

natural bodies. Following Dokučaev, the Swiss soil scientist Jenny (1941) then defined soils (S) as a function of their **genetic factors**: parent material (P), climate (C), organisms (O), relief (R) and age (T). Furthermore, in the last 5000 years of the Earth's history, soils have increasingly been affected until today by humans (H) through various forms of land use (Chap. 7):

$$S = f\ (P, C, O, R, H) \cdot T$$

With their complex interactions, the genetic factors trigger soil-forming processes, which are divided into transformation and translocation processes. The former include mainly rock weathering and mineral transformation, loamification and brunification, as well as the decomposition of organic matter and humification. Translocation processes are triggered by percolating and ascending soil water, e.g. leaching and salinization, decalcification and carbonatization, clay migration (lessivage) or podzolization. Depending on their intensity and duration, transformation and translocation processes lead to characteristic soil properties, e.g. the soil horizons typical for the various soils, which are litter-like at the top and become more rock-like with depth. Altogether, this results in the following causal chain of pedogenesis:

Genetic factors → soil-forming processes
→ soil characteristics

Read in the inverse sequence, the characteristics of soils today allow conclusions to be drawn on processes that took place in the past, as well as the genetic factors they depended on, and thus contribute to a reconstruction of the landscape history (Chap. 7). Using the causal chain of pedogenesis, predictions can also be made on future soil and landscape development. Thus, when one of the genetic factors changes, e.g. the climate as a result of global warming, predictions can be made on the changing pedogenic processes in various regions of the Earth, and therefore also on the future soil properties and their changing options for land use.

Figure 1.1 Shows a typical soil as a **natural body**. This loose soil (a Cambisol) developed from solid rock (granite), called R horizon. Weathering caused the hard rock to break down into fragments (stones) and its minerals (quartz, feldspars, micas), which together with newly formed minerals (clay minerals, iron oxides etc.) as particles of different sizes (stones, sand, silt, clay), form the inorganic solid matter. Voids are created when the rock breaks down: The coarser pores are mostly filled with air, the finer ones with water. The formation of clay minerals caused the A and B horizons to become loamy and colored brown from iron oxide. A small portion of the dead plant residues was transformed by the soil fauna and flora into brown to black humic substances, and mixed together with minerals to ultimately form the brownish-black colored A horizon, above which an organic layer (O horizon) is found.

All soils collectively form the **soil cover** or **pedosphere** (pedon, Greek: soil), which evolved together with the biosphere in the overlapping zone of the atmosphere, lithosphere and hydrosphere (Chap. 8). The **ecosphere** (Fig. 1.2) comprises the entirety of all ecosystems, and thus

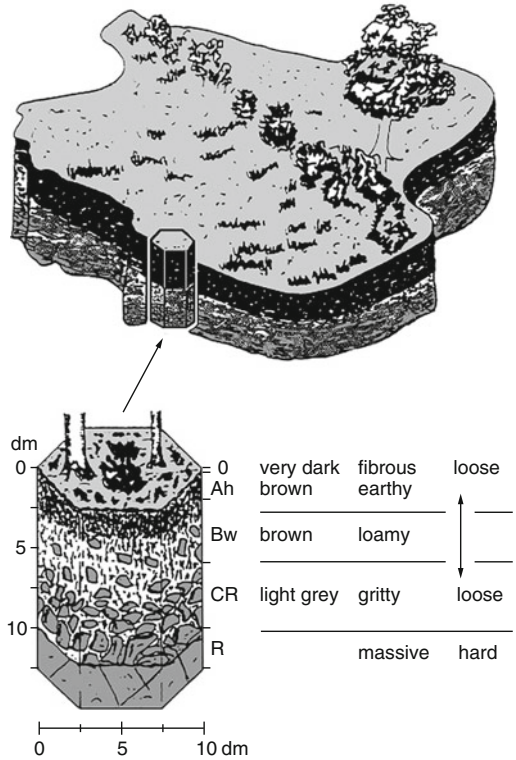

Fig. 1.1 Typical soil as a natural body

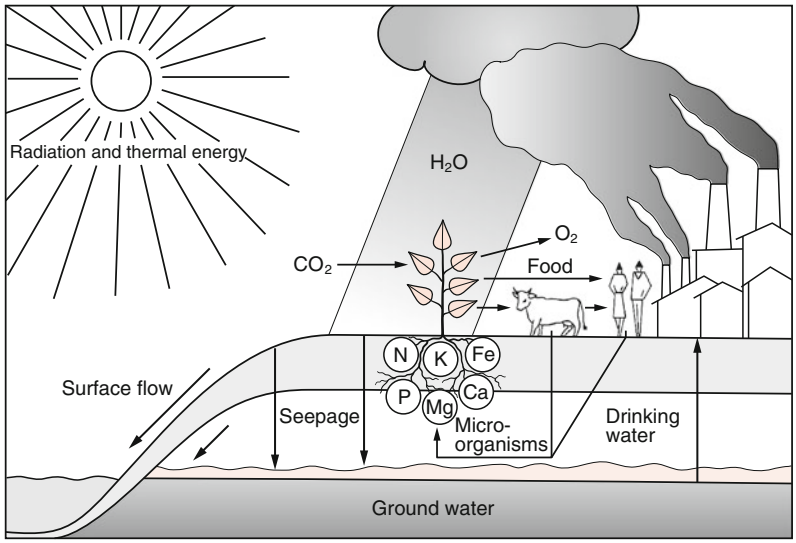

Fig. 1.2 Position and functions of soils in the ecosphere (explanations in the text) (Brümmer 1978, 1984, 1992)

also includes the pedosphere. Similar and different soils are closely associated (Fig. 1.1 top) in **landscapes**, which are characteristic sections of the ecosphere. The soils of a landscape are connected with each other through flows of energy, water and material (Fig. 1.2). Thus, soils in depressions are enriched with weathering products dissolved by surface flow and seepage water from soils on the neighboring hills. Soils on slopes are often eroded by surface flow, and the neighboring soils in depressions are covered by their erosion material. Substances that are dissolved in the seepage water and translocated to greater depths reach the groundwater, and are transported with the base flow into the depressions. Through surface flow, interflow and base flow, substances are transported from the hills to the depressions, and finally to the surface waters (streams, lakes and rivers) draining the landscape. Thus, depending on the constituent substances and including anthropogenic or natural contaminations, soils influence the composition and quality of the groundwater and runoff water. The latter, in turn, influences the **biocenosis** in the surface waters of the various landscapes. Therefore, there is a close substance connection both between the soils of a **catena** (lat. chain) from the summit to the depression, and also between the soils of a landscape and their groundwater and surface waters.

Soils are (usually) covered with vegetation and penetrated by roots (Fig. 1.1), and are populated with animals and microorganisms; they are always part of an **ecosystem**. Together with the surface-near layer of air, they form the habitat (=biotope) of a community consisting of plants, animals and microorganisms (=**biocenosis**). Accordingly, there are close interactions between the biotope and the biocenosis, and also between the surface and subsurface life communities.

The soil's **root zone** offers the plants anchoring and provides **water**, **oxygen** and **nutrients** (Chap. 9). The latter also applies to soil animals and microorganisms. The supply is mainly determined by the respective reserves and the availability of water, oxygen and nutrients in the root zone.

1.2 Functions of the Soils in the Ecosphere

The concept and definition of the functions of soils in the ecosphere (Fig. 1.2) were introduced by G.W. Brümmer in the period from 1976–1993, and further developed by the scientific

advisory board of the Federal Government of Germany in 1994. The ecosphere includes the area at the ground surface, which is populated by living organisms and characterized by various interacting cycles of energy, air and water, as well as inorganic and organic substances. It is also called the Earth's Critical Zone. Within the ecosphere, soils represent the basis on which human and animal life can exist. They form the sites where higher plants take root, making use of solar energy from the carbon dioxide in the atmosphere, from the water entering the soil through precipitation, and from the soil's nutrients, to build biomass and are producing oxygen. This is then available to humans and animals as food. At the same time, plants primarily provide organic wastes and thus litter to the soil. The litter serves as a food source for soil animals and microorganisms. They consume the greater portion of the incoming organic matter and transform it back to CO_2. The organic substances in the bodies of all dead organisms are subject to decomposition and transformation processes in the soil, mineralizing the bound nutrients and returning them to the cycles of elements in the biosphere. In the German Soil Protection Act from 1998, these **natural soil functions** are defined as **habitat functions** (Chaps. 10 and 11).

Furthermore, natural soil functions include the **regulating functions** of soils, which also play a decisive role for life on Earth. Soils are effective **storage, filtering, buffering and transformation** systems, which can hold and transform water, dissolved and suspended nutrients, as well as contaminants from natural sources and from anthropogenic emissions. For this reason, after passing through intact soils, rainwater is generally available as filtered clean groundwater for drinking, irrigation and industrial water supplies. Soils and sediments also have a strong influence on the water balance of a landscape. In doing so, their water storage capacity acts as a regulator in the landscape's water balance (Fig. 1.2). Another important function of soils is the storage of carbon, which is a climate-relevant element in the form of its gases CO_2 and CH_4. Carbon is stored as humus in mineral soils and especially in bogs and fens, or in the form of dissolved carbonic acid anions, which can cause calcium ions, liberated by weathering and other pedogenic processes, to precipitate as carbonate. The German Soil Protection Act from 1998 defines the regulating and habitat functions as natural soil functions (Chaps. 10 and 11).

The **utilization functions** of soils define functions useful to man, such as their suitability for agricultural and forestry use. Soils are also used for waste deposits or as building ground, and they supply raw materials such as clay, sand, gravel, limestone, brick clay, etc. Furthermore, soils provide the surfaces for residential, commercial and traffic areas, but also for green areas that provide residents with space for recreation and relaxation, thus promoting their health.

As the foundation and as part of ecosystems, soils shape the character of a landscape together with the relief, rocks and climate, as well as the biocenosis that developed based on these primary factors and the respective anthropogenic effects. Thus, soils represent **records of landscape history**, and their respective soil characteristics are a reflection and **archive of the natural and cultural history** of a landscape.

Soil functions vary both qualitatively and quantitatively in different soils, and determine the soils' properties and thus their **potential use**. Life on Earth depends on the soils' various functions, as well as their sustainable use and conservation (Chaps. 10 and 11).

In addition to **natural soils**, there are also **cultivated soils** that are influenced by humans. The capacity of natural and cultivated soils to serve as a site for plant growth is called **soil fertility**. Soils can be evaluated according to this capacity (Chap. 11). Cultivated soils mainly serve for food production, but also for the production of feed, organic raw materials, and renewable fuels. In addition to its fertility, the actual **yield performance** of a soil as a site for crop production is also influenced by numerous non-soil factors, such as climate, plant species, soil tillage, fertilization, pest infestation etc. Using soil information systems that were developed for many countries worldwide, detailed information can be obtained on the properties and state of the soils, as well as their potential for use and their yield performance.

1.3 Soils as an Open System Worth Protecting

Energy and substances pass through cycles in ecosystems, which are often not completely closed since ecosystems and soils represent open systems. Thus, soils are subject to the input and removal of substances from both natural and anthropogenic origins, and therefore have close chemical and matter relationships with other compartments of the ecosystem. Depending on the properties of the soil and substances, a transfer of substances can take place from the soil into the food chain, groundwater, surface waters, and the atmosphere (e.g. of CO_2 and CH_4). The percolation of seepage water in soils under humid climate conditions causes the dislocation and leaching of soil substances. Over the course of hundreds to millions of years, this leads to a natural acidification, nutrient depletion and degradation of the soil. Under arid conditions, in contrast, ascending groundwater (and also dust deposition and rainfall) can lead to salt and carbonate accumulation in the soil.

In addition to the removal of natural substances under humid conditions, the leaching of substances of human origin also plays an important role. As a general rule, most substances produced and processed by man eventually reach the soils or waters through various transport and dispersion processes. As a result of the soil's filtering, buffering and storage functions, this often leads to an **accumulation of potentially toxic substances** such as heavy metals and persistent organic contaminants in terrestrial, semiterrestrial and subhydric soils. Contrary to air and water, contaminated soils can often not be remediated, or only at high costs.

The agricultural use of soils can also lead to soil contamination and degradation. Thus, particularly the agricultural use of land promotes **erosion** by water or wind, and traffic with heavy machinery promotes **compaction**. Especially in arid regions, irrigation can lead to soil **salinization**, and overgrazing in areas bordering on deserts can lead to **desertification**. Because the removal of primary and secondary harvest products (e.g. cereals, vegetables, milk, meat, wood, fuel) removes nutrient elements from soils used for the production of biomass, the soil must be fertilized to avoid **degradation**. Soil degradation generally leads to a reduction in **soil biodiversity**. Severe nutrient depletion of soils (as is the case today in many developing countries) decreases soil fertility and increases destruction of the soil structure and erosion, jeopardizing agricultural production and food security. However, the application of excess fertilizer can result in contamination of the groundwater and surface waters, and also of the atmosphere if the soil's buffering capacity is exceeded.

Because of the soil's natural (habitat, regulating), utilization and archiving functions mentioned here, soils—together with water and air—belong to humanity's most precious resources, to be protected at all costs. This has already been expressly stated in the ***Soil Charter*** of the European Council in 1972. In addition, soils are a **non-renewable resource**. An estimated area of 0.22 ha of agricultural land is available per person to supply food for the current world population of about 7 billion people. With population growth until 2050 reaching more than 9.6 billion people, the harvested yields must be increased by about 40 % under the optimistic assumption of a constant soil area, in order to maintain a food supply comparable to today's situation. This is a problem that has yet to be solved. For this reason, the ***UN Convention to Combat Desertification*** (***CCD***) was approved in 1996 to protect soils. The functions of soils are protected in Germany since 1998. The ***Act on Protection against Harmful Changes to Soil and on the Rehabilitation of Contaminated Sites*** (***Soil Protection Act***) is based both on the natural and the utilization and the archiving functions of our soils (Chap. 11). Harmful soil changes are to be avoided according to the law, and if harm has already been done, it is to be rehabilitated in order to maintain an intact basis for our habitat and to enable sustainable land use. Most investigation methods required for this purpose are internationally standardized. Founded in 2000,

the ***European Land and Soil Alliance*** (***ELSA***) is, among other things, committed to active soil protection in cities and municipalities. The EU Commission published an overview of the soils of Europe and their endangerment, and since 2006, develops a ***Soil Protection Strategy*** with a ***Soil Framework Directive*** for Europe.

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2 Inorganic Soil Components—Minerals and Rocks

2.1 The Rock Cycle

The soil's position in the material cycle of the lithosphere (Fig. 2.1) shows that a large number of processes are involved in the formation of rocks, lithogenesis, in the form of a cycle. At the beginning of lithogenesis, rocks are formed through crystallization when the molten magma cools down. They are subject to further diverse changes through the processes of weathering, erosion, transport, deposition, diagenesis, metamorphism and anatexis, which are connected to one another in a cycle. Soils are a significant station in this cycle. On the one hand, they are the result of the transformation of rock in contact with the atmosphere, hydrosphere and biosphere (pedogenesis), and on the other, they deliver material for the formation of new rocks. For this reason, soils cannot be understood and classified without knowledge of the rocks; however, the same is true for many rocks without knowledge of the soils (Kittrick 1985).

2.2 Minerals

2.2.1 General

Minerals are homogeneous components of rocks. They are natural, predominantly inorganic and chemically uniform compounds, whose elemental components are arranged in a defined, regular-periodical manner; they are crystalline. The smallest geometrical unit of these crystals, which have exactly the same chemism and symmetry properties as the mineral, is called **elementary cell** (Ramdohr and Strunz 1978).

The occurrence of the elements can be derived from the average chemism of the Earth's crust (Table 2.1): Half of the mass can be attributed to oxygen, one quarter to silicium, and the rest consists almost entirely of Al, Fe, Mg, Ca, Na and K cations.

The dominance of the O ion and its large diameter (Table 2.2) indicate that most minerals consist of more or less densely packed O^{2-} ions, whose negative charges are neutralized by the often much smaller cations in the gaps of the O-packing. In doing so, the smaller cations such as Si^{4+} have four O^{2-} ions (ligands) as their next neighbours (coordination no. = 4), the somewhat larger cations such as Al^{3+} have six (coordination no. = 6), and particularly large ones like K^{+} can also have eight or twelve O^{2-} ions. In addition to O^{2-}, the equally large hydroxyl anion OH^{-} and S^{2-} anions also act as ligands. Due to the various sizes of the ions, their volume fractions in the lithosphere may deviate considerably from their mass fractions: Table 2.1 shows that oxygen takes up 88 % of the volume, while important cations like the comparatively large K^{+}, Ca^{2+} and Na^{+} ions only account for 1–3 % by volume.

The average chemical composition of the lithosphere also shows that compounds consisting of O and Si, i.e. salts of silicic acid and the pure oxide SiO_2 predominate. Corresponding to the cation occurrence, the first eight minerals are

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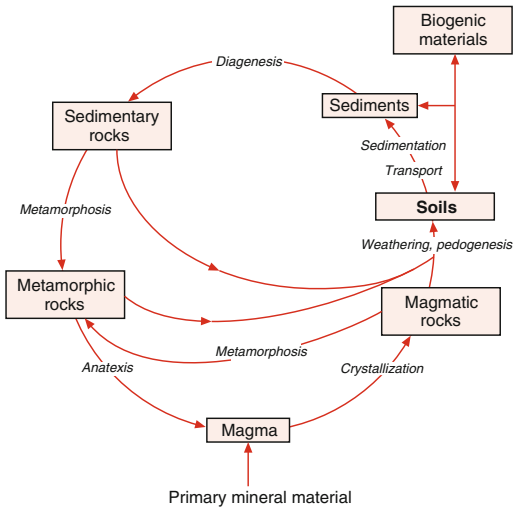

Fig. 2.1 The position of soils in the cycle of the lithosphere

Al, Fe, Mg, Ca, Na, and K silicates (Table 2.1). This is also true for most soils, which inherit the silicates not only from the parent material, but also form their own (pedogenic) silicates.

The conditions under which **primary** silicates crystallize out of the magma differ fundamentally in terms of temperature, pressure, oxygen and water content from the environmental conditions in the soil, where the crystal growth of the **secondary** minerals is usually strongly inhibited. **Lithogenic** minerals, originating from rocks, differ from **pedogenic** minerals, formed in the soil, not only in their grain size, but also in other properties, e.g. the sorption capacity. For this reason, the two groups will be discussed separately (Dixon and Weed 1989).

Table 2.1 Average chemism, mineral and rock constituents of the lithosphere (mass 2.85×10^{19} t)

Oxides	Mass (%)[a]		Elements	Mass (%)	Vol. (%)	Mineral constituents	Vol. (%)	Rock constituents[b]	Vol. (%)
SiO_2	57.6	52.5	O	47.0	88.2	Plagioclases	39	Basalts, gabbros basic igneous rocks etc	42.6
Al_2O_3	15.3	10.5	Si	26.9	0.32	Quartz	12	Gneisses	21.4
Fe_2O_3	2.5	4.0	Al	8.1	0.55	K feldspars	12	Granodiorite, diorite and syenite	11.6
FeO	4.3		Fe^{3+}	1.8	0.32	Pyroxenes	11	Granites	10.4
MgO	3.9	3.3	Fe^{2+}	3.3	1.08	Micas	5	Crystalline schists	5.1
CaO	7.0	11.1	Ca	5.0	3.42	Amphiboles	5	Clays, clay schist	4.2
Na_2O	2.9	2.8	Mg	2.3	0.60	Clay minerals	4.6	Carbonate rocks	2.0
K_2O	2.3	4.6	Na	2.1	1.55	Olivines	3	Sands, sandstones	1.7
TiO_2	0.8	–	K	1.9	3.49	Calcite, dolomite	2.0	Marble	0.9
CO_2	1.4	–				Magnetite	1.5		
H_2O	1.4	–				Other minerals	4.9		
MnO	0.16	–							
P_2O_5	0.22	–							

[a]The 2nd column shows the average composition of superficial rocks (Hudson 1995)
[b]The predominance of basic rocks is due to the surface area dominance of the oceanic crust

Table 2.2 Effective radii of various ions (pm) in crystals related to the coordination number IV or VI

$^{VI}Na^{+}$	102	$^{IV}Al^{3+}$	39	^{IV}C	15	P^{5+}	38
$^{VI}K^{+}$	138	$^{VI}Al^{3+}$	53.5	^{IV}Si	26	O^{2-}	140
$^{VI}NH^{4+}$	147	$^{VI}Fe^{2+}$	78.0	$^{IV}Ti^{4+}$	42	OH^{-}	137
$^{VI}Mg^{2+}$	72	$^{VI}Fe^{3+}$	64.5			S^{6+}	30
$^{VI}Ca^{2+}$	100	$^{VI}Mn^{2+}$	83			S^{2-}	182
		$^{VI}Mn^{4+}$	53			Cl^{-}	153

2.2.2 Silicate Structure

The structure of silicates helps to explain their diversity and properties, e.g. their weatherability. The basic building block of SiO_2 and silicates is a tetrahedron, in which the small tetravalent Si atom is surrounded by four large oxygen ions (Fig. 2.2 top). This creates a dense oxygen packing that fills the space and only allows cations to fill the gaps. If the centers of the O^{2-} ions are connected with each other, it creates a tetrahedron consisting of four triangles of the same size (Fig. 2.2). Every SiO_4 tetrahedron has four negative charges and is linked with other SiO_4 tetrahedra via oxygen bridges. The types and extents of the various cross-linking result in different silicate structures: The tetrahedra in **tectosilicates** are completely cross-linked in all three spatial directions. Types of incomplete tetrahedron cross-linking include, **layered** or **phyllosilicates** with extensive 2-dimensional cross linking, as well as **band** and **chain silicates** with one-dimensional cross linking. If there is no cross-linking at all, they are called **nesosilicates** or **orthosilicates**. The tetrahedron basic units of this structure types are the tectosilicate-SiO_2^0, phyllosilicate-$Si_2O_5^{2-}$, band-$Si_4O_{11}^{6-}$, chain-SiO_3^{2-} and the insular or nesosilicate SiO_4^{4-}, characterized by an ascending O/Si ratio of 2.0, 2.5, 2.75, 3.0 and 4.0, and increasing demand for cations for the spatial connection of the tetrahedron units (Fig. 2.3).

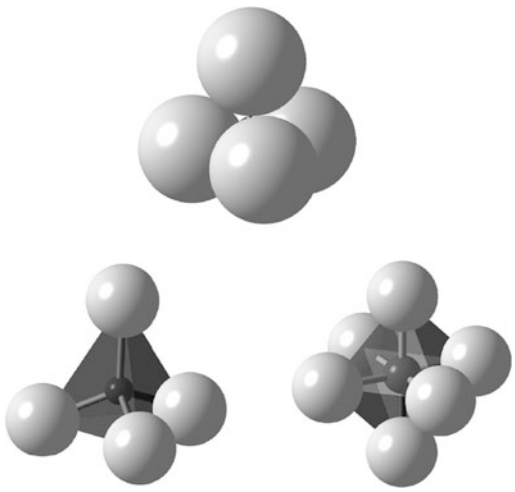

Fig. 2.2 Spherical model of a tetrahedron (*top*) and an octahedron (*right*) in combination with a polyhedral representation (*left*) to emphasize the coordination around the *central* ion (coordination polyhedron). Only the *upper* representation is to scale, the ions were drawn smaller in the other two representations to improve clarity

Mainly K^+, Na^+, Al^{3+}, Fe^{2+}, Fe^{3+}, Mg^{2+} and Ca^{2+} are involved, and together with the linking variations, they give rise to the chemical diversity of the silicates. Both the structure and the chemism have a significant effect on the weatherability of the various silicates (see Sect. 2.4).

Another variation of the silicates arises when, instead of the Si^{4+}, the approx. 50 % larger Al^{3+} (Table 2.2) occupies the centre of the tetrahedron, without changing the 'morph' of the structure (therefore **isomorphic substitution**). However, it does change the charge conditions: The charge of Al^{3+} that is missing relative to Si^{4+} is compensated by the uptake of additional cations, e.g. K^+, Na^+ or Ca^{2+} into the structure.

With 80 % per volume (including quartz >90 %), silicates are the most frequently occurring minerals in igneous rocks. They are also the most important primary products for those minerals that are newly created by weathering and thus by pedogenesis. The ranges of variation in the chemical composition of the predominant igneous silicates fluctuate strongly (Table 2.3). The ranges show that silicates often do not

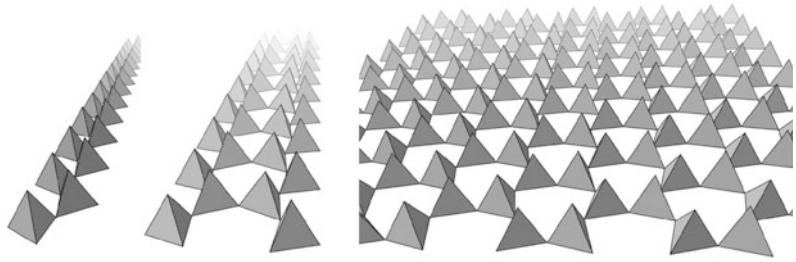

Fig. 2.3 Types of bonding in silicates: chain (*left*), band (*centre*) and layered structure (*right*)

Table 2.3 Chemism (mass %) of important minerals of igneous and metamorphic origins

	Olivines	Pyroxenes[a]	Amphiboles[b]	Muscovites	Biotites	K-feldspars	Plagioclases
SiO_2	38–47	47–53	39–54	39–53	33–45	63–66	43.5–69
TiO_2	–	<4.4	–	<3.9	<10	–	–
Al_2O_3	–	1–7	–	20–46	9–32	19–21	19–36
Fe_2O_3	–	0.4–7.6	0.2–23	<8.3	0.1–21	<0.5	–
FeO	8–12	4–21	<9	–	3–28	–	–
MnO	–	–	–	<2.3	–	–	–
MgO	38–47	10–18	3–25	<2.4	0.3–28	–	–
CaO	–	13–22	10–14	<4.5	–	–	<19.5
Na_2O	–	–	0.5–2.3	<5.2	–	0.8–8.4	<12
K_2O	–	–	<1.7	7.3–13.9	6–11	3–16	–
H_2O	–	–	0.2–2.7	2–7	0.9–5	–	–

[a]Augite
[b]Common hornblendes

correspond to the ideal formula. This is mainly due to isomorphic substitution.

2.2.3 Primary (Lithogenic, Pyrogenic) Silicates

2.2.3.1 Feldspars

Feldspars are pale or weakly colored Na–K–Ca–Al silicates with good cleavage and a hardness of 6. They belong to the tectosilicates, i.e., they consist of a three-dimensional tetrahedral framework. In the tetrahedra, $^1/_4$ (alkali feldspars) or $^1/_2$ (anorthite) of the tetrahedron centers are substituted by Al^{3+}. To balance the charge, the relatively large K^+, Na^+ or Ca^{2+} ions are incorporated into the gaps in the silicate structure (Fig. 2.4).

The most important types of feldspar are the **orthoclase** (potassium feldspar, $KAlSi_3O_8$), **albite** (sodium feldspar, $NaAlSi_3O_8$) and **anorthite** (calcium feldspar, $CaAl_2Si_2O_8$). These pure types are rarely found in rocks. Thus, potash feldspars usually contain Na (e.g. sanidine, anorthoclase, microcline); in which case, together with albite, they are called alkali feldspars, whose K_2O content lie between 2.5 and 14.7 %. Between albite and anorthite, there is a continuous series of intermediates called **plagioclases** (Ca–Na feldspars), where Na and Ca are completely interchangeable due to their similar ionic radius (Na 102 pm; Ca 100 pm), contrary to Na and K (138 pm). For this reason, with decreasing albite and increasing anorthite fractions, Ca and Al contents increase, while the Na and Si content decreases. This also explains the variation in the chemical composition of plagioclases (Table 2.3). In basic igneous rocks, in addition to Ca-rich plagioclases, Si-poorer **feldspar representatives** (foids), nepheline ($NaAlSiO_4$) and

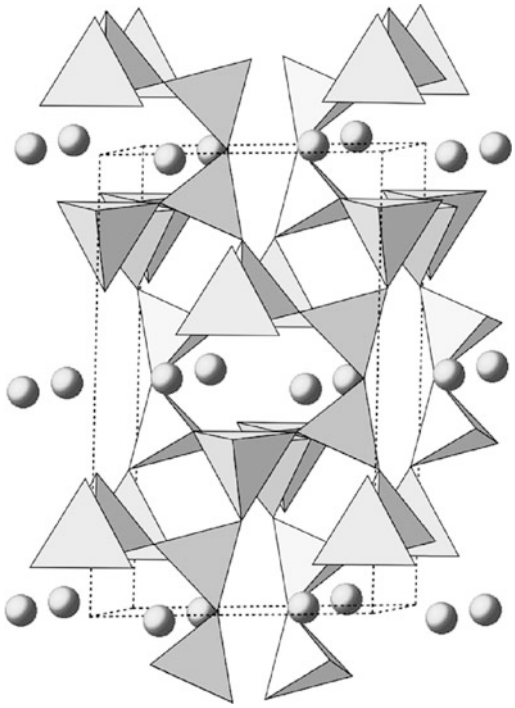

Fig. 2.4 Tetrahedral model of an albite. The *spheres* are the Na ions, the tetrahedra contain Si^{4+} and Al^{3+} at a ratio of 3:1. The *dotted lines* surround the elementary cell

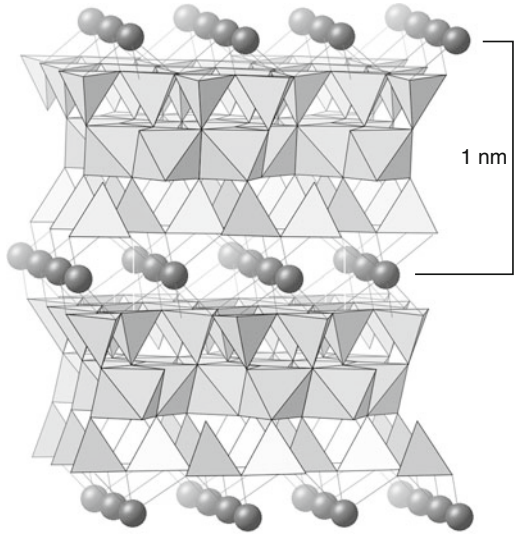

Fig. 2.5 Model of a mica structure. The *spheres* are K^+ ions. The *thickness* of one elementary layer is labeled

leucite ($KAlSi_2O_6$) can occur, which are also tectosilicates.

2.2.3.2 Micas and Chlorites

Micas are K–Mg–Fe–Al phyllosilicates with extremely good cleavage, which is due to the laminar arrangement of their structure (sheet-like or phyllosilicates). The most common micas are the light-colored **muscovite** and the dark **biotite**. Muscovite is predominantly of metamorphic origin, but also igneous (only in intrusive rocks) and sedimentary. Biotite is usually igneous, and the darker it is in color, the higher its Fe content. The K content of both minerals lies between 6 and 14 % K_2O.

In the sheet-like structure of the micas, the SiO_4 tetrahedra are each linked with three (of 4) O^{2-} ions laying on one plane, i.e. two-dimensional (Figs. 2.3 and 2.5). The fourth O^{2-} ion that is not linked to the neighboring tetrahedron links the tetrahedral layer with the octahedral layer, in which Al^{3+}, Mg^{2+} or Fe^{2+} ions are six-fold coordinated. This octahedral layer is followed by another tetrahedral layer; however, it is rotated by 180°, so that the oxygen ions at the tips also point to the octahedral layer. Two of the six octahedrally coordinated oxygen ions from the octahedral layer bond with both the tetrahedral layers, and two form hydroxyl ions (OH^-) with H^+. The remaining two oxygen ions link the octahedra via common edges to form sheets, which is why micas are also referred to as 2:1 or **three-layered minerals** (Fig. 2.5).

Three octahedron centers form one formula unit, and altogether, their central cations have six negative charges to be compensated. In **dioctahedral** muscovite, two of the three centers are occupied with Al^{3+}, and in **trioctahedral** biotite, in contrast, all three are occupied with variable proportions of Fe^{2+} and Mg^{2+}. For muscovite, this results in the idealized formula $KAl_2(Si_3Al)O_{10}(OH)_2$, and accordingly for biotite $K(Mg, Fe^{2+})_3(Si_3Al)O_{10}(OH)_2$.

In micas, the three-layered structural units are linked vertically to the layer planes by potassium ions, which penetrate into the central gaps of the 6-O rings of the outer oxygen layer of the tetrahedron (see Fig. 2.6), and thus hold the silicate layers together (=**interlayer cations**). Because 6

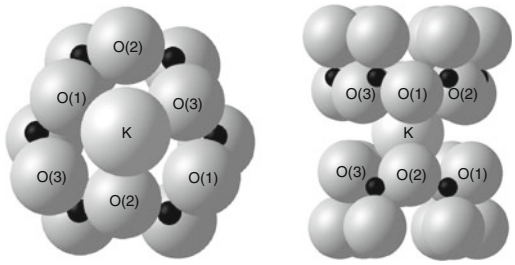

Fig. 2.6 Spherical model of the tetrahedral layer of mica seen from the front (*left*) and from the side (*right*) (true to scale). The oxygen and the potassium are labeled, the *small black spheres* are the Si^{4+} ions

oxygen ions on each side of the tetrahedral layer contribute to the bonding, K^+ with its O^{2-} ions has a coordination number of 12.

In a polyhedral model, the silicate sheets of micas are shown as a sequence of tetrahedral and octahedral layer at a ratio of 2:1 (Fig. 2.5), in a spherical model, as a package of two O and two (O, OH) layers. Together with the layer of K^+ ions between the silicate layers, these form the elementary layer with a thickness of 1 nm. The actual crystal sheet consists of a more or less large number of such elementary layers.

The so-called layer charge ξ determines whether there are interlayer cations or not: In micas, one of each of the four Si^{4+} ions is substituted by Al^{3+}. The lacking positive charge is therefore compensated by an interlayer K^+. However, the layer charge can vary over a great range (see Sect. 2.2.4).

The strong cohesion of the silicate layers in micas is not only a result of the high layer charge, but is also due to the fact that the K^+ ion is only slightly larger than the gap at the center of the oxygen hexagonal rings, and therefore penetrates into these gaps (Fig. 2.6). Furthermore, K^+ is relatively easily polarized, so that its positive charge is slightly shifted under the influence of the negative excess charge, which can strengthen the bond.

The strength of the cohesion of the layers in trioctahedral biotite is lower than in dioctahedral muscovite, and therefore the availability of the K^+ ions for plant growth is higher in biotite than in muscovite. Possible explanations are: (a) the K–O bond in trioctahedral minerals is somewhat longer and thus weaker than in dioctahedral minerals, (b) in trioctahedral three-layered minerals, the vector of the OH-bond is approximately perpendicular to the layer plane, while it forms and angle of $\sim 74°$ in dioctahedral minerals. As a result, in trioctahedral micas, the distance between the H^+ and the K^+ ions is smaller, i.e., the repulsion between the two ions is stronger than in dioctahedral micas. This also explains why K^+ is much more difficult to liberate, as soon as the Fe^{2+}–OH groups are converted by oxidation to Fe^{3+}–O groups.

The vertical linking can also occur without interlayer cations only through the VAN DER WAAL forces, as is the case with pyrophyllite ($Al_2Si_4O_{10}(OH)_2$) or talc ($Mg_3Si_4O_{10}(OH)_2$). The interlayer distance is then only 0.9 nm. The bonding strength between the silicate layers mainly depends on the charge per area; this is demonstrated by the following sequence of scratch hardness H: Talc ($\xi = 0$, $H = 1$), smectite-vermiculite group ($\xi = 0.3$–0.9, $H \sim 1^1/_2$), muscovite ($\xi = 1$, $H = 2$–$2^1/_2$), margarite ($\xi = 2$, $H = 4$).

The phyllosilicates also include the generally green in color, Mg–Fe(II)-rich **chlorite** (gr. *chlorós* = green), which, like the micas, consist of trioctahedral 2:1-layers. However, contrary to the micas, it is not K^+ that is inserted between the layers, but rather an independent, mainly trioctahedral hydroxide layer with the molecular formula (Mg^{2+}, Fe^{2+}, Fe^{3+}, $Al)_3(OH)_6$ (Fig. 2.7). The substitution of M^{2+} by M^{3+} in both hydroxide layers generates a positive charge, which compensates for the negative charge of the tetrahedral layers. The latter comes from the partial substitution of Si^{4+} by Al^{3+} (Bailey 1991). Because the two octahedrally coordinated layers are similar in their structures and chemistry, chlorites can be grouped according to the general formula:

$$(M^{2+}_{6-x-3y}M^{3+}_{x+2y}\square_y)(Si_{4-x}M^{3+}_x)O_{10}(OH)_8$$
$$\text{with } M^{2+} = Mg^{2+}, Fe^{3+} \text{ and } M^{3+} = Fe^{3+}, Al^{3+}.$$

$\square$ represents an empty space, i.e. an unoccupied position in the structure. In addition to the purely

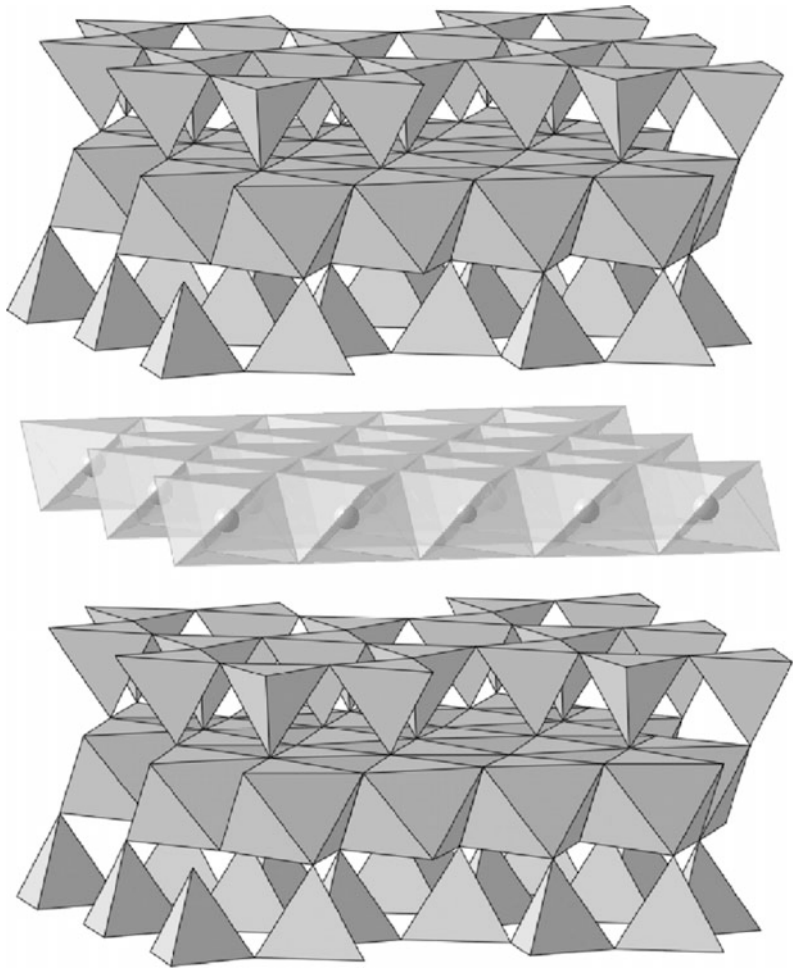

Fig. 2.7 Polyhedral model of the structure of chlorite. The *light octahedra* with the implied cation represent the hydroxide interlayer

electrostatic attraction, there are also H-bridge bonds between the OH-groups of the hydroxide layer and the O^{2-} ions of the two neighboring tetrahedral layers.

2.2.3.3 Pyroxenes, Amphiboles and Olivines

In contrast to the tecto- and phyllo-silicates, the generally dark **pyroxenes** and **amphiboles** are built with tetrahedral chains (Figs. 2.3 and 2.8) or bands (chain silicates arranged in parallel. In the tetrahedron centers, in turn, some of the Si^{4+} ions were substituted by Al^{3+} ions. The cations inserted to equalize the charge, mainly Ca^{2+}, Mg^{2+} and Fe^{2+}, link the chains and bands. Because this bond is weaker than the Si–O and Al–O bonds within the chains and bands, they are cleaved and weathered parallel to the chains and bands.

Pyroxenes include mainly **augite** (Ca, Mg, Fe, Al, Ti)$_2$(Si, Al)$_2$O$_6$ and the minerals enstatite, hypersthene and diopside, and the amphiboles include the **hornblendes** (Ca$_2$(Mg, Fe, Al)$_5$(Si, Al)$_8$O$_{22}$(OH)$_2$) and actinolite, mainly found in metamorphic rocks. On average, hornblende contains more Al and less Ca than augite. It is greenish-black to black in color, similar to biotite, because it contains both Fe^{2+} and Fe^{3+} (given as FeO or Fe_2O_3 in Table 2.3).

The olive-green nesosilicate/orthosilicate **olivine**, (Mg, Fe^{2+})$_2$SiO$_4$, is often found in basic igneous rocks. Like the plagioclases, olivines form a completely isomorphic series of intermediates with the end members forsterite (Mg$_2$SiO$_4$)

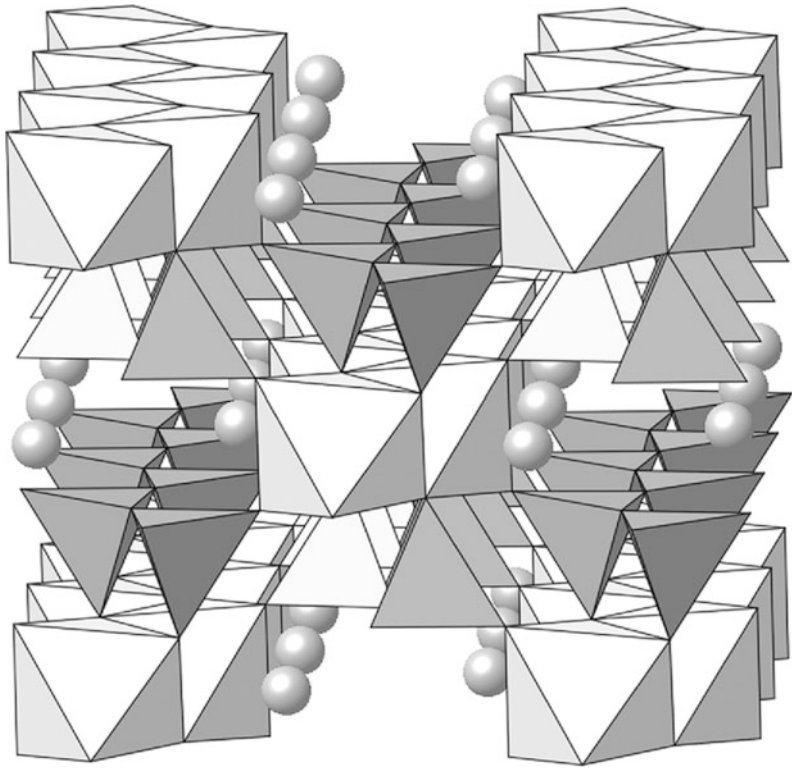

Fig. 2.8 Polyhedral model of the pyroxene structure (diopside) with chain-like bonding of the SiO_4 tetrahedra. The *octahedra* contain Mg^{2+}, the *spheres* are the Ca^{2+}

and fayalite (Fe_2SiO_4). The SiO_4 tetrahedra are not linked by shared O^{2-} ions, but rather only by Mg^{2+} and Fe^{2+} ions. There is no isomorphic substitution with Al^{3+}. Olivines weather readily, leading to the formation of serpentine.

2.2.3.4 Rare Silicates

Almost all igneous rocks contain small fractions of several silicates, which belong to the so-called **heavy minerals**, i.e. minerals with a density >2.9 g cm^{-3}. These include titanite ($CaTiOSiO_4$), zircon ($ZrSiO_4$) and tourmaline (idealized as $MA_3X_6[(OH)_4|(BO_3)_3|Si_6O_{18}]$ with M = Na, Ca; A = Mg, Fe, Li, Al, Ti; Cr; X = Al, Mg, Fe). Tourmaline is an important supplier of boron for plants.

Typical silicates of metamorphic origins are: Garnet, $(Ca, Mg, Fe^{2+}, Mn)_3(Al, Fe^{3+}, Cr^{3+})_2(SiO_4)_3$, andalusite and sillimanite, Al_2OSiO_4, staurolite, $(Fe^{2+}, Mg)_2(Al, Fe^{3+})_9O_6(SiO_4)_4$ (O_9OH_2) and epidote, $Ca_2(Al, Fe^{2+})Al_2[O/OH/SiO_4/Si_2O_7](OH)$ and also serpentine, $Mg_3Si_2O_5(OH)_4$.

Igneous rocks that cooled very quickly contain large amounts of non-crystallized silicates, **volcanic glass**, the chemical composition of which varies in a wide range according to the magma.

In building materials such as concrete, poorly crystallized, hydrated calcium silicates with the composition $mCaO \cdot SiO_2 \cdot nH_2O$ occur as a reaction product from clinker phases with the mixing water, where m is ~ 1.5–2, depending on the water addition. Morphologically, they form needles and copings or bendings, and structurally, these silicates resemble the mineral **tobermorite**, in which the water molecules are embedded between the silicate layers. From the clinker phases containing Al, tetracalcium aluminate hydrates are formed when the concrete hardens, and in the presence of sulfate, analogous sulfates are also formed, such as ettringite, $Ca_6Al_2[(OH)_4SO_4)]_3 \cdot 24H_2O$.

2.2.4 Clay Minerals

2.2.4.1 General Properties

Clay minerals are defined here as silicate minerals occurring in the clay fraction (<2 μm). Clay minerals formed from the weathering products of primary silicates are important constituents of many soils and sediments, which are lacking in igneous and metamorphic rocks. Structurally, they are related to the phyllosilicates, however, they have a very small particle size (<2 μm), and therefore give mudstones, clayey rocks and clayey soils their plasticity, their swelling properties and their capacity to adsorb ions and molecules. Their chemical composition and their charge can vary even within the same mineral type (Table 2.4). Their nonstochiometric chemical composition is expressed in the molecular formulas (see Table 2.5). They have "low" crystallinity, which, together with the layer charge, result in the reaction capacity of clay minerals in soils. All of these properties can be attributed to the environmental conditions during formation in the earth surface: low temperatures, low pressure as well as the "impurity" and fluctuating compositions of the weathering solutions (Brindley and Brown 1984; Jasmund and Lagaly 1993).

2.2.4.2 Crystal Structure and Classification

In addition to the structural similarities with the micas, clay minerals have the following characteristics (Newman 1987).

1. Like with the micas, the basic building units of clay minerals are SiO_4 tetrahedral and octahedral layers. Among the octahedral layers, a distinction is made between dioctahedral (Al, muscovite type) and trioctahedral (Mg, Fe, biotite type).
2. The charge is highly variable and can range from almost 0 to >1. The tetrahedral charge is always negative, the octahedral can be

Table 2.4 Variation ranges for the chemical composition of important clay mineral groups (in mass %)

Clay mineral	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O
Kaolinites	45–47	38–40	0–0.2	0–0.3	0	0	0	0
Smectites	42–55	0–28	0–30	0–0.5	0–3	0–2.5	0–0.5	0–3
Vermiculites	33–45	7–18	3–12	0–0.6	0–2	20–28	0–2	0–0.4
Illites	50–56	18–31	2–5	0–0.8	0–2	1–4	4–7	0–1
Chlorites	22–35	15–48	0–4	0–0.2	0–2	0–34	0–1	0–1

Table 2.5 Examples for chemical structures of common clay minerals

Clay mineral	Interlayer occupancy	Central cations octahedral layer	Central cations tetrahedral layer	Anions and water
Kaolinite	$X_{0.04}$	$(Al_{1.91}Fe^{3+}_{0.04}Ti_{0.04})$	$(Al_{0.05}Si_{1.95})$	$O_5(OH)_4$
Halloysite	$x_{0.04}$	$(Al_{1.96})$	$(Al_{0.05}Si_{1.95})$	$O_5(OH)_4 \cdot 2H_2O$
Illite (dioct.)	$K_{0.64}X_{0.10}$	$(Al_{1.46}Fe^{3+}_{0.21}Fe^{2+}_{0.08}Mg_{0.28})$	$(Al_{0.45}Si_{3.55})$	$O_{10}(OH)_2$
Glauconite	$K_{0.72}X_{0.06}$	$(Al_{0.48}Fe^{3+}_{0.96}Fe^{2+}_{0.17}Mg_{0.41})_{2.05}$	$(Al_{0.26}Si_{3.74})$	$O_{10}(OH)_2$
Vermiculite (trioct.)	$X_{0.71}$	$(Al_{0.14}Fe^{3+}_{0.34}Fe^{2+}_{0.09}Mg_{2.40})$	$(Al_{1.13}Si_{2.87})$	$O_{10}(OH)_2$
Montmorillonite (dioct.)	$X_{0.39}$	$(Al_{1.50}Fe^{3+}_{0.12}Fe^{2+}_{0.01}Mg_{0.38})$	$(Al_{0.05}Si_{3.95})$	$O_{10}(OH)_2 \cdot nH_2O$
Palygorskite	–	$(Al_{0.34}Fe^{3+}_{0.06}Mg_{0.60})_4$	Si_4	$O_{10}(OH)_2(H_2O)_8$

X exchangeable cations in equivalents, *K* interlayer potassium, *n* changing proportions of H_2O, *dioct*. dioctahedral, *trioct*. trioctahedral

negative or positive. The total charge is then approx. 0.2–1.0.

3. In clay minerals, interlayers can occur between the silicate layers. These can consist of ions (K), hydrated ions ($Mg \cdot H_2O$) or octahedral layers.
4. Among platy clay minerals with "endless" silicate layers, a distinction is made between two-layer or 1:1, three-layer or 2:1, and four-layer or 2:1:1 minerals. In the latter, the interlayer consists of an octahedral layer. If the layers are not charged, they are connected by hydrogen bridges, dipole interactions or VAN-DER-WAALS forces.
5. A special type are band silicates, where five or eight octahedra form a band, which is then connected to other bands through Si–O–Si bridges, and thus results in tubular structures (palygorskite and sepiolite).
6. When there is a very rapid supply of Si and Al from the weathering solution, clay minerals can be formed that consist of one single tetrahedral-octahedral double layer. These double layers are then bent to form hollow spherules (allophane) or tubes (imogolite).

Clay minerals are classified according to the occurrence of these properties (Table 2.6).

2.2.4.3 Kaolinite and Halloysite

As virtually pure Al silicates, these two clay mineral groups are the most common dioctahedral two-layer minerals, $Al_2Si_2O_5(OH)_4$, while trioctahedral serpentine, $Mg_3Si_2O_5(OH)_4$, occurs more rarely.

In kaolinite and halloysite, every silicate layer on the tetrahedron side is bordered by O^{2-} ions, and by OH^- ions on the octahedron side (Fig. 2.9). The silicate layers in kaolinite are held together by hydrogen bridges OH–O between the OH^- ions of the octahedra and the O^{2-} ions of the tetrahedra in the neighboring silicate layer. The octahedron centers are occupied by Al^{3+}, and the tetrahedron centers by Si^{4+}. The layer distance is 0.7 nm. In halloysite, in contrast, there is a H_2O layer between the silicate layers; its layer distance is therefore larger by the thickness of one H_2O sheet (0.28 nm) and is of 1.0 nm. When heated, but sometimes also already when air drying, halloysite looses the interlayer of water and contracts to 0.7 nm to form metahalloysite. In kaolinite and halloysite, the amount of isomorphic substitution of Si by Al in the tetrahedra, and thus the charge of the silicate layers is very low. In the octahedra, there is usually a little substitution of Al^{3+} by Fe^{3+} (see formulas in Table 2.5).

Table 2.6 Classification of the most important clay minerals

Structure type	Example	Height of the negative layer charge per formula unit	Occupancy of the interlayer space
1:1 or two-layered-minerals	Kaolinite	0	–
	Halloysite	0	H_2O
	Serpentine	0	–
2:1 or three-layered-minerals	Illite	>0.6	K
	Vermiculite	0.6–0.9	Exchangeable cations
	Smectite	0.2–0.6	Exchangeable cations
	Chlorite	Variable	Hydroxide layer
Fibrous pyroxene-like	Palygorskite	0	–
Variable	Allophane	?	–
	Imogolite	?	–
	Hisingerite	?	–

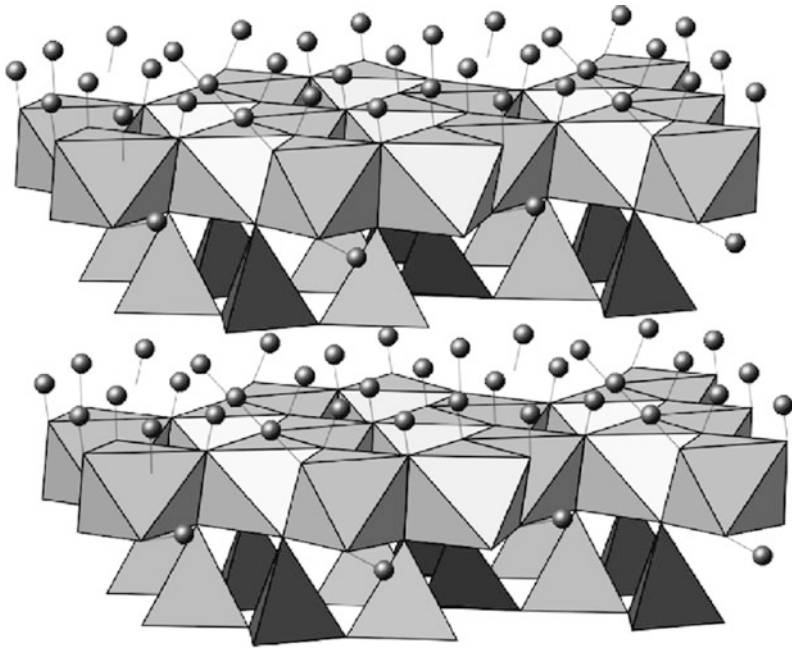

Fig. 2.9 Polyhedral model of a two-layered silicate (kaolinite). The *spheres* symbolize the H^+ ions

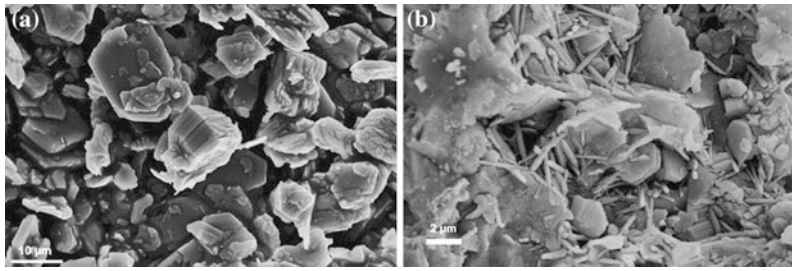

Fig. 2.10 **a** Pseudo hexagonal contour of kaolinite minerals (San Juanito, Chihuahua, Mexico). **b** Halloysite and kaolinite from the weathering of granite (Podzol, Bärhalde, Cv horizon) (*image* M. Zarei)

Kaolinite usually forms hexagonal µm-sized platelets, and halloysite forms tubes, rolled-up platelets (Fig. 2.10) or hollow spherules. Pedogenic kaolinite crystals are often smaller (several tenths of a µm) (Fig. 2.10a) and more rich in Fe than the many kaolin deposits. With increasing Fe incorporation, the crystal size and crystal arrangement (both combined in **crystallinity**) are decreasing. Kaolinite, as main component of the kaolins, is used to make high-quality ceramic and as filling material.

2.2.4.4 Illites and Glauconites

Illites show the closest similarity to the micas. They are like these three-layer minerals, however, their negative layer charge with 0.6–0.9 per formula unit is lower than that of the micas (1.0), and other than through the Si–Al substitution in the tetrahedra, also originate from the substitution of Al^{3+} by Mg^{2+} and Fe^{2+} in the octahedra. Due to the lower layer charge, the K content of illites with 4–6 mass % is lower than that of mica. Like with the micas, the silicate layers are held together by K at approx. 1 nm layer distance. In soils, illites are formed through the physical and chemical weathering of micas. During the diagenesis of sediments, illites are mainly formed from smectites through recrystallization and chemical incorporation of potassium between the layers. If the conversion is incomplete, a portion of the layers inside the crystal remains smectitic and thus expandable. Due to this chemical heterogeneity, illite is not classified as a defined mineral in the strict sense.

Under the electron microscope, illites appear as irregularly shaped platelets. Their crystals often only consist of 100–300 silicate layers, i.e. they have a thickness of approx. 0.1–0.3 µm.

The green-colored glauconites are related to the illites. They are found in marine sediments and differ from the illites through a higher Fe content in the octahedral layers. The glauconites also contain generally K-depleted, partially expanding layers.

2.2.4.5 Vermiculites and Smectites

Vermiculites and smectites are expandable three-layer minerals, whose negative layer charge is compensated by various exchangeable cations in the interlayer space (Fig. 2.11). By definition, the two minerals are separated by their layer charges: Those with a charge of 0.6–0.9 per formula unit are classified as vermiculites, those with 0.2–0.6 as smectites. With the addition of potassium, vermiculites contract due to their high charge to an interlayer distance of 1 nm, and therefore turn into illites and contribute to the so-called **K-fixation** of soils (Chap. 5), however, smectites do not.

Vermiculites generally originate from biotites through the **oxidation** of octahedral Fe^{2+}–Fe^{3+}. Due to the increase in the positive charge, the negative layer charge is reduced, the mineral expands and K is liberated from the interlayer space. Vermiculites also differ from smectites in the location of the isomorphic substitution and in the chemical composition. When heated, vermiculites expand to many times their original volume, and are used in this form as isolation and packaging material.

Due to their lower layer charge, smectites store more water and therefore expand more than vermiculites. The expansion height depends on the height of the layer charge and the type of interlayer cations. A smectite saturated with Ca^{2+} or Mg^{2+} stepwise stores up to four ~0.28 nm-thick water layers, so that its interlayer distance increases to approx. 2 nm. Sediments rich in

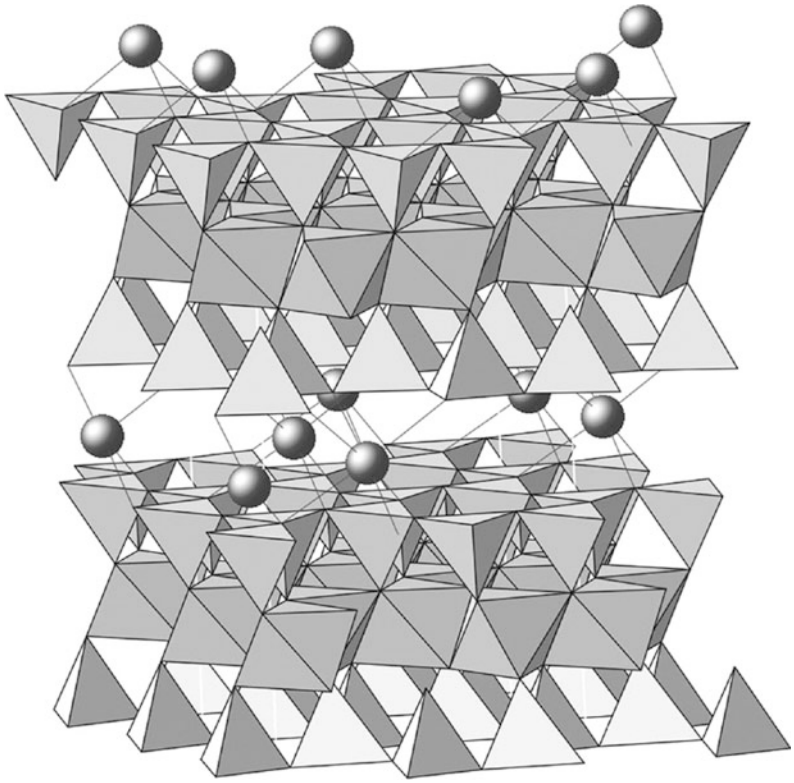

Fig. 2.11 Polyhedral model of a smectite. The *spheres* (not true to scale) between the silicate layers are the exchangeable cations

smectites and soils, such as Vertisols (Chap. 8), therefore swell and shrink strongly with fluctuating water contents. The swelling can trigger landslides and can lead to structural degradation in soils. The various smectites differ from one another in the height of the layer charge, the proportion of tetrahedral and octahedral charges, and the chemical composition. Mg^{2+}-rich forms with mainly octahedral charge are called montmorillonite, Al^{3+}-rich with mainly tetrahedral charge are beidellite, and Fe^{3+}-rich are nontronite. Pure smectite deposits are usually montmorillonite, while smectites in soils generally have higher Fe and lower Mg contents. Their charge is of 0.3–0.4 per formula unit and is 40–80 % tetrahedrally localized. Thus, they are Fe-rich, beidellitic smectites. Under the electron microscope, smectites appear as very thin and therefore flexible sheets that are often folded or rolled up at the edges, have an irregular boundary, and are riddled with many structural faults.

Smectites are the main minerals of the economically significant bentonites, as they occur e.g. in Lower Bavaria and in Wyoming and Mississippi, and have a multitude of technical applications (e.g. as adsorbents, binding agents for molding sands, additive for rinsing in deep drilling).

2.2.4.6 Pedogenic Chlorites

Soil chlorites (secondary chlorites) are similar to the 'primary' chlorites from rocks (Sect. 2.2.3.2) in that they both contain between the 2:1 layer a more or less complete hydroxide (Fig. 2.7) interlayer, and their stacking distance is therefore 1.4 nm. Their dioctahedral silicate layers are like those of vermiculite or smectite, and contrary to the primary chlorites from rocks, their layer interspace is sporadically occupied by an Al hydroxide octahedral sheet (also called Al chlorite) (Fig. 2.12). The Al hydroxides have a structure similar to gibbsite (Sect. 2.2.6.2).

Through the imperfect filling of the interlayer Al-hydroxy polymers, the properties of the formerly expandable three-layer minerals change: They loose their expandability and their capacity to contract with the addition of K. Already small amounts of Al-hydroxy polymers are sufficient

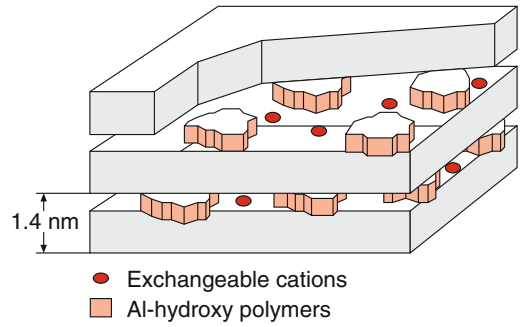

Fig. 2.12 Diagram of a pedogenic chlorite

(approx. $^1/_6$ of the possible interlayer sites) to cause this effect. The cation exchange capacity decreases with increasing filling.

Treatment with NaOH, NaF or Na citrate (100 °C) can dissolve the Al-hydroxy interlayer polymers and reverse the above-mentioned changes. Liming can cause a similar effect, if the clay particles are not too big and the degree of chloritization is not too high. The increase in pH neutralizes the positive charges of the Al-hydroxy polymer cations (OH/Al = 3; layer charge = 0), which can then no longer be held by the negatively charged silicate layers and exit the interlayer space.

Pedogenic chlorites only occur naturally in acidic soils, because only these release sufficient Al. Favorable conditions for deposition are a pH range of 4–5 and not too much organic matter, because SOM binds the Al complex and thus impedes deposition. If the pH drops even further, in the interlayers no more Al-hydroxy polymers are formed, and the soils can be "dechloritized" (podzolization).

2.2.4.7 Palygorskite and Sepiolite

The two Mg-rich, trioctahedral clay minerals palygorskite and sepiolite consist of bands of 2:1 silicate layers, which are staggered by one layer thickness vertical to the layer plane. Both minerals differ only in the width of the bands (palygorskite has 5 octahedra, sepiolite has 8 octahedra per band). This band structure is expressed physically in the fiber form of the crystals. There are channels between the bands that are filled with H_2O molecules. The octahedra are mostly

occupied with Mg, but sometimes also with Al, Fe and Ti. Their excess negative charge is low. Both minerals are formed in the alkaline range and/or in saline soils. For this reason, they are mainly found in semi-desert soils (Chap. 8).

2.2.4.8 Allophane, Imogolite and Hisingerite

Allophanes are hydrous secondary aluminum silicates with an Si/Al molar ratio of 0.5–1.0, in some cases up to 4, originating mainly from the weathering (Chap. 8) of volcanic glasses (Sect. 2.4.2) in humid climates. They consist of tiny hollow spherules with 3.5–5 nm outer diameter and walls with a thickness of approx. 0.7–1 nm (Fig. 2.13). The walls of the hollow spherules consist of a curved Al–O–OH octahedral layer, where incomplete Si–O–OH-tetrahedral layers are bound by O bridges on the inner surface. In contrast to the other clay minerals, the crystal arrangement only extends over the range of the very small hollow spherules (short range order), so that the allophanes were long considered to be amorphous. Due to their similarity to imogolite, Al-rich allophanes (Si/Al = 0.3–0.4) are called proto-imogolite allophane. The very rare hisingerite contains Fe in the octahedral layer instead of Al.

In contrast, imogolite has a one-dimensional long range order, since it consists of several µm-long, very fine tubes with 1 nm inner and 2 nm outer diameter. The outside of the tubes form a dioctahedral Al hydroxide layer, which is connected to an incomplete layer of Si–O_3OH tetrahedra on the inside via O bridges. Therefore, the outer surface of the tubes consists of Al–OH groups, and the inside of Si–OH groups (Fig. 2.14). This results in the chemical structure $(HO)_3$ Al_2O_3SiOH, according to the sequence from the outside to the inside, and an Si/Al ratio of approx. 0.5.

2.2.4.9 Interstratified Minerals

The clay mineral crystals in soils often have different elementary layers arranged in a regular or irregular sequence (Fig. 2.15). Such minerals are called interstratified minerals. With irregular mixed layers, which occur more frequently in soils than regular sequences, the relative proportions of the elementary layers can fluctuate across a wide range. This includes those between

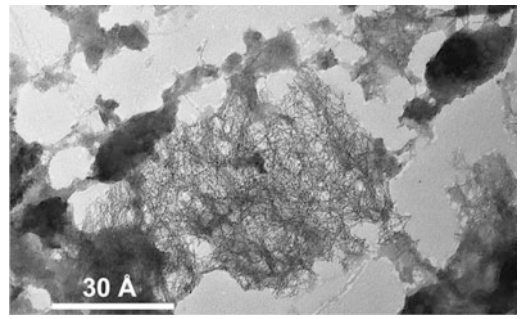

Fig. 2.13 Thread-like structures of imogolite, Bw horizon of an Andosol in Iceland (*image* M. Zarei)

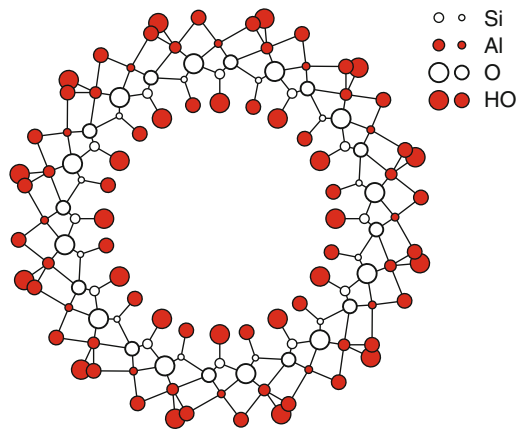

Fig. 2.14 Structure of imogolite: Cross section through an imogolite tube. The smaller structural elements lie somewhat underneath the plane of the drawing, and the larger ones above

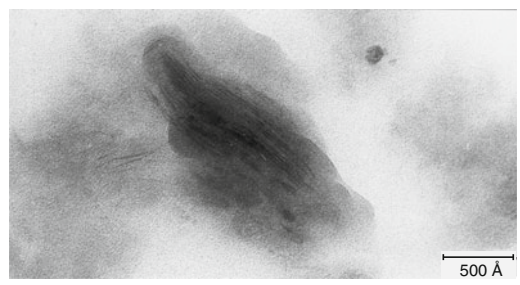

Fig. 2.15 Section through an expanded smectite with 1.0–1.8 nm layer sequence from the Bwk horizon of a Calcic Luvisol on Lanzarote (*image* M. Zarei)

chlorite and vermiculite, or between illite and smectite, generally originating from the partial weathering of chlorite or illite. There occur also mixed layers between kaolinite and smectite. The more rare, regular mixed layers—e.g. at a ratio of 1:1—are formed by the transformation of biotite to vermiculite (hydrobiotite) or from chlorite to smectite (corrensite) through the loss of the interlayer K or of the hydroxide layer in every second elementary layer. However, silicate layers with different charges can be combined to a crystal with mixed layers already during the formation of the clay minerals from the solution.

The properties of the interstratified minerals result from the type and the proportions of the components. In general, the interstratified minerals are transitions that are more reactive than pure clay minerals.

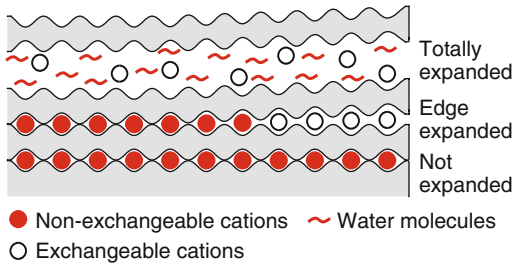

Fig. 2.16 Diagram of mica with a vermiculite or smectite layer that is not expanded, expanded at the edges, and completely expanded

2.2.5 Clay Mineral Formation and Transformation

2.2.5.1 Changes in the Interlayer Filling

Among the phyllosilicates, the micas muscovite and biotite as well as the primary chlorites are most important for clay mineral formation (Niederbudde 1996). Typical for these transformations is the preservation of the silicate layers, even if they do not remain unaltered, while the occupancy in the interlayer space changes. Supported by mechanical crushing, K^+ ions (Sect. 7.2) are extracted from the edges of the micas and substituted by other cations such as Ca^{2+} and Mg^{2+}, which, as hydrated interlayer cations, are not pulled into the bowl-shaped depressions in the O hexagonal ring like the K^+ ions, but rather remain substitutable with other cations. This initially leads to partly expanded layers at the edges of the crystals, and with increasing K-loss, to completely expanded layers (Fig. 2.16).

The decrease in the negative layer charge facilitates or even enables the expansion. In the micas containing Fe^{2+} (biotite), this is a result of the oxidation from Fe^{2+} to Fe^{3+}, i.e. through an increase in the positive charge. However, the decrease in the negative charge is generally lower than the extent of the $Fe^{2+} \rightarrow Fe^{3+}$ oxidation, because some of the Fe^{2+}–OH groups are transformed into Fe^{3+}–O groups by releasing H^+, so not only the positive, but also the negative charge increases and/or part of the octahedral Fe^{3+} and Mg^{2+} is released (Fe) or bound but still exchangeable (Mg). With the dioctahedral micas, the negative charge probably decreases through O → OH transformation.

This process ultimately results in a completely K-free and expanded clay mineral, which, depending on the layer charge, is a vermiculite or smectite. In the same way, primary chlorites are transformed into vermiculite or smectite when their (Mg, Fe, Al) hydroxide layer is dissolved by protonation.

The transformation of micas into expandable three-layer minerals takes place in the soil faster the more the pH values drops and the K concentration in the soil solution decreases; the equilibrium solution for biotite is of 10–15 mg K L^{-1}, for muscovite approx. 0.01 mg K L^{-1}. This demonstrates that biotite weathers much more easily than muscovite. Plant roots and K-fixing clay minerals can lower the K concentration so much that biotite turns into vermiculite within a relatively short time (Nahon 1991).

2.2.5.2 New Formation from the Weathering (Decay) Products of Silicates

During chemical weathering, feldspars, pyroxenes, amphiboles, olivines and also phyllosilicates break down into their individual ionic components. The new minerals can form either inside (pseudomorphosis) or in the immediate vicinity of the original mineral, but also after transport of the weathering products to other soils or waters (rivers, lakes, oceans).

Close spatial contact between weathered and newly formed mineral demonstrate that structurally related parts can be adopted. Such a process is improbable for feldspars as tectosilicates, because during their transformation, e.g. to kaolinite, tetrahedral Al is transformed to octahedral Al and therefore the (Si, Al) tetrahedral bond structure must be broken; thus, in contrast to the primary phyllosilicates (mica, chlorite), the structural relationship is minor.

The type of clay mineral that is formed under a given set of conditions can be derived from the pH and the composition of the solution as well as the solubility products of the individual minerals using stability diagrams (Fig. 2.25). They indicate that smectite is formed in neutral to slightly alkaline environments and with high concentrations of Si and Mg, illite with higher K concentrations, kaolinite in the acidic range with moderate Si concentrations, and at very low Si concentrations ($<10^{-5}$ mol L^{-1}), no more silicate is formed, only gibbsite. Smectite and gibbsite are therefore mutually exclusive. This concurs with observations in nature (see Sect. 2.4.4). With the formation of new clay minerals, Fe is generally precipitated separately as an oxide, because these are very poorly soluble.

2.2.5.3 Clay Mineral Transformation

Clay minerals develop from the weathering of rock to form soil. They may originate from rocks and can be further transformed because the conditions change in a particular direction with progressive weathering. For example, the degree of acidification increases with time in soils of humid areas. As a result of this, aluminum can be liberated from various minerals and embedded between the layers of expanded three-layered minerals, and they become pedogenic chlorites. If the parent material contains vermiculite in addition to biotite, they can absorb K^+ from the potassium-releasing biotite and turn into illite (**illitization**). With long-term tropical weathering, the Si concentration decreases so much that the initially formed smectite, as can be read from the stability diagram (Fig. 2.25), is transformed into kaolinite, and in extreme cases, even into gibbsite (**desilification**, Chap. 8). Allophane and imogolite are transformed over the course of time into the better crystallized minerals kaolinite and halloysite. Figure 2.17 summarizes the described formation and transformation pathways of clay minerals.

2.2.6 Oxides and Hydroxides

Minerals in this group can be both of primary and secondary origin. The most common oxide

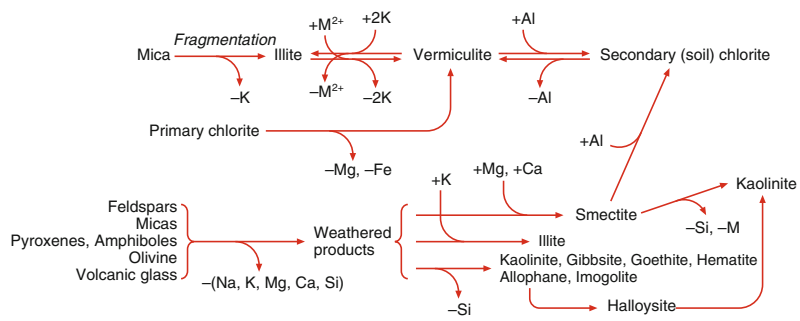

Fig. 2.17 Formation and transformation paths of clay minerals (M = metal cation)

in rocks and soils is quartz. In contrast, Al, Fe and Mn oxides and hydroxides, as well as some Si and Ti oxides, are generally characteristic new formations of weathering, i.e. of secondary origin, and are therefore present in most soils and sediments. In primary minerals, metals are mainly bound in silicates, and are liberated during weathering by hydrolysis and protolysis (Stanjek 1997, 1998; Waychunas 1991). In doing so, their silicate (SiO_4) ligands are substituted by O and OH ligands (M = metal):

$$]-M-O-Si- + H_2O \rightarrow I]-M-OH + HO-Si-O \quad (2.1)$$

The affinity to the new ligands increases with increasing charge and decreasing size of the metal cation. If metals are oxidized when they are liberated from the silicate bond, e.g. Fe^{2+} and Mn^{2+}, their tendency towards oxide formation increases, while the tendency to form clay minerals decreases. The list of oxide minerals that are found in rocks and soils reflects a great diversity (Table 2.7).

2.2.6.1 Silica Oxides

The most important Si oxide by far in the Earth's crust is **quartz** (SiO_2). Most quartzes are of igneous and metamorphic origins (primary

Table 2.7 The oxide, oxihydroxide and hydroxide minerals of Si, Al, Fe, Mn and Ti in rocks and soils

Element	Name	Formula	Color
Si	[Quartz][a]	SiO_2	Colorless
	Opal	$SiO_2 \cdot nH_2O$	Colorless
	[Cristobalite]	SiO_2	Colorless
Al	Gibbsite	γ-$Al(OH)_3$	Colorless
	(Boehmite)[b]	γ-AlOOH	Colorless
	(Diaspore)	α-AlOOH	Colorless
	(Corundum)	α-Al_2O_3	Colorless
Fe	Goethite	α-FeOOH	Yellowish-brown (7.3–1.6Y)
	Lepidocrocite	γ-FeOOH	Orange (4.9YR–7.9YR)
	Hematite	α-Fe_2O_3	Red (3.5R–4.1YR)
	Maghemite	γ-Fe_2O_3	Brownish-red (6.2YR–9.4YR)
	[Magnetite]	Fe_3O_4	Black
	Ferrihydrite	$5\ Fe_2O_3 \cdot 9H_2O$	Reddish-brown (2.8YR–9.2YR)
	{Schwertmannite}[c]	$Fe_8O_8(OH)_6SO_4$	Orange (6.2YR–0.3Y)
Mn	Vernadite	γ-$MnO_2 \cdot nH_2O$	Blackish-brown
	Birnessite[d]	$(Mn_2^{3+}Mn_7^{4+})O_{18} \cdot R(H_2O)_n$	Blackish-brown
	Lithiophorite[e]	$[Al_2Li(OH)_6]\ [Mn_5^{4+}Mn^{3+}O_{12}]$	Blackish-brown
	(Pyrolusite)	MnO_2	Blackish-brown
Ti	Anatase	TiO_2	Light black
	[Rutile]	TiO_2	
Fe + Ti	[Ilmenite]	$FeTiO_3$	Black?
	Pseudorutile	$Fe_{2-x}Ti_3O_{9-x}(OH)_{3x}$	

[a][] Usually only lithogenic
[b]() Rare in soils
[c]{} More common in mine piles
[d]The interlayer cation R(=Na, K, Ca) is surrounded by water molecules
[e]Li/Al < 0.5 in soils

quartz), a smaller fraction is formed in the soil. It accounts for 12 % vol. of the composition of the lithosphere (Table 2.1). It has a density of 2.65 g cm^{-3}, conchoidal fracture and is usually transparent/clear to white. Quartz consists exclusively of SiO_4 tetrahedra forming a continuous 3-dimensional network. Therefore, there are 4 half O^{2-} ions for each Si^{4+} ion; this results in the formula SiO_2. The framework structure contributes greatly to the high hardness (scratch hardness 7 on the Mohs scale from 1 to 10) and weathering resistance, so that quartz is accumulated during weathering and transport processes (Headnay et al. 1994; Dixon and Weed 1989).

As a second SiO_2 modification, **cristobalite is found in volcanic rocks and their soils**. Often found in soils and sediments, **opal**, $SiO_2 \cdot nH_2O$, is a mixture of amorphous SiO_2, poorly crystallized cristobalite and **tridymite**, another SiO_2 modification. The H_2O content of opal, depending on its degree of aging, usually ranges from 4 to 9 %, its density from 2.1 to 2.2 g cm^{-3}.

In the tropics and subtropics, Si originating from weathering can accumulate in depressions as quartz or opal. Si indurations are called **silcrete** (Chap. 8). In many other soils, opal is of biogenic origin. Topsoils contain up to several percent opal in many different shapes. This so-called **bio-opal** either comes from the supporting tissues of plants (phytoliths), especially from grasses, or the needles of siliceous sponges. Straw from cereals contains 1–1.5 % and grasses ~5 % SiO_2 by weight. The plant-specific form of the bio-opal/phytolith particles (e.g. strips or needles) often provides information on the history of the origin of the soil.

The majority of the Si liberated by weathering is used in the formation of secondary silicates. Only a small portion is precipitated as pedogenic Si oxide. It is formed from the dissolved Si that is present in the solution as orthosilicic acid H_4SiO_4 (also formulated as $Si(OH)_4$). With higher concentrations and in the pH range from 5 to 7, the silicic acid tends towards polymerization and its solubility decreases. Finally, a hydrous, amorphous Si oxide is formed, which, passing through opal, slowly turns into more or less well arranged cristobalite, tridymite or quartz. In doing so, the solubility decreases from approx. 60 to 1.4–3.3 (quartz) mg Si L^{-1}. The solubility of bio-opal is of 2–9 mg Si L^{-1}. Polymerization can be inhibited by adsorption of Si on other minerals, e.g. Fe and Al oxides. In the range of pH 2–8, the solubility of Si oxides is almost independent of the pH. Above pH 8–9, they depolymerize to form silicate anions and the solubility increases.

The Si concentration of the soil solution generally lies between the solubility of the amorphous SiO_2 and of quartz. Its formation is therefore thermodynamically possible, however, it is kinetically inhibited because of the high crystallization energy. This is why quartz is only seldom found as a newly formed mineral in soils.

2.2.6.2 Aluminum Oxides

Among the crystallized Al hydroxides found in soils, **gibbsite** ($Al(OH)_3$) is by far the most common. The Al^{3+} ions form octahedra with six OH^- ions that are connected via shared OH^- ions to form layers, in which $^2/_3$ of the octahedral centers are occupied with Al. The crystals consist of stacks of such Al–OH octahedron layers and often form hexagonal platelets or columns of clay or silt size (Fig. 2.18).

Furthermore, weathering produces two AlOOH forms, **diaspore** and **boehmite**, which mainly occur in bauxites (aluminum ore) and have the same crystal structure (isotypic) as the two Fe oxides goethite and lepidocrocite (see Sect. 2.2.6.3).

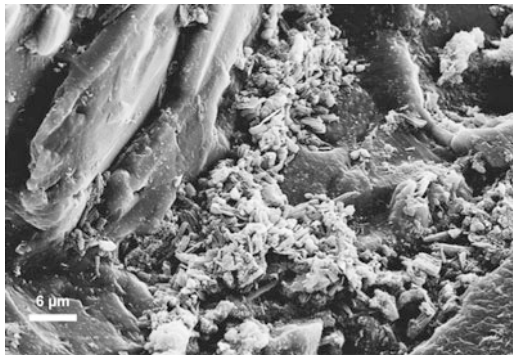

Fig. 2.18 Gibbsite crystals on quartz (Ferralsol in Northern Thailand, *image* M. Zarei)

Corundum (Al_2O_3) is generally of lithogenic origin, and was also formed in tropical soils, probably during fires.

Gibbsite is formed through slow hydrolysis of the Al liberated during the weathering of silicates containing Al (feldspars, micas, clay minerals, etc.); however, this only occurs if, as is the case in some tropical soils, the Si concentration drops below 0.5 mg Si L^{-1} due to strong desilification, and is therefore no longer sufficient for clay mineral formation (Fig. 2.26). Here, for example, plagioclases can be directly transformed into gibbsite. Similarly, gibbsite results from the progressive desilification from clay minerals.

In acidic soils under temperate humid climates, no gibbsite is formed from the liberated Al, because apparently the formation of Al silicates (clay minerals) or Al sulfates, of hydroxy-Al polymers in the interlayer of expandable three-layered clay minerals, of Al complexes with humic matter, or of amorphous Al hydroxide seems to be preferred. The composition of soil solutions and the solubilities of these compounds often imply the presence of amorphous Al hydroxide or Al-hydroxy-sulfates (e.g. alunite, $KAl_3\ (SO_4)_2(OH)_6$ or jurbanite, $AlSO_4(OH)\cdot 5H_2O$); direct identification of these compounds has not yet been possible.

At a pH of 5, the solubility product $K_{sp} = a_{Al}\cdot a_{OH}$ (a = activity) of gibbsite (approx. 10^{-34}) results in an Al concentration of only approx. 3 mg Al L^{-1}. The amorphous form is 1–2 orders of magnitude more soluble ($K_{sp} \sim 10^{-32}$). However, because the solubility increases with decreasing pH by three powers of ten per pH-unit, gibbsite is no longer stable in the highly acidic range.

2.2.6.3 Iron Oxides

The greatest portion of iron liberated from minerals by weathering is bound in Fe^{3+} oxides and not, as with Al, in clay minerals. Because the iron in primary minerals (biotite, amphibole, pyroxene, olivine, magnetite) is usually divalent, it is oxidized by oxygen from the atmosphere in the presence of water and liberated from the silicate bond. The Fe^{3+} hydrolyzes to Fe(III) oxides already at the weathering site (see Eq. 2.12 in Sect. 2.4.2.3), giving the soil a uniform brown or red color (Cornell and Schwertmann 1996). The ratio of the oxidized to the total iron (corrected by the Fe oxides in the rock) is therefore an indicator of the soil's degree of weathering. The ratio is 0.2–0.3 in young soils from Pleistocene sediments, and of 0.8–0.9 in old soils in the humid tropics. As very stable weathering products (see Sect. 2.4.4), the Fe hydroxides remain in the soil as long as aerobic conditions exist. Under anaerobic conditions, they are reduced with the microbial oxidation of biomass (simplified to CH_2O), i.e. they serve as an electron acceptor (Chap. 4). In doing so, they are dissolved:

$$4\ FeOOH + CH_2O + 8H^+ \rightarrow 4\,Fe^{2+} + CO_2 + 7\,H_2O \qquad (2.2)$$

The Fe^{2+} moves along a redox gradient on a cm to km scale, until it reaches aerobic areas, where it is oxidized again and precipitated as Fe(III) oxide. This results in local, sometimes hardened Fe oxide accumulations in the form of mottles, concretions and horizons (**ferricrete**, Sect. 8.2.6.2).

In soils where the Fe oxides are evenly distributed, the Fe oxide contents generally range from 0.2 to 20 %; it especially depends on the texture (sand < clay), on the parent material and on the stage of pedogenesis. In accumulation zones, like rust mottles, concretions and ferricretes, it can increase up to 80–90 %.

On the one hand, the significance of iron oxides for the matter balance of soils and landscapes lies in their capacity to incorporate trace elements during their formation, such as chromium and vanadium, and on the other, they bind anions such as phosphate, arsenate, chromate, selenite, but also heavy metals, firmly on their surface and reduce its mobility in soils (see Chaps. 5 and 9).

(a) **Forms and properties**

The two most common Fe(III) oxides in soils and rocks (Table 2.7) are the generally needle-shaped **goethite** (α-FeOOH), and the hexagonal platelet crystals of **hematite** (α-Fe_2O_3). Less common, but by no means rare, are **lepidocrocite** (γ-FeOOH), which

usually forms strongly lobed or toothed platelets or ledges, **maghemite**, the ferrimagnetic form of Fe_2O_3, and the very poorly crystallized, hydrous **ferrihydrite** (formerly: amorphous Fe(III) hydroxide), which mostly occurs as aggregates with small crystals 2–5 nm in size. Small amounts of lithogenic **magnetite** (Fe_3O_4) are found in many rocks, which weathers relatively slowly. There are also bluish-green colored Fe(II,III) hydroxides, the so-called green rusts, which are formed under anaerobic conditions and can contribute to the bluish-green color of reduced horizons in groundwater (Gleysol) soils.

The only structural element of the most common Fe(III) oxide is an octahedron, where the central Fe^{3+} is surrounded by six O^{2-} or by three O^{2-} and three OH^- ions. The individual minerals differ only in the spatial arrangement of the octahedra (Fig. 2.19). The basic pattern of the hematite structure are two FeO_6 octahedra that share three oxygen ions. These double octahedra are connected to each other at the edges (i.e. two shared O^{2-} ions respectively) and form a three-dimensional framework. In goethite, $FeO_3(OH)_3$ octahedra are connected at the edges to form double chains and these are linked at octahedral corners (i.e. via one shared O^{2-} ion and H^+ bridges). In lepidocrocite, the double chains form zigzag layers due to octahedral edges that are held together by H^+ bridges. In pedogenic or soilborne goethites and hematites, some of the Fe^{3+} ions are isomorphically substituted by Al^{3+} ions (in goethite up to $^1/_3$, in hematite up to $^1/_6$ of the Fe^{3+}). Because the Al^{3+} ions are smaller than the Fe^{3+} ions (Table 2.2), the elementary cell of the Al-substituted Fe(III) oxides is somewhat smaller than that of the pure minerals.

All Fe(III) oxides are poorly soluble compounds. The solubility products $a_{Fe}^{3+} \cdot (a_{OH})^3$ of goethite and hematite are of 10^{-42}–10^{-44}, that of lepidocrocite is of about 10^{-40}, and of ferrihydrite 10^{-37}–10^{-39}. A typical characteristic of Fe oxides in soils is that, because of the very low solubility and crystallization-inhibiting substances in the soil solution, they only form very small crystals (nanoparticles) (goethite and hematite 10–100 nm, ferrihydrite 2–5 nm). Therefore, they have a very large specific surface (50–200 $m^2\ g^{-1}$), and can contribute significantly to the total surface area of the soil substance even at low contents.

(b) **Occurrence and formation**

The mineral form and the properties of iron oxides reflect the conditions of pedogenesis in many ways. Because of its high stability, **goethite** is found in soils of all climate regions and is thus the most common pedogenic Fe oxide. In the absence of hematite, it gives the soil the typical yellow to rusty-brown color. The conditions under which the Fe oxides were formed in soils can be deducted both from field observations and from synthesis trials in the laboratory. Both Fe^{2+} and Fe^{3+} are possible initial forms of iron, both of which do not exist as naked ions, but rather are initially surrounded by six water molecules. In the first step, one of these water molecules dissociates

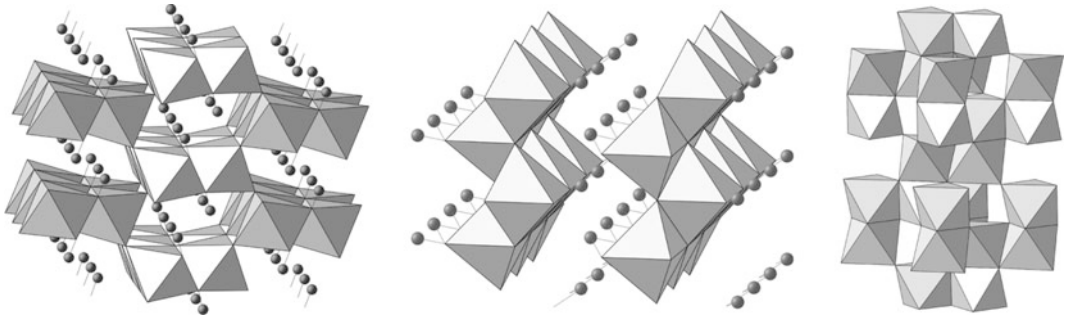

Fig. 2.19 Octahedral model of goethite (*left*), lepidocrocite (*centre*) and hematite (*right*). The *smaller spheres* are H^+ ions

a proton and thus reduces the charge of the dissolved species. This (reversible) reaction step, which takes place both with Fe^{2+} and Fe^{3+}, is called **hydrolysis**:

$$\left[Fe(OH_2)_6\right]^{3+} + H_2O \Leftrightarrow \left[Fe(OH_2)_5OH\right]^{2+} + H_3O^+ \quad (2.3)$$

The now lower-charged monomers dimerize according to:

$$2\left[Fe(OH_2)_5OH\right]^{2+} \Leftrightarrow Fe_2\left[(OH_2)_5OH\right]_2^{4+} \quad (2.4)$$

and then polymerize, forming –Fe–OH–Fe– and –Fe–O–Fe bonds, resulting in crystalline iron oxides:

$$n Fe_2\left[(OH_2)_5OH\right]_2^{4+} + 4n\, H_2O \Leftrightarrow 2n\, FeOOH + 4\, n\, H_3O^+ \quad (2.5)$$

Which oxide is formed by this reaction depends, among other things, on the rate with which the low-molecular components are supplied, and whether the crystallization is disturbed by other components in the solution. If there is a rapid supply and/or strong disturbances, the poorly crystallized **ferrihydrite** is formed, e.g. with rapid oxidation of waters containing Fe^{2+} or in the presence of organic compounds, as in the B horizons of Podzols. The oxidation of Fe^{2+} by chemolithotrophic bacteria (e.g. species from the *Leptothrix*, *Crenothrix* or *Gallionella* genera) also often leads to ferrihydrite, which can fully incrustate the dead cells or be slimy in texture. Ferrihydrite is found in lake ores, bog irons and in the B horizons of Podzols. In general, ferrihydrite can be called a young Fe oxide; it is lacking in older, more strongly developed soils.

Orange-colored schwertmannite, $Fe_8O_8(OH)_6SO_4$, occurs in acid sulfate mine waters and soils (*acid sulfate soils*) as a bacterial oxidation product of pyrite. It is structurally related to akaganeite, β-FeOOH, but probably contains sulfate in the tunnel instead of chloride.

When Fe is supplied at a slower rate, like e.g. with the weathering of silicates containing Fe^{2+} (mafic), the better crystallized mineral goethite is formed. Goethite is promoted by carbonate ions when present during the oxidation of Fe^{2+}. Because there are transitions between all formation environments in soils, ferrihydrite and goethite are often associated in temperate climates; this is also because ferrihydrite is a less stable oxide that transforms into goethite through solution in the course of time. This is also delayed by substances such as silicate and organic molecules that are sorbed on the ferrihydrite.

Hematite is widespread and is closely associated with goethite in tropical and subtropical soils, giving them their red color (see Table 2.7). Synthesis trials under simulated soil conditions show that ferrihydrite is transformed into hematite and goethite in two parallel reactions. Isotope trials also show that the two reactions take place in the solution, i.e., water is required. Compared to goethite, hematite is promoted by lower moisture contents and higher temperatures. The formation of goethite, in contrast, is promoted with increasing distance from the solubility minimum of the ferrihydrite, which is in the neutral range (pH 6–8) and coincides with the zero charge point.

Because of their high stability, goethite and hematite in soils do not directly transform into each other through dehydroxylation or rehydroxylation. Hematite is not formed from goethite through the loss of water (except for fires), and goethite is also not formed when hematite absorbs water. This is not contradicted by the observation that red tropical soils containing hematite turn into yellowish-brown soils from top to bottom (Xanthization), because under more humid conditions today, hematite is preferentially dissolved by reduction or complexing with the participation of microorganisms and organic substances, and goethite remains behind.

Lepidocrocite is mainly formed through slow oxidation of Fe^{2+} at low carbonate ion concentrations. Although it is metastable compared to

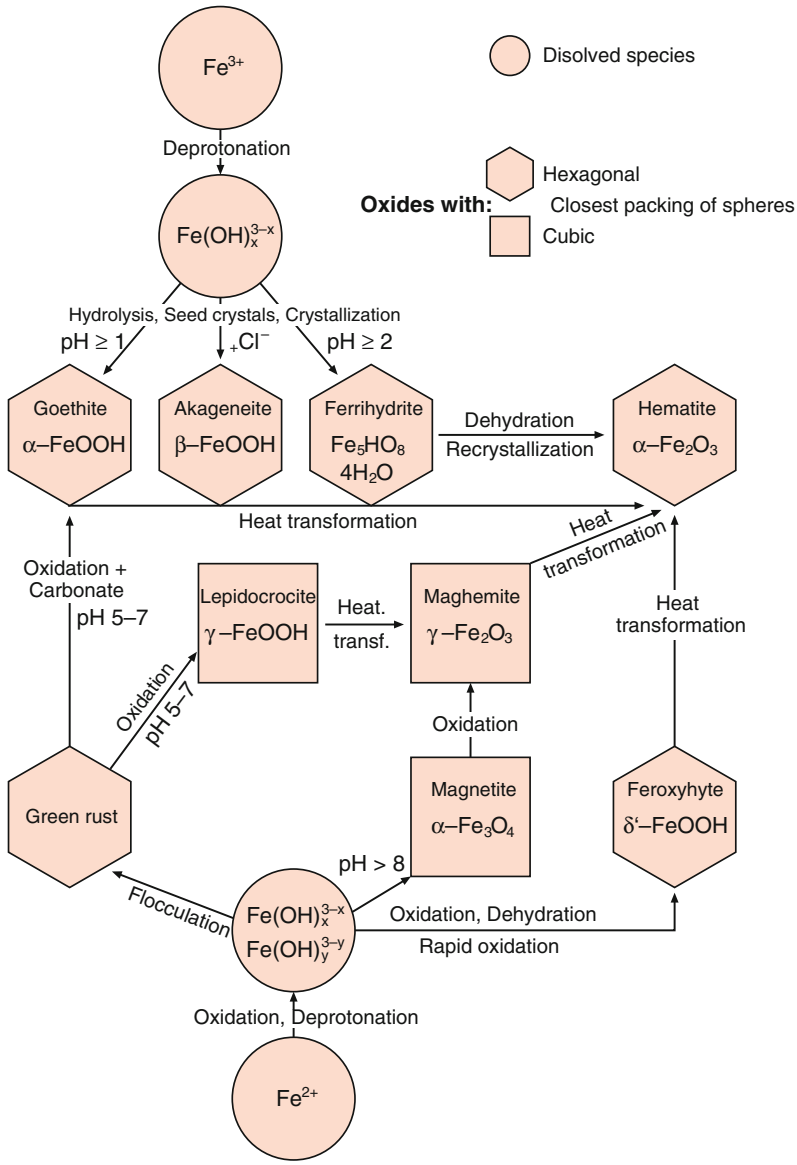

Fig. 2.20 Formation and transformation paths of iron oxide minerals (after U. Schwertmann)

goethite, it only transforms into goethite very slowly, so that it is persistent over a longer period of time. It mainly occurs in clayey, carbonate-free, waterlogged soils in the form of orange mottles or bands (Chap. 7).

Bacterially formed **magnetite** has been found in soils influenced by groundwater. **Maghemite** is either formed through the oxidation von lithogenic magnetite especially in basic volcanic rock, or through the effect of heat (fires) on other Fe(III) oxides in the presence of organic substances. The association with charcoal and corundum suggests the effect of fire. Maghemite and Feroxyhite are mainly finely distributed in tropical and subtropical soils or widely spread in concretions, because the frequency of forest fires here is high. Figure 2.20 shows a sketch of the explained formation and transformation paths for the different iron oxides.

Thus, Fe oxides reflect the pedogenic conditions in many ways. This is especially true for the goethite-hematite ratio in soils. Soils in temperate

and cool climates are usually free of hematite, while many (sub)tropical soils also contain hematite in addition to goethite. The soil hydrosequences in these regions contain less hematite with increasing water saturation. At the same time, they are toposequences where the upper, drier soils are red, and the lower, more humid soils are yellow. Even within the profile itself, yellow topsoils are often observed above red subsoils, which is a sign that hematite is not formed or is not stable in the humic topsoil of such soils. Lepidocrocite in soils of temperate zones usually indicates a reducing, $CaCO_3$-free environment, ferrihydrite the presence of crystallization inhibitors (see above) or rapid oxidation of Fe^{2+} in reductomorphic soils.

The extent of Fe substitution by Al also depends on the pedogenic environment. In acidic, strongly weathered soils (e.g. Ferralsols), the Al substitution of goethite is generally high (up to $^1/_3$ of the Fe), in neutral or reduced soils, in contrast, it is much lower ($<^1/_6$). The spatial proximity to a source of Al (e.g. clay minerals) also plays a role. Finally, the crystallinity also reflects the pedogenic environment. Thus, humic soils in cool-humid climates contain more poorly crystallized goethite associated with ferrihydrite, while humus-free, strongly desilified, oxide-rich tropical soils contain more well-crystallized goethite.

2.2.6.4 Titanium Oxides

Rocks contain Ti in silicates and oxides; among the latter, **rutile** (TiO_2), **ilmenite** ($FeTiO_3$) and **titanomagnetite** ($\approx Fe_{2,4}Ti_{0,6}O_4$) dominate. The Ti liberated by weathering is derived from primary, easily weathered silicates (biotite, amphiboles and pyroxenes), while the poorly weatherable oxides are relatively accumulated in the soil. Titanium is not only subordinately incorporated into clay minerals during weathering, but is rather mainly precipitated as **anatase** (TiO_2), in which the Ti is partly substituted by Fe^{3+}. Anatase can also be synthesized at room temperature. **Pseudorutile** is an Fe–Ti oxide of variable composition that is formed from the weathering of ilmenite. Titanomagnetites weather (oxidize) to titanomaghemites.

The Ti content in strongly weathered soils can increase to more than 1 %, in some tropical soils on Ti-rich rocks to even more than 10 %, while in younger soils of temperate climate zones, it is usually only of 0.1–0.6 %.

2.2.6.5 Manganese Oxides

During the weathering of silicates containing Mn (e.g. biotite, amphiboles and pyroxenes), the Mn^{2+} is precipitated under aerobic conditions mainly as blackish-brown to black colored, poorly soluble Mn(IV) oxide. Mn oxides occur in soils, like the Fe(III) oxides, as mottles, particle coatings (Mangans), concretions and crusts.

The mineralogy and chemism of Mn oxides (Table 2.7) are more diverse than those of Al and Fe oxides, because in addition to the tetravalent Mn, they may also contain Mn^{3+} and Mn^{2+}, and absorb cations such as Li, Na, K, Ca, Ba, Al and Fe for charge compensation. For this reason, like the clay minerals, Mn oxides are often non-stoichiometrically composed.

Only a few of the oxides have been reliably identified in soils until now. They belong to the **phyllomanganates**, consisting of MnO_6 octahedral layers with an interlayer distance of 0.7 or 1.0 nm. The 0.7 nm mineral with an H_2O layer is called **birnessite**, and the form that is expanded to 1 nm due to the embedding of a second H_2O layer is called **buserite**. The substitution of Mn^{4+} by Mn^{3+} and Mn^{2+} creates a negative charge in the MnO_6 layers, which is compensated by cations like Na^+, K^+, Mg^{2+} and Ca^{2+} between the layers. In **lithiophorite**, a Li–Al hydroxide layer is incorporated between the MnO_2 layers. Poorly crystallized forms of the layer types are called Vernadite (ə-MnO_2).

Tunnel manganates occur more rarely in soils, in which the MnO_6 octahedral chains form tunnels of variable size that absorb exchangeable cations and water. These include the MnO_2 forms **todorokite**, K-containing **cryptomelane**, Ba-containing **hollandite**, and rarely found in soils **pyrolusite**.

The Mn oxides, like the Fe oxides, have a low solubility, but can be subject to microbial reduction and thus dissolved. Because Mn(IV) oxides are more easily reduced than Fe(III)

oxides (Sect. 4.3) and Mn^{2+} is only reoxidized with the help of bacteria, manganese is more mobile in a reducing environment. For this reason, manganese oxides are more likely to occur in soils as separate accumulations and are less likely to be associated with iron oxides. Manganese oxides have a high affinity to many heavy metals, especially to Co, Ni, Pb and Zn, and therefore co-accumulate these metals.

2.2.7 Carbonates, Sulfates, Sulfides and Phosphates

The most common carbonate is $CaCO_3$, which occurs as calcite, more rarely as aragonite. Carbonates with several cations are also widespread, such as **dolomite** ($CaMg(CO_3)_2$, 13.1 % Mg) and **ankerite**, $CaFe(CO_3)_2$, which usually also contains Mg and Mn. Calcite and dolomite are the main minerals of carbonatic rocks: limestone and dolomite (Alaily 1996, 1998 and 2000).

In soils, calcite and dolomite are generally inherited from the rocks. In the lower part of soils in temperate humid regions, calcite is formed from dissolved $Ca(HCO_3)_2$ that was eluviated from the upper profile sections. It coats the inside of the pores, or often occurs in loess soils as lime concretion (loess puppet). Calcitic precipitations from $CaCO_3$-rich groundwater are called meadow, spring or floodplain lime. In semi-arid regions, lime crusts are formed, called **calcretes**. The formation of dolomite (dolocretes) in soils has only been observed in isolated cases. **Siderite** ($FeCO_3$) is formed both in sediments and in soils under predominantly anaerobic conditions, e.g. in fens and in association with goethite in bog iron.

Anhydrite ($CaSO_4$) and **gypsum** ($CaSO_4 \cdot 2H_2O$, hardness 2) are the main components of gypsum rocks. Gypsum occurs in small amounts in many sediments and soils, especially in arid areas. Furthermore, it is formed as an oxidation product from sulfides.

For example, a K-Fe hydroxysulfate, the light yellow **jarosite**, $KFe_3(OH)_6(SO_4)_2$, is found as an oxidation product of sulfides, in addition to gypsum, in acid sulfate soils at pH 2–3.

The occurrence of **baryte** ($BaSO_4$) is more rare. Other salts, especially soluble sulfates and chlorides, and to a lesser extent also nitrates and borates of Na, K and Mg, are sometimes found in large quantities in marine and continental deposits (salt deposits), but also in soils of arid regions.

Among the sulfides, the two forms of iron disulfide (FeS_2), **pyrite** and **marcasite**, are the most common representatives. Finely-grained and therefore black FeS_2 is widely distributed in clayey sediments that were formed under anaerobic conditions, but also in reduced soils, coloring them dark. Iron monosulfide with variable composition ($Fe_{1-x}S$) and low crystallinity is usually a young formation in anaerobic sediments and soils, and could be the instable precursor of pyrite ($FeS + S \rightarrow FeS_2$). Sulfides such as **greigite** (Fe_3S_4) can also be directly formed by bacteria in sediments and soils. The forms of heavy metal sulfides (e.g. those of Cu, Pb, Zn etc.) are particularly diverse.

Apatite, $Ca_5(PO_4)_3(OH, F, CO_3)$ is the most important phosphate mineral that primarily supplies the nutrient phosphorous to the pedosphere and biosphere. It has both igneous and pedogenic origins. Another, frequently occurring pedogenic Fe^{2+} phosphate, e.g. in fens (ground water peat), is **vivianite**, $Fe_3(PO_4)_2 \cdot 8H_2O$, which is white oxidizes at the surface when exposed to air and turns bright blue.

2.3 Rocks

Rocks are solid or unconsolidated, natural mineral mixtures of the crust of the Earth. Their mineralogical composition must be uniform over a certain spatial, geologically significant extent. The most important or highest classification criterion of rocks is their genesis. The three main types of origin are: hardening or cooling down of magma (magmatism), sedimentation in the ocean or on land (sedimentation), and transformation under the effect pressure and heat (metamorphism). Classifications at lower levels and designations of the types of rocks are based on the

mineralogical composition (e.g. mica schist), the chemism (e.g. acidic, intermediary, basic igneous rock), the texture and structure (e.g. coarse-grained/fine-grained granite), the formation site (e.g. plutonite, vulcanite), the fossil content (e.g. Bryozoan limestone) and the type locality (adamellite, tonalite) (Wedepohl 1969; Wimmenauer 1985).

2.3.1 Igneous Rocks

Igneous rocks are formed from the hardening of molten magma either deep in the Earth's crust (plutonites or intrusive rocks) or at the Earth's surface (vulcanite or extrusive rocks). In both groups, the rocks are classified according to their chemical SiO_2 contents into acidic, intermediate, basic and ultrabasic igneous rocks. The designation "acidic" or "basic" refers to the silicic acid content. The mineral constituents essentially depend on the SiO_2 content, which is used to define the various igneous rocks. Figure 2.21 shows this for the most important representatives of the plutonites (top row) and vulcanites (bottom row), and Table 2.8 summarizes their chemism. In Si-rich 'acidic' rocks, quartz, alkali feldspars, Na-rich plagioclases and micas dominate, and Si-poor 'basic' rocks are dominated by Ca-rich plagioclases and dark, Fe-containing pyroxenes, amphiboles and olivines. Therefore, acidic igneous rocks are usually light in color, and the basic igneous rocks are dark (Carmichel et al. 1974).

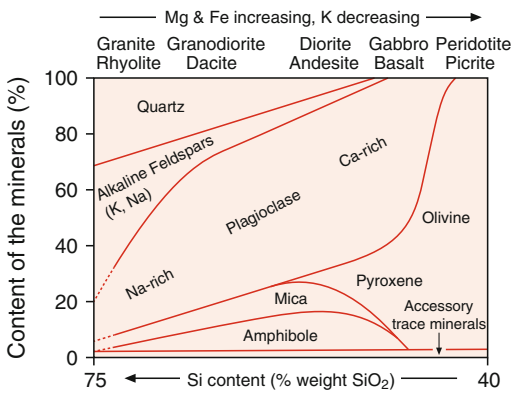

Fig. 2.21 The most common igneous rocks and their mineral constituents (after E. Murad)

The chemism of igneous rocks varies according to the mineralogical constituents. As can be seen in Table 2.8, the Ca, Mg, Fe, Mn and initially also the P content increase when the Si content decreases, while the K content decreases. The corresponding intrusive and extrusive rocks concur largely in their chemical composition, however, they differ significantly in their structure (Fig. 2.21). In plutonites, the slow cooling results in relatively coarse grained minerals (e.g. with granites; from the Latin *granum* = grain), while the fast cooling of vulcanites results in a fine crystalline or even glassy matrix, in which individual coarser crystals (inclusions) can be embedded that were formed as early crystallisations out of the liquid magma (e.g. porphyric structure).

Among the igneous rocks in the crust (mass $\sim 2.85 \times 10^{19}$ t), the granites and granodiorites account for 22 % vol., the basalts and gabbros for about 43 % vol. The rest are sedimentary and metamorphic rocks (Table 2.8). However, igneous rocks are only found to a limited extent at the surface of the earth, and are often restricted to mountainous terrain (Fig. 2.22). Granites are widely distributed in the Bohemian Massif with its bounding ranges (Riesengebirge, Erzgebirge, Fichtelgebirge, Bavarian Forest and Bohemian Forest), in the Black Forest and in the Harz, while continuous basalt masses are only found in the regions of the Vogelsberg and the Rhön, as well as in Bohemia. Larger areas of acidic igneous rocks are found in Scandinavia, the Central Alps, the Carpathians, in China, Canada, West Africa and the pacific cordillera of North and South America. Large areas of terrestrial basalts ('plateau basalts') and andesite as well as their glass-rich equivalents are found e.g. in East Africa, Central India, Asia (China, Japan, Indonesia, Philippines), South Brazil (Paraná basin) and again in the cordillera of North and South America. Basic plutonites (gabbro, norite) are known in Germany from the Odenwald and Harz, much larger occurrences lie in Greenland, Scandinavia, Russia, Canada and Africa (South Africa, Zimbabwe).

Table 2.8 Average chemism (mass %, acc. to Nockolds in Wedepohl 1969) and mineral constituents (vol. %, acc. to Wedepohl 1969 and Wimmenauer 1985) of common igneous rocks

	Plutonites				Vulcanites		
	Granites	Grano-diorites	Gabbros	Peridotites	Rhyolites	Andesites	Tholeiitic basalts
SiO_2	72.8	66.9	48.4	45.5	73.7	54.2	50.8
TiO_2	0.37	0.57	1.3	0.81	0.22	1.3	2.0
Al_2O_3	13.9	15.7	16.8	4.0	13.5	17.2	14.1
Fe_2O_3	0.86	1.3	2.6	2.51	1.3	3.5	2.9
FeO	1.7	2.6	7.9	9.8	0.75	5.5	9.0
MnO	0.06	0.07	0.18	0.21	0.03	0.15	0.18
MgO	0.52	1.6	8.1	34.0	0.32	4.4	6.3
CaO	1.3	3.6	11.1	3.5	1.1	7.9	10.4
Na_2O	3.1	3.8	2.3	0.56	3.0	3.7	2.2
K_2O	5.5	3.1	0.56	0.25	5.4	1.1	0.82
H_2O	0.53	0.65	0.64	0.76	0.78	0.86	0.91
P_2O_5	0.18	0.21	0.24	0.05	0.07	0.28	0.23
Quartz	27	21	–	–	30	5	–
K feldspar	35	15	–	–	40	11	–
Plagioclase	30	46	56	–	25	55	40
Biotite	5	3	–	–	2	–	–
Amphiboles	1	13	1		2	15	–
Pyroxenes	–	–	32	26	–	10	40
Olivine	–	–	++[a]	70	–	–	5
Magnetite and Ilmenite	+	+	2	3	+	2	6
Apatite	+	+	+	+	+	++	+

[a]+ and ++ indicate contents below the percent range

2.3.2 Sediments and Sedimentary Rocks

2.3.2.1 General

The rocks on land are exposed to the 'weather', i.e., they are weathered. As explained in Sect. 2.4, this results in solid and dissolved degradation products and new minerals, which form soils together with the transformation products from the vegetation (Fig. 2.1). Solid and dissolved products are eroded or eluviated by ice, water, wind and gravity, and deposited or precipitated (sedimented) at other, generally lower sites (valleys, lakes and oceans); unconsolidated sediments are formed. These consist of more or less unaltered minerals (detritus) as well as newly formed minerals (Füchtbauer 1988; Tucker 1996).

The formation of sediment is therefore based on the process sequence weathering → erosion → transport → deposition and is often caused by soil formation (Fig. 2.1). This process sequence varied during the course of Earth history, e.g. due to climate change, fluctuations in the sea level, glaciation or tectonics. As a result of this, periods of soil formation on stable land surfaces with weathering and vegetation-friendly climate alternated with periods of soil degradation and sediment formation under vegetation-hostile climates.

If the sediments consist mainly of mechanically transported, largely unchanged rock

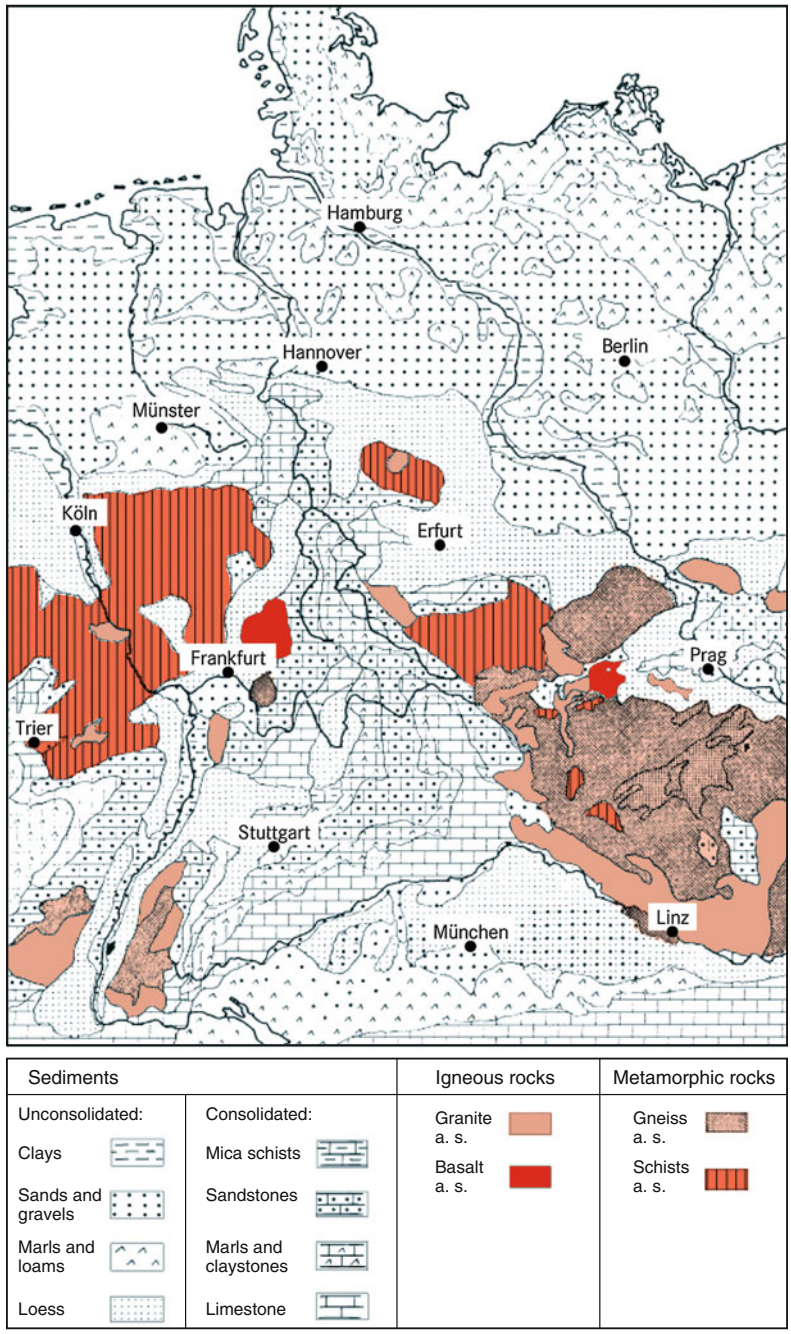

Fig. 2.22 Distribution of igneous rocks, metamorphic rocks and sediments in Central Europe (adapted by E. Schlichting) (a.s. = and similar rocks)

material, they are referred to as **clastic** sediments. Their grain size depends on the mobility of the grains in the transport medium (wind, water, ice) and the length of the transport path, i.e. unsorted (e.g. in moraines) or relatively homogeneous, i.e. sorted (e.g. in eolian sands). In contrast, if the sediments owe their mineral composition mainly to precipitation from the solution or biological processes (biomineralization), they are called **chemical** or **biogenic** sediments. Furthermore, sediments can be designated according to the transport medium (e.g. ice: glacial; wind: eolian)

and the deposition site (mainland: terrestrial; river: fluvial; lake: lacustrine; ocean: marine).

For clastic sediments, the different grain sizes are sorted according to the transport strength of the transport medium depending on their weight, and are thus predominantly sorted by size. Fine-grained sediments are formed with low transport forces, coarse grained with high transport forces. Rapid changes in the transport force, e.g. in river valleys, river deltas, basins and coasts, therefore lead to mixed layers between clays, silts, sands and gravels. Such mixed layers are found e.g. in the pre-alpine Molasse basin, where the erosion material from the forming Alps and the surrounding continents accumulated with alternating depositional environments (partly marine, partly fluvial and lacustrine).

All sedimentary rocks are initially deposited in loose beds, but can be consolidated over the course of time through cementation and/or the load from overlying sediments through the process of **diagenesis** to form **sedimentary rocks**. Cementation is caused by clays, Ca–Mg carbonates as well as Si and Fe oxides, which are precipitated out of correspondingly composed aqueous solution in the pore space. The load increasingly presses water out of the sediments, beds them more densely and arranges parallel sheet-formed structure of sediments. These processes both increase the contact area between the mineral grains and also the strength of the rock. In general, more and more consolidated sedimentary rocks are found with increasing geological age; Quaternary sedimentary minerals are therefore predominantly (unconsolidated) sediments, while Mesozoic and Paleozoic deposits are sedimentary rocks. These can be weathered, eroded and transported again (Fig. 2.1), so that in some cases, sediment can be subject to repeated cycles of weathering, transport and redeposition (see Sect. 2.1). Sediments can be usually recognized because they are layered and typically contain minerals in sedimentary environments such as clay minerals, carbonates, and fossils, and they accumulate stable primary minerals (e.g. quartz, rutile, zircon, heavy minerals).

The chemical and mineralogical composition of sediments varies greatly, even among those with the same name. In general, the quartz content increases and the silicate content decreases with increasing Si content (Table 2.9). Higher K contents usually indicate rocks with higher contents of potassium feldspars, micas or illites (graywackes, claystones, loess), higher Mg contents indicate rocks rich in chlorite and clay mineral (graywackes, claystones) or dolomite (dolomite), and higher Ca contents indicate calcite-rich rocks (carbonate rocks, loess).

Sediments and sedimentary rocks only account for approx. 8 % of the earth's crust, and about half of these are claystones, the rest are sand and carbonate rocks in about equal proportions (Table 2.1). However, sediments and sedimentary rocks cover about 75 % of the surface of the planet, and are therefore very significant for soils. Therefore, the average chemical composition of surface-near rocks sometimes differs greatly from that of the earth's crust (Table 2.1). The (consolidated) sedimentary rocks mostly form mountainous landscapes, while plains and valleys are filled with loose sediments.

The distribution of the individual types of sediment is generally on a smaller scale than that of igneous and metamorphic rocks, so that only a few large-scale occurrences are mentioned in the following.

2.3.2.2 Coarse Grained Sediments (Psephites)

Coarse-grained (>2 mm) sediments include scree (angular rock fragments) and pebble or gravel (rounded rock fragments). The predominant particle sizes >2 mm in angular rock fragments are called grit, and in rounded rock fragments, correspondingly, are called gravel/pebbles. Angular rock fragments indicate a high transport force, and are found in mountainous areas near the erosion site and in the valleys, where they are mainly glaciofluvial. Angular rock fragments are consolidated to form breccia, and pebbles form conglomerate (e.g. Nagelfluh). Sediments containing very coarse components in a fine-grained

Table 2.9 Average chemism (mass %) and mineral constituents (vol. %) of sediments (from Wedepohl)

	Sand-stones[e]	Gray-wackes	Claystones Pelites	Carbonate rocks	Eolian sand[a]	Loess[a]	Marly glacial till[a]
SiO_2	70.0	66.7	58.9	8.2	96.8	72.8	64.2
TiO_2	0.58	0.6	0.78	n.d.[f]	n.d.	0.77	0.48
Al_2O_3	8.2	13.5	16.7	2.2	1.3	8.6	6.3
Fe_2O_3	2.5	1.6	2.8	1.0	0.2	2.4	n.d.
FeO	1.5	3.5	3.7	0.68	n.d.	n.d.	3.2
MnO	0.06	0.1	0.09	0.07	n.d.	n.d.	0.06
MgO	1.9	2.1	2.6	7.7	0.1	0.85	1.0
CaO	4.3	2.5	2.2	40.5	0.1	5.1	9.7
Na_2O	0.58	2.9	1.6	n.d.	n.d.	n.d.	0.7
K_2O	2.1	2.0	3.6	n.d.	1.1	2.6	2.1
H_2O	3.0	2.4	5.0	n.d.	~0.5[c]	n.d.	2.4[c]
P_2O_5	0.1	0.2	0.16	0.07	n.d.	n.d.	0.11
CO_2	3.9	1.2	1.3	35.5	n.d.	3.4	7.7
Quartz	82	37	20	–	85	40–45[d]	38
K feldspars	5	28	10–15	12	13	10–15	16
Mica[b]	8	29	45–55	12	2	20	22.5
Chlorite	–	29	14	–	–	1	2
Kaolinite	–	29	14	–	–	2	–
Calcite	3	3	3	53	–	10–15	17.5
Dolomite	3	3	3	35	–	–	4
Sulfides	0.07	–	0.8	0.3	–	–	0.7

[a]Individual analyses by E. Schlichting and H.P. Blume (eolian sand, marly glacial till) and D. Schroeder (loess)
[b]Including three-layered clay minerals
[c]Including organic matter
[d]Values for Central German loess
[e]The chemism is based on sandstone in the broad sense, the mineral constituents on sandstones in a more strict sense
[f]Not determined

matrix indicate special deposition conditions. Bomb tuffs are formed when lava fragments fall into volcanic ash, or suevite when molten fragments fall into debris, or with mudflows into lakes or marginal seas like with greywackes.

2.3.2.3 Sands and Sandstones (Psamments)

Sands and sandstones are sediments or sedimentary rock with more than 50 % of the particle size fraction being sand (0.063–2 mm). The second most common components can be added to the name (e.g. silty sandstone with 25–50 % silt).

Sands are generally coastal or continental Cenozoic deposits by water, e.g. from the melt water of glaciers, as well as by wind (eolian sands, dune sands). Various proportions of fine, medium and coarse sand characterize the particle size distributions of the different sands.

Sandstones are found in all geological periods. In the strict sense, sandstones contain >75 % quartz. Red sandstones colored by hematite from the Paleozoic and Mesozoic (old red and young red sandstones) are widespread.

Greywackes are dark grey sandstones containing mica and chlorite and rich in rock

fragments, while arkoses contain kaolinite and are rich in feldspars.

2.3.2.4 Silts and Siltstones, Clays and Claystones (Pelites)

The texture of silt sediments is dominated by the 2–63 µm particle size fraction. The most well-known and significant silt sediment in soil science is **loess** (see Sect. 2.3.2.6). Silt-rich sediments are also formed in lakes with high sediment input.

Clays are sediments with high contents in the <2 µm particle fraction. They are dominated by the generally platy clay minerals, giving clays their plasticity. **Silt sediments,** in contrast, are non-plastic. In addition to clay minerals, quartz, feldspars and micas occur in both types, but also calcite, pyrite, Fe oxide and other minerals. Clays are generally formed under calm sedimentation conditions with low water transport forces.

With the diagenesis of clays and silts, water is pressed out and the platy clay particles are bedded densely parallel to each other, so that they turn into claystones and silt stones. In doing so, they progressively loose their plasticity. Claystones and siltstones are widespread in the Southern German cuesta landscapes, and claystones in the Rhenish Slate Mountains on either side of the Middle Rhine.

Poorly consolidated claystones are often easily eroded, and therefore form plains. Naturally, claystones give rise to clayey soils (Vertisols, *germ*. Pelosols).

2.3.2.5 Carbonate Rocks and Marls

Carbonate rocks are rocks with >5 % Ca and Ca–Mg carbonates, predominantly as calcite and dolomite. They can be classified according to their carbonate content into **limestones** with >75 % and **marl** with 25–75 % carbonate. There are transitions to claystones and sandstones. Carbonate rocks usually contain a few percent Mg, which is mainly attributed to additions of dolomite. If the dolomite content is >50 % (Mg content > 6.6 %), they are called **dolomites**. Most carbonate rocks were formed biogenically in the ocean, so that they often have a high fossil content. They occur as unlayered compact limestones (e.g. 'reef limestone') and as broad-bedded to thin-layered limestones.

During soil formation from carbonate rocks, the carbonates are dissolved and transported away. The non-carbonate dissolution residues (mainly layered silicates and quartz) form the mineral constituents of these soils (e.g. Rendzic Leptosol, Lixisol).

2.3.2.6 Quaternary Sediments

Unconsolidated sediments that were formed during and after the Quaternary glaciation are very significant for soils. They are discussed here separately according to their genesis, although they could also be classified into the scheme above.

(a) **Loess, sands, floodplain sediments and mud**
During the Quaternary glaciation, silt-rich material was blown out of the periglacial, vegetation-poor melt water and frost debris or rubble floodplains, tundra and arctic arid regions, which was then deposited with rainfall, decreasing winds or on the lee side of hills: loess. In recent times, wind-blown silts mainly come from hot deserts (e.g. Sahara). The Pleistocene loess belt stretches from France over the northern edge of the central European low mountain range in the Ukraine and towards Central Asia. There are other large loess areas in North America and in Argentina. In Germany, the loess thickness varies from a few decimeters up to 140 m, but it can also reach several 100 m, e.g. in China. However, a thin loess layer (4–6 dm) also covers large areas of higher terrain up to 600 m a.s.l.
Loess usually contains carbonates, is yellow in color and has a pronounced maximum grain size between 10 and 60 µm in diameter; its clay content in Central Europe is of 10–25 %, the silt content of 65–80 %, and the sand content of 10–15 % (mainly fine and medium sand). Illite dominates the clay mineral constituents in Central German loess (Table 2.9); in contrast, Southern German loess contains higher proportions of smectite. Because it was blown out of carbonate-rich deposits, the

carbonate content of Southern German loess can account for up to 35 %; in Central Germany, it is usually of 5–20 %. A coarse--grained variation of loess is **sand loess**, occurring in several patches in North and South Germany, but also at the border of loess belts like Western China, Southern Argentina or Southern Israel.

Pedogenesis began under the humid climate conditions of the post-glacial period. During this time, the carbonates in the loess of Central Europe were leached up to depths of about 0.8–1.5 m (decalcification), and the light-yellow loess was transformed into yellowish-brown loess loam through iron oxide and clay formation (brownification). Soils with higher natural fertility were formed, e.g. Chernozems and Luvisols.

In addition to loess, sands were also blown out of areas with little or no vegetation, so-called **eolian sands**, which are found all over the world as shifting sand covers or hill systems (dunes). They are found especially at coastal or valley margins, where they were populated by plants during the Holocene and thus included in pedogenesis. In deserts, eolian sands cover large areas (e.g. Sahara 28 %, Arabia 26 %, Australia 31 %). The maximum grain sizes of eolian sands are of 0.2–0.6 mm; they are generally rich in quartz, and can also be rich in calcite or gypsum in arid areas.

Loose sediments are deposited in river valleys, deltas and at the coasts around the world, their grain size ranging between gravel and clay depending on the transport conditions. The sediments in river valleys are called **fluvial sediments** (or floodplain loams), and those at the coasts are called tidal flat muds and **sands** (Chaps. 7 and 8). Young anthropogenic sediments with variable grain sizes are called **colluvium**, which are often formed at the hillside toe when soils on slopes are used for agriculture and are therefore more strongly eroded (see Chap. 7).

(b) **Glacial sediments**

When glaciers are melting, they leave moraines and lake basins behind in the areas formerly covered by the glacier, and river terraces and sands in the areas in front of the glacier. **Moraine** material is usually poorly sorted and contains large rocks, the so-called boulders, and depending on the texture and carbonate content, is called **glacial till, boulder clay, boulder marl** or glacial sand. The former glacier boundaries were marked by wall-shaped, often sandy-gravelly terminal moraines, in which the crushed gravelly sediments are better sorted than in the ground moraines, because the fine material was washed out by melt water during the glacier's retreat. The fluvioglacial gravels of the river terraces formed at the foot of the glaciers, sands of the melt water areas, and lacustrine silts and clays in glacier tongue formed closed basins are also better sorted than moraine material.

Glacial sediments cover large areas of the Pleistocene Arctic glaciation in the northern part of the entire northern hemisphere, and of the alpine glaciers in high mountains and at their base (Alps, Himalayas, Cordilleras etc.).

(c) **Periglacial cover beds (scree) and cryogenic substrates**

Periglacial cover beds (scree) and cryogenic substrates are loose sediments that moved freely on slopes (>2°) as a slurry over frozen underground. They occur at annual mean temperatures around −2 °C in permafrost regions. In the today temperate zones, they were formed during the Pleistocene and are mainly found now in low mountain ranges as a 1–4 m-thick cover, consisting of several layers above various unconsolidated rocks or bedrock. **Solifluction material** can be recognized by the arrangement of stones parallel to the slope, flow patterns, and often platy structure.

They often display a regular sequence of basis (Basislage), main (Hauptlage), top (Oberlage) and cover layers (Decklage) (German soil description rules). The texture and mineral constituents of **solifluction material** are determined by the parent material and can therefore vary considerably. **Solifluction material** is often rich in silts,

because thin loess layers are transported and mixed with frost debris from the underlying rock. Stone-rich **solifluction material** is called solifluction debris. Cryogenic soils occur on level terrain due to **cryoturbation** triggered by freeze/thaw cycles.

2.3.3 Metamorphic Rocks

Igneous and sedimentary rocks can be so strongly altered by high pressure, high temperature and tectonic movement (metamorphism) that they sometimes turn into an entirely different rock, called metamorphic rock. Metamorphic rocks originating from igneous rocks have the prefix **ortho-** (e.g. **orthogneiss**), and accordingly, those originating from sediments have the prefix **para-**. Depending on the parent material and the degree of metamorphism, they can have very different chemical properties and especially mineralogical properties. Higher pressures and/or temperatures result either from the high load applied by overlying thick layers of rock, or from the formation of mountains (regional metamorphism). Furthermore, rocks can be transformed by contact with hot magma (contact metamorphism).

Metamorphism begins at about 200 °C and, except for contact metamorphism, 200 MPa (corresponding to a depth of 7 km), and reaches up to about 600–700 °C and 1–2 GPa (corresponding to a depth of 35–70 km). Typical for metamorphism is the transformation of a mineral inventory defined by the parent material into a new mineral association adapted to the pressure and temperature conditions. It changes the rocks much more drastically than diagenesis (Sect. 2.3.2.1), because the minerals are aligned, coarsened and transformed. The chemism of the rocks hardly changes, unless there is migration of pore solutions (metasomatism).

The alignment of the minerals, i.e. the parallel arrangement of sheet or platy minerals perpendicular to the main direction of pressure, results in schistosity, a characteristic feature of many metamorphic rocks. The position of the schistosity areas in the crystalline rock is usually not identical with the position of the layers in the parent sediments. Coarser calcite crystals (sugar like grains) result e.g. from the metamorphism of carbonate rocks to **marble**. Typical new minerals include mica (sericite), epidote, chlorite, serpentine, talc, garnet, disthene, staurolite, andalusite and sillimanite.

Gneiss is a common metamorphic rock, originating from granite (orthogneiss) or various Si-rich sediments (paragneiss) and accounting for approx. 20 % of the lithosphere (Table 2.1). In terms of their mineralogy, they are often similar to granites or diorites (>20 % feldspars), but differ from these because especially the mica plates or platelets are arranged in parallel. **Phyllites** and **mica schist** (<20 % feldspars) are also widespread, usually originating from clays, claystones greywacke**s**. While there are hardly any micas in claystones, they can already be clearly seen in phyllites as fine flakes, and in the form of larger crystals in mica schists. Si-poor igneous rocks (e.g. basalt) are transformed into **green schist**, **amphibolites** and **eclogites**. High-purity limestones are changed into marble, marls are transformed into mica schist with highly variable mineral constituents, depending on the degree of metamorphism. **Quartzites** are formed from the metamorphism of quartz-rich sands and sandstones. Contact metamorphism of siliceous rocks results in very fine, massive **hornfels**. Under very strong metamorphic conditions, there is initially partial melting (anatexis) and finally, total melting (diatexis) of the rocks.

Metamorphic rocks are most commonly found worldwide in the old continental shields (cratons), which were later exposed through erosion or covered with younger rocks (basal complex or basement). They form large areas in Scandinavia and Canada, where they are often covered with Quaternary sediments. There are continuous areas of metamorphic rocks in the tropics and subtropics (West and Central Africa, Brazil, West Australia, India). Younger metamorphic rocks are found in the alpinotype mountains (Alps, Himalayas, Andes etc.). In Central Europe, metamorphic rocks are found e.g. in the Black Forest, in the Vosges, the Bavarian-Bohemian Massif, the Rhenish Massif, the Harz and the Central Alps.

2.3.4 Anthropogenic Substrates

Especially in urban industrial areas, humans relocate naturally developed soil or rock material, and/or deposit technogenic substrates. Soils also develop from such anthropogenic substrates or mixed substrates.

Relocated natural substrates are usually from soil removal by leveling and excavation for construction projects (buildings, verges and road cuts, railroad cuts and canals), some of which are spread over an area, and some are piled up in banks, dams or hills. Large-scale mine piles, some of which were populated at a later time, were created due to the mineral extraction of e.g. coals and ores. A very special form of natural substrate is the broken igneous rock used as rail pavement in railway construction, where the interstices of the crushed rocks can contain transported dusts (soil material, emissions) and formerly also soot from steam engines; it serves as a harsh rooting medium and arid site for wild plants. The fill can be attributed to dumping or flushing. Both lead to stratification: In general, dumped rock is bedded more loosely than flushed material, but it can be compacted with leveling.

The relocated substrates are divided according to their textures, because these strongly influence the ecological properties of the soils that develop from them.

Most mine piles from coal mining (e.g. in the Ruhr, Saxon, British and American coal mining areas) contain pyrite. Within a few years, the pyrite is oxidized with the participation of bacteria (e.g. *Thiobacillus ferrooxidans*) to form Fe (III) oxides and sulfuric acid (Chaps. 5, 6, Sect. 8.2). Depending on the pH, jarosite, schwertmannite, ferrihydrite or goethite are formed.

Already during Roman and medieval times, dwelling mounds were often covered with topsoil material or sod. The current building regulations prescribe that the 'topsoil' be separately removed and spread back over the surface after termination of the construction measures.

Artificial **technogenic substrates** are defined as fill made of material that was created or strongly altered by humans, such as brick, mortar, concrete, slag, waste, sewage sludge or ashes. It is not only characteristic for these substrates to contain highly variable solids, minerals are per definition of natural origin but also a pronounced heterogeneity in the composition and the contaminants. These substrates therefore differ greatly in their properties and lead to very different soils (Sect. 8.7.4).

Building rubble usually consists of a mixture of brick and mortar debris with 20–75 % porous rocks, 5–10 % limestone, and various proportions of gypsum. Brick debris from the Middle Ages can also be completely free of carbonates. Secondary components may include ashes, coal, concrete, gypsum, metals, glass and porcelain fragments, leather and bones.

Ashes may occur as fine-grained fly ash, or as more coarse-grained boiler ash from coal fired power station or waste incinerating plants. They generally react strongly alkaline (pH values 8–12). Ashes from coal combustion are low in carbonates (<0.5 %), and those from waste incineration are rich in carbonates (>10 %). They were spread over areas or dumped on mine piles, but fly ashes also hydraulically pumped and cover large areas.

Slags from blast furnaces (with lump slag, foamed slag and slag sand) or steelworks are coarse-grained, porous, calcareous and react strongly alkaline (pH values 9–12), in contrast, gasworks slags react very acidic. They are found in mine piles or as building material for structural, underground and traffic route engineering.

Waste is divided into household waste, oversize waste, trade waste, road litter and industrial hazardous waste. Household waste contains materials such as ashes, metals, glass and ceramic fragments, rubber, cardboard, leather, bones, plastics, wood and other substances. Since the introduction of waste separation, plant material should mainly be disposed of in the organic waste bin, making it rich in protein and thus readily decomposable by macro- and micro-organisms. Waste is fine to coarse grained and reacts alkaline. Its lime content fluctuates greatly (especially depending on the proportion of building rubble). Waste was formerly disposed of over large areas

or used to fill depressions (e.g. gravel quarries), and today, it is stored in the form of compact, supervised dumps or incinerated in waste combustion facilities (thermal power plants); the resulting slags and ashes are landfilled.

Sewage sludge is the residues from wastewater treatment. Fresh sludge from the mechanical treatment is inhomogeneous; in contrast, decayed or rotten sludge is fine-grained and homogeneous. Sewage sludge is rich in readily decomposable organic matter, however, depending on the type of conditioning, it may also contain higher amounts of carbonates and metal sulfides. It reacts strongly alkaline and is generally landfilled as rinsed material, unless it can be used as a soil conditioner on fields (see Sect. 7.4).

Industrial sludge comes from the treatment of commercial and industrial wastewater. There are more than 100 different kinds of sludge, depending on the sector, with highly variable properties: sludge from the metal-working industry is generally rich in metals and poor in carbonates; tar and oil sludge as well as lacquer and paint sludge contains a wide variety of organic compounds, lime sludge is rich in carbonates; paper pulps represent a mixture of cellulose, lime and kaolin clay, sludge from flue gas desulfurization is rich in gypsum; sludge from breweries, distilleries, dairies and the food industry is rich in readily decomposable organic matter, contains bentonite or diatomaceous/infusorial earth.

2.4 Weathering

Minerals in igneous and metamorphic rocks were formed under completely different physicochemical conditions, as they occur in soils, the direct contact between the lithosphere, atmosphere, hydrosphere and biosphere. As a result, parent materials and their minerals weather in soils. In addition to humification, weathering is the most important matter-altering process of soil formation; it comprises a multitude of physical, chemical and biotic processes.

2.4.1 Physical Weathering

Physical weathering causes the decay of rocks and minerals into smaller particles, without altering the minerals chemically. It is mainly initiated by pressure release of overburden, by temperature, ice and salt bursts, through root pressure, as well as through mutual mechanical strain in the rocks.

When solid bedrock is gradually freed from overlying rock or ice masses by erosion, the load is reduced and they expand as a result of the **pressure release**. This leads to the formation of joints, and cracks, where the other forces of physical weathering can attack.

Among these forces, the effect of **temperature bursting** increases the greater the range of the temperature fluctuations and the greater the speed of temperature change. Extreme values are reached e.g. in high mountains and in subtropical and tropical deserts. Daily fluctuations of 30–50 °C were measured in deserts with annual mean temperatures of >17 °C. The temperatures of rock surfaces reached up to 84 °C, and then dropped to 20–30 °C within a short time due to rain. Because the thermal conductivity of rocks is low, their outside and inside are warmed or cooled at different rates through rapid changes in temperature. Therefore, they expand or contract differently, leading to pressure differences reaching up to 50 MPa. This results in fissures parallel to the surface, but also to cracks straight through larger boulders (core cracks). Rock flakes break off the surface and rock boulders fall apart into sharp-edged rubble. This process is accelerated by different color and expansion coefficients in adjoining mineral grains. Granite is more easily decayed than basalt, because it has a coarser structure and consists of light- and dark-colored minerals.

The effect of **ice bursting** (cryoclastic) can be even stronger than the bursting effect caused by temperature differences. This is based on the properties of water, which increases its volume by about 10 % when it freezes. For this reason, ice is able to develop a considerable bursting effect in rock fractures and cracks. Jointed rocks and minerals with good cleavability, such as

micas and feldspars, are particularly vulnerable. The bursting effect, which can reach a pressure of 210 MPa with temperatures dropping down to −22 °C, only reaches its maximum potential if the ice cannot expand into voids that are filled with air, i.e., if the cracks or pores are closed by a firmly adhering ice plug during cooling. As a result, the effect of ice bursting increases with the size of the joint and pore volume, the degree of water saturation, and above all, the frequency of freeze-thaw cycles. Ice bursting transforms solid rock into angular rock fragments, grit, sand, silt and even coarse clay. Its effect is particularly strong in climate regions where there are frequent alternations between freeze and thaw periods (e.g. in periglacial regions; see Sect. 8.2.1.1).

Salt bursts work similarly to ice bursting. In arid regions (hot and cold deserts), dissolved substances are not eluviated, accumulating in the soil and on the outer surfaces of rocks with the evaporation of water. If salts crystallize out of oversaturated salt solutions, significant pressure can arise if the sum of the volumes of the saturated solution and the precipitated crystals is greater than the volume of the oversaturated initial solution. The volume can also increase through the formation of hydrates, e.g. when anhydrite, $CaSO_4$, turns into gypsum, $CaSO_4 \cdot 2 H_2O$. This may result in pressures of several tens of MPa. Analogous to with ice bursting, salt burst is promoted by frequently alternating drying and wetting cycles.

Mechanical weathering of rocks can also take place through swelling and shrinking processes in layered silicates. The hydration of cations in the interlayer space of such silicates takes place in stages, where, e.g. in smectites, up to four layers of water molecules are incorporated (**intracrystalline swelling**). The swelling pressure arising from the embedding of the first water layer is of ~400 MPa, and from the second and third layers of ~110 and ~27 MPa. If claystones with dehydrated layered silicates are exposed at the surface through erosion, the load becomes lower than the swelling pressure and the layered silicates can take up water layers and increase in volume.

Further expanding takes place through **osmotic swelling**, where the water between the clay particles diffuses, and dilutes the higher ion concentration in the diffuse double layer surrounding it relative to the outer solution. However, the pressures generated by osmotic swelling are much lower, only around 2 MPa.

Plant roots can also penetrate into fissures and cracks and press rocks (root burst) apart through their growth (thickening). This results in pressures of max. 1–1.5 MPa.

The rock fragments formed by physical weathering are rubbed and hit against each other during transport by ice, water or wind. This mechanical strain rounds the rock fragments and creates fine material, occurring faster and more strongly when the individual mineral grains are softer and easily divided. Feldspars, micas and amphiboles and pyroxenes are therefore more rapidly reduced to small fragments than quartz. For example, to be reduced to a size of 2 cm in a creek with 0.2 % slope, a 20 cm large granite boulder would have to be transported over a distance of approx. 11 km, a boulder of gneiss of the same size over 5–6 km, and a soft sandstone only 1.5 km.

In vegetation-poor regions, sand transported with the wind can contribute to the physical weathering of solid rocks (**abrasion**).

The significance of physical weathering for soil formation is presumably low in humid tropical and subtropical regions, where chemical weathering dominates. In former glacial regions of the northern hemisphere, in contrast, it generated large amounts of fine material from solid rocks (see Sect. 2.3.2.6), in which pedogenesis could take place faster than on solid bedrock.

2.4.2 Chemical Weathering

Chemical weathering includes all heterogeneous reactions, i.e. occurring between the solution and solids, causing the minerals, contrary to physical weathering, to change their chemism or be fully dissolved. Because it attacks the surface of the minerals, its effect increases with decreasing

grain size of the minerals. In this respect, physical weathering is a forerunner of chemical weathering.

In addition to oxygen, the most important agent of chemical weathering is water, which dissolves the minerals, cleaves them hydrolytically or disintegrates them. The effect of water is increased through inorganic (H_2CO_3) and organic acids as well as through rising temperatures (exception: poorly soluble carbonates). In addition to readily soluble minerals, chemical weathering also includes poorly soluble minerals, especially the silicates. It breaks them down into their components, from which new minerals are then formed, either at the weathering site, i.e. in the soil cover (pedogenic minerals), or after transport of the dissolved weathering products into depressions, lakes and oceans.

Many of these newly formed minerals differ from the parent minerals of igneous and metamorphic origin, in that they are more finely grained, more poorly crystallized, oxidized and/or richer in OH-groups and water. In this way, they reflect the specific conditions of mineral formation at the Earth's surface.

2.4.2.1 Dissolution Through Hydration

Dissolution is defined as the transition of a mineral in the aqueous weathering solution, without involving a chemical reaction in the strict sense. The driving force of dissolution is the striving of the ions at the mineral surface to surround themselves with H_2O molecules in the presence of water, i.e. to hydrate and thus to dissociate. The bonds of these H_2O molecules to the ions of the mineral are stronger than those of the ions within the crystals of such minerals. Accordingly, energy is released during hydration (hydration energy, see Table 5.8).

This is the process involved in the weathering (dissolution) of most alkaline and alkaline earth chlorides, sulfates and nitrates, whose solubility is quite high at several 100 g L^{-1} (Table 2.10). Readily soluble salts are those that are more soluble than gypsum. Dissolution weathering is significant in soil formation from salt and gypsum rocks, and in saline soils (Chap. 8). Salts such as NaCl and gypsum, which enter soils in humid regions through seawater, irrigation, fertilization and road salt, are rapidly leached out.

Table 2.10 Solubility of salts that also occur as minerals in water at 20 °C

Salt	Mineral name	Solubility/ g L^{-1}
$CaSO_4 \cdot 2H_2O$	Gypsum	2.4
Na_2SO_4	Thenardite	48
$NaHCO_3$	Nahcolite	69
$Na_2SO_4 \cdot 10H_2O$	Mirabilite	110
$MgCl_2 \cdot 6H_2O$	Bischofite	167
$Na_2CO_3 \cdot 10H_2O$	Natrite (soda)	216
KNO_3	Nitrocalite (potash saltpeter)	315
KCl	Sylvine	344
$MgSO_4 \cdot 7H_2O$	Epsomite	356
NaCl	Halite	359
$CaCl_2$	Hydrophilite	745
$NaNO_3$	Sodium nitrate Nitrohalite (chile salpeter)	921
$Ca(NO_3)_2 \cdot 4H_2O$	Nitrocalcite	1212

2.4.2.2 Hydrolysis and Protolysis

If the components of the minerals react chemically with the H^+ and OH^- ions of dissociated water, it is referred to as hydrolysis. Especially compounds that consist of a weak acid and/or weak base, e.g. carbonates and silicates, are subject to hydrolysis. Thus, the majority of rock-forming minerals are affected.

In soils of humid climate regions, the reaction with the H^+ ions of the solution is the actual driving force of this type of weathering. Here, oxygen bridge bonds between metals M (Fe, Al, Ca, Mg, K, Na etc.) and Si (silicates), C (carbonates) or P (phosphates) are broken, the Si–O–M, C–O–M and P–O–M groups are protonized to form –Si–OH (silanol), –C–OH (hydrogen carbonate) or –P–OH (hydrogen phosphate), and the metals are liberated:

Table 2.11 Solubility of $CaCO_3$ in water depending on the CO_2 partial pressure at 25 °C

CO_2 partial pressure (kPa)	Solubility (mg $CaCO_3$ L^{-1})
0.031[a]	49
0.33	117
1.6	201
4.3	287
10	390

[a]Corresponds to the average partial pressure of air

$$-\mathrm{Si}-\mathrm{O}-\mathrm{M} + \mathrm{H}^+ = -\mathrm{Si}-\mathrm{OH} + \mathrm{M}^+ \quad (2.6)$$

$$-\mathrm{C}-\mathrm{O}-\mathrm{M} + \mathrm{H}^+ = -\mathrm{C}-\mathrm{OH}^- + \mathrm{M}^{++} \quad (2.7)$$

$$-\mathrm{P}-\mathrm{O}-\mathrm{M} + \mathrm{H}^+ = -\mathrm{P}-\mathrm{OH}^- + \mathrm{M}^{++} \quad (2.8)$$

Equations 2.6–2.8 show that the equilibrium shifts to the right side with increasing H^+ concentration (decreasing pH) of the solution; acidic solutions therefore weather more strongly than neutral solutions.

These weathering processes will first be described using the example of carbonates. Poorly soluble dolomite is decomposed by carbonic acid to form readily soluble Ca^{2+} and Mg^{2+} hydrogen carbonates:

$$\mathrm{CaMg(CO_3)_2} + 2\ \mathrm{H_2CO_3} = \mathrm{Ca(HCO_3)_2} + \mathrm{Mg(HCO_3)_2} \quad (2.9)$$

The concentration of carbonic acid in the weathering solution increases according to $CO_2(g) + H_2O = H_2CO_3$ (g = gaseous) with the CO_2 partial pressure of the air it is in equilibrium with. For this reason, the solubility of the carbonates increases in the same direction (Table 2.11).

Contrary to many other weatherable minerals, the solubility of carbonates drops with increasing temperature, because the solubility of CO_2 in water decreases in the same direction. Thus, at a CO_2 partial pressure of 0.03 kPa, the solubility of calcite at 25 °C is of 49 mg, at 15 °C of 60 mg and at 0 °C of 84 mg $CaCO_3$ L^{-1}. Still, carbonates in a warm soil are generally more readily dissolved than in cool soils, because the CO_2 partial pressure of the soil air is higher due to the more intensive biological activity. Carbonate weathering leads to the degradation of carbonate rocks, and to the decalcification of soils containing carbonates formed from loess, calcareous glacial till, and other rocks containing carbonates.

The hydrolysis of silicates is explained using the example of feldspar. Figure 2.23 shows feldspar crystals at different weathering intensities from a soil. The holes in the surface and its regular form indicate that during weathering, the feldspar dissolved without preference to individual components (e.g. Ca^{2+}), i.e. **congruent**, and the geometry of the leaching of the components depends on the crystal structure (here the framework structure). The same is true for the weathering of a hornblende, which then exhibits other weathering forms, corresponding to its band structure.

As solid products of hydrolytic cleavage of potash feldspars, clay minerals such as kaolinite are formed from the ionic and molecular decomposition products (Eq. 2.10)

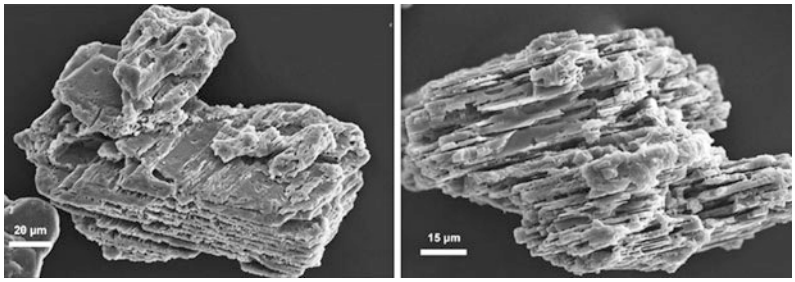

Fig. 2.23 Structure-oriented dissolution examples of mineral grains from a soil; potash feldspar (*left*) and plagioclase (*right*) with advanced weathering (*image* M. Zarei)

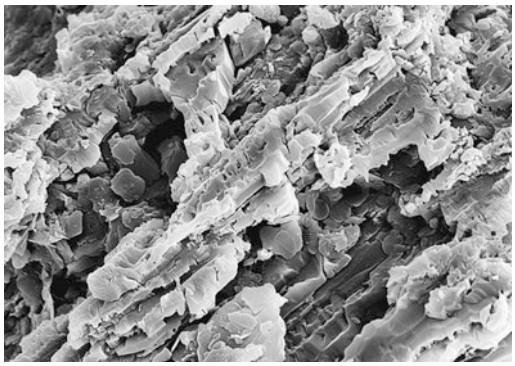

Fig. 2.24 Kaolinite newly formed by weathering in dissolution caverns of a potash feldspar (*image* width 56 μm; SEM image by M. Zarei)

$$2\,KAlSi_3O_8 + 2\,CO_2 + 11\,H_2O \rightarrow 2\,K^+ + 2\,HCO_3^- + 4\,H_4SiO_4 + Al_2Si_2O_5(OH)_4 \quad (2.10)$$

In contrast, incorporation of liberated potassium leads to the formation of illite (Fig. 2.24).

Equation 2.10 is an example for an **incongruent** dissolution reaction, because the activities of the dissolved species are controlled and altered by the newly formed solid phase (in this case kaolinite), and no longer corresponds to the chemism of the parent mineral. However, the formulation of the equation does not say anything about the mechanisms of dissolution on an atomic level. In the first step, the K^+ ions at the surface of the fresh feldspar are replaced by H^+ ions and enter the solution. If this reaction takes place in pure water, KOH is formed, which can be seen in the alkaline reaction of a suspension of feldspar powder in water:

$$\begin{array}{l} \equiv Si{-}O{-}Al\equiv + H_2O \rightarrow \equiv Si{-}O{-}Al\equiv + K^+ + OH^- \\ \quad\;\; | \qquad\qquad\qquad\qquad\quad H \\ \quad\;\; K \quad (6) \end{array} \quad (2.11)$$

The protonation destroys the Si–O–Al bond and leads to the complete dissolution of the feldspar with the liberation of dissolved ions, from which secondary (clay) minerals are formed if their solubility products are exceeded. Si–O–Si bonds must also be broken. The stability of the Si–O–Si bond depends on the type of structurally neighboring metal ions. It is higher the stronger its tendency towards covalent bonding; the bond therefore becomes stronger in the sequence K < Na < Ca < Mg < Al. For this reason, pure Al silicates such as andalusite are found detrital and unaltered in some sandstones.

The newly formed minerals can be deposited at the surface of feldspars, or when the feldspar is dissolved, they can fill its volume and take on its former shape (**pseudomorphosis**), as is often observed with kaolinite and gibbsite.

The transformation explained for potash feldspars can be also applied, in a more or less modified form, to other silicates such as plagioclase, pyroxene and amphibole and olivine. A special characteristic of platy phyllosilicates (mica, chlorite) is that in the first weathering stage, they only loose the embedded components between the elementary layers (e.g. K^+ in micas), so that although the layer bonding is weakened, the sheet-like structure as a whole is initially maintained (cf. Sect. 2.2.5).

2.4.2.3 Oxidation and Complex Formation

Many minerals such as biotite, pyroxene, amphibole and olivine contain Fe and Mn in the reduced, divalent form. They are therefore oxidized in weathering environments containing O_2, i.e. in contact with the atmosphere. This breaks the bonds in the mineral and liberates the oxidized Fe and Mn, which are hydrolytically transformed to oxides and hydroxides. For silicates, this results in the following basic reaction (with] as solid phase):

$$]{-}Fe^{2+}{-}O{-}Si{-}[+ 1/2\,O_2 + 2\,H^+ \rightarrow]{-}Fe^{3+}{-}OH{+}]{-}Si{-}OH \quad (2.12)$$

The oxidation of iron can also take place inside the mineral structure, so that the positive charge increases. To equalize the charge, other cations, e.g. K^+ in biotite, can exit the structure or OH groups can be transformed into O groups. With the weathering of biotite, Fe^{2+} is liberated in addition to K^+ and precipitated as Fe(III) oxide. Biotite thus looses its black color and becomes

bleached. Protolysis is also involved in the oxidative weathering of Fe(II) silicates, as shown by the following weathering reaction for pyroxene:

$$4\,CaFeSi_2O_6 + O_2 + 8\,H_2CO_3 + 14\,H_2O \rightarrow 4\,FeOOH + 4\,Ca(HCO_3)_2 + 8\,H_4SiO_4 \quad (2.13)$$

The oxidation of magnetite, Fe_3O_4, results in maghemite or hematite (Eq. 2.14), and the oxidation of titano-magnetite correspondingly in titano-maghemite or titano-hematite:

$$4\,Fe_3O_4 + O_2 \rightarrow 6\,Fe_2O_3 \quad (2.14)$$

Oxidation processes in minerals therefore promote their further degradation. In addition to Fe (II) silicates, siderite ($FeCO_3$) and other Fe(II) minerals are also subject to oxidative-hydrolytic weathering. Because the formed Fe(III) oxides have a pronounced brown, yellow or red color, the weathering of most rocks is accompanied by the corresponding coloration (e.g. brunification, browning).

With iron sulfides such as FeS and FeS_2 (pyrite), the sulfide ions are also oxidized in addition to Fe^{2+}. This oxidation results in goethite (FeOOH) and sulfuric acid (H_2SO_4):

$$4\,FeS_2 + 15\,O_2 + 10\,H_2O \rightarrow 4\,FeOOH + 8\,H_2SO_4 \quad (2.15)$$

If the pH falls below 3, Fe^{2+} can only be oxidized bacterially by *Thiobacillus ferrooxidans*. Furthermore, at these low pH values, the Fe^{3+} ion is no longer fully hydrolyzed ($OH/Fe^{3+} < 3$), and instead of Fe(III) oxides, Fe(III) hydroxysulfates such as schwertmannite or jarosite are formed, where the potassium comes from the weathering of minerals containing K. If the sulfate concentration drops or the pH changes, schwertmannite is hydrolyzed to goethite:

$$Fe_8O_8(OH)_6SO_4 + 2\,H_2O \rightarrow 8\,FeOOH + H_2SO_4 \quad (2.16)$$

Depending on the proton buffering capacity of the accompanying minerals, the pH may drop to such low levels in oxidizing mining dumps containing pyrite or in marshes that they significantly impede plant growth. The toxic effect of low pH values is even amplified by the liberation of Al^{3+} from silicates. Mine pile contamination can be counteracted either by liming or preferably by covering (air exclusion) to prevent oxidation.

2.4.3 Role of the Biota

Weathering is generally more intensive in a living, rooted soil than in a lifeless environment. This is particularly due to the contribution of plant roots and the lower representatives of the soil flora (bacteria, algae, fungi).

In principle, the mechanisms taking place with biotic weathering are the same as for chemical weathering. The main effect is from the biotically produced acids, e.g. during the decomposition of litter. In addition to carbonic acid, these are especially low-molecular organic acids such as oxalic acid, tartaric acid, malic acid and citric acid, but also aromatic acids such as benzoic acid. The liberation of metals, which form stable complexes with organic ligands (e.g. citrate), is promoted by organic complexing agents. Mainly Al, Fe and Mn, as well as heavy metals like Cu and Pb, are bound by organic complexing agents. Humic substances, especially fulvic acids, also participate in the complex formation with metals (see Chap. 3).

Furthermore, the microbial oxidation of organic sulfur and nitrogen favors the formation of H_2SO_4 and HNO_3. Finally, this also includes proton release from plant roots in exchange for absorbed metal cations (see Chap. 4).

In soils, the surfaces of the crystals of primary silicates are often densely covered with fungal hyphae, bacteria or algae, so that there is close contact between the organisms and the mineral surface. This contact can lead to more intensive weathering due to the excretion of organic acids and complexing agents. Lichens produce e.g. oxalic acid, which reacts with Ca^{2+} and Mg^{2+} from the rocks to form Ca- and Mg-oxalate. The low solubility of these oxalates promotes weathering because the liberated metals are

excluded from the weathering solution. Thus, biotites lost potassium after spending a longer period in the A horizon of acidic forest soils. Here, the hyphae penetrated between the exfoliated biotite crystals. From 1 kg of granite fragments within a period of 30 days, 160 mg Fe, 100 mg Al and 220 mg Mn were dissolved in the presence of a complex soil microflora; in contrast, only 0.2 mg Fe, 0.5 mg Al and 10 mg Mn were dissolved in a sterile environment.

Such dissolution processes are important for plants because of the mobilization of phosphate from poorly soluble Ca-phosphates, e.g. apatite. Similar dissolution phenomena were also observed in the rhizosphere (=immediate root periphery). Iron-complexing root exudates, so-called **siderophores**, dissolve the Fe(III) oxides and thus ensure the Fe supply for some plants.

2.4.4 Weathering Stability

Minerals are thermodynamically stable, if they are in equilibrium with their chemical surroundings under the given pressure and temperature conditions. This definition only has limited applicability for soils, since equilibrium is seldom reached between the minerals and weathering solution in nature, because the weathering products are constantly being extracted by: (a) removal in dissolved form, (b) formation of poorly soluble new minerals (clay minerals, carbonates, oxides and hydroxides), and (c) the formation of organic complex compounds with Al and Fe, especially in soil horizons that are rich in humus. Soils are not closed, but rather open systems, with substances added to and/or removed from the system. For this reason, dynamic equilibria are established with time, where the mineralogical composition continuously adapts to the substance changes. This is why weathering always is a never-ending process. Chemical weathering and formation processes in soils should therefore always be considered both thermodynamically and kinetically.

2.4.4.1 Thermodynamic Stability Conditions

The stability of minerals against chemical weathering correlates with the water solubility. Readily soluble minerals such as salts (e.g. rock salt) therefore weather most rapidly. The sequence continues with the slightly less soluble gypsum, the carbonates (calcite > dolomite) and finally the even less soluble primary silicates.

The stability of primary silicates depends on several factors, which often interact. These include the structure type, the Si–Al substitution, the type of metal cations, which connect the SiO_4 tetrahedra, and the content of oxidizable cations like Fe^{2+} and Mn^{2+}. In general, the stability of the various structure types increases in the sequence orthosilicates- < chain silicates- < phyllosilicates- < tectosilicates, since the linking of the SiO_4 tetrahedra and therefore the proportion of Si–O–Si(Al) bonds increases in the same sequence. In the same structure type, the stability decreases with increasing substitution of Si by Al, i.e. in the sequence quartz > orthoclase > nepheline, and for the plagioclases from albite to anorthite. This is because the four oxygen atoms of the tetrahedra are pressed apart by the about 50 % larger Al ion.

The type of cations that link the SiO_4 tetrahedra influences the stability through their size and charge. The stability increases with the charge and decreases with the size of the linking cation. For this reason, structures where the larger cations Mg^{2+}, Ca^{2+} and Fe^{2+} (Table 2.2) link the tetrahedra are less stable than those linked by Al, e.g. biotite compared to muscovite. Because this influence can superimpose any other influence related to the structure, the orthosilicates exhibit the stability sequence zircon > andalusite, staurolite > olivine. The SiO_4 tetrahedra in zircon ($ZrSiO_4$) are linked by Zr^{4+}, in andalusite (Al_2OSiO_4) and staurolite by Al^{3+}, and in olivine by Mg^{2+} and Fe^{2+}.

The content of oxidizable metal ions such as Fe^{2+} and Mn^{2+} reduces the stability, because their oxidation disturbs the charge and structural ratios (in sixfold coordination, Fe^{3+} is 13 % smaller than Fe^{2+}, cf. Table 2.2) in the mineral.

Table 2.12 Average lifetime of a 1 mm crystal of various silicates in years in soils (acc. to Lasaga 2014)

Anorthite	Diopside	Albite	K feldspar	Muscovite	Quartz
1.1×10^2	6.8×10^3	8.0×10^4	5.2×10^5	2.7×10^6	3.4×10^7

The fact that biotite weathers more readily than muscovite is therefore closely related to its generally high Fe^{2+} contents. Pyrite is also particularly readily weatherable, because it can be oxidized although it is poorly soluble.

Altogether, these observations result in the following approximate sequence of increasing weathering stability for the rock-forming silicates: olivine < anorthite < pyroxene < amphibole < biotite < albite < muscovite ~ orthoclase < quartz. Values for the lifetime of 1 mm crystals of various silicates are listed in Table 2.12; they correspond to the previously mentioned sequence. Under aerobic, surface-near conditions, clay minerals as end products of weathering are about equally as stable as the structurally related muscovite.

The weathering stability can be qualitatively assessed using **stability diagrams**, where the stability fields for the individual minerals are represented as a function of the composition of the weathering solution at a state of equilibrium. They are calculated from the thermodynamic parameters (enthalpy of formation) of all of the participating phases. Stability diagrams such as Fig. 2.25 can be used to assess whether a mineral is stable with a given weathering solution or if it dissolves. Orthoclase and muscovite weather more readily the lower the K and Si activity and the higher the H activity (pH) in the weathering solution (Fig. 2.26). For the kinetics (see Sect. 2.4.4.2), a large deviation of the solution concentration from the equilibrium concentration (see Eq. 2.17) results in a rapid dissolution rate.

However, the precise location of the stability boundaries is uncertain and can thus only be used for a qualitative prediction, because (1) the free energies of the individual minerals differ only slightly from one another, and therefore the energies of the transformation reaction cannot be determined with sufficient precision; (2) equilibrium is seldom reached in the weathering environment, i.e. at low temperature and low pressure; (3) metastable phases are preferentially formed, which only transform very slowly (if at all) into stable phases. Thus, for example, although the Si concentration in many weathering solutions is significantly above that of equilibrium with quartz, the latter is only formed very slowly, if at all.

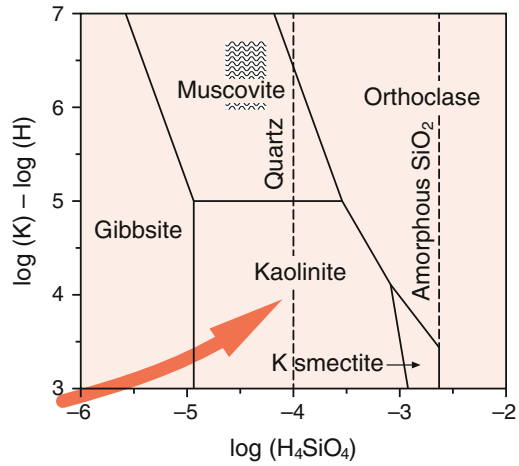

Fig. 2.25 Stability range of orthoclase, muscovite, kaolinite, smectite and gibbsite at 25 °C as a function of the activity (mol L^{-1}) of K^+, H^+ and H_4SiO_4. The two *dotted lines* mark the H_4SiO_4 saturation activities of quartz and amorphous SiO_2, the *wavy lines* show the average composition of seawater. The *arrow* symbolizes the changing of strongly undersaturated rainwater, which becomes increasingly enriched with K^+ and H_4SiO_4 in contact with minerals

2.4.4.2 Kinetics of Chemical Weathering

Stability diagrams (Fig. 2.25) have already been used here to show that although undersaturation forecasts that a mineral is not stable and will dissolve, the stability diagrams do not say anything about the rate at which dissolution takes place. A quantitative description of the rate R at which a mineral is chemically weathered can be formulated as follows (White and Brantley 1995):

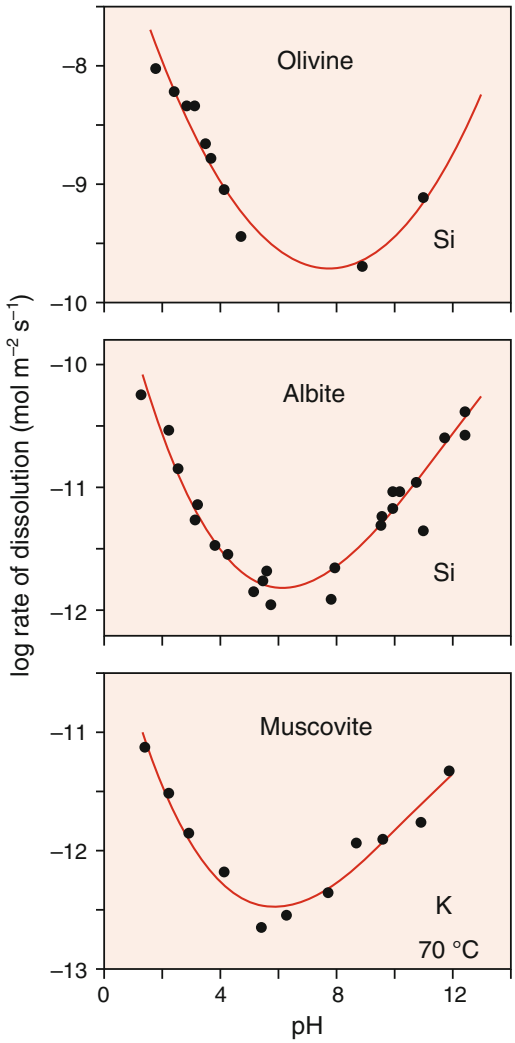

Fig. 2.26 Liberation rates of Si from olivine and albite, and of K from muscovite at 70 °C depending on the pH (after Knaus and Wolery 1986)

$$\text{Rate } R = k_0 A_{\min} \exp\frac{E_a}{RT}(a_{H+}^n) g(I)(\Pi_i a_i^n) f(\Delta G_r) \tag{2.17}$$

The individual terms in Eq. 2.17 can at least be qualitatively linked to important soil properties: The mineral type determines the mineral-specific rate constant k_0, which is of $\sim 10^{-10}$–10^{-14} mol m^{-2} s^{-1} for silicates. The reactive surface A_{min} increases with decreasing grain size, which in turn is a function of the parent material. Thus, the coarse-grained minerals of acidic plutonite (e.g. granite) have less reactive surface than the fine-grained minerals of basic vulcanites such as basalt. The temperature-dependency of the reaction is accounted for by the exponential term, which comprises the activation energy E_a, the temperature T and the BOLTZMANN constant R. The chemical composition of the soil solution is accounted for by the next three terms: The first term is the proton activity (pH value), which is raised to the power of the number n of protons involved in the solution reaction. The liberation rates of Si from olivine and albite (Fig. 2.26) drop with rising pH in accordance with Eq. 2.10. The rerise of the rates above pH 7 is due to an increase in the silicic acid solubility in the alkaline range. Such changes in the solubility behavior (e.g. also through complexing reactions) are accounted for by the rate equation in the product term $\Pi\ a_i^n$. The term $g(I)$ takes account of the fact that dissolution rates also depend on the ionic strength.

Finally, the term $f(\Delta G_r)$ takes in account that the rate depends on the degree of undersaturation and varies between 1 (i.e. maximum rate k_0 at maximum undersaturation) and zero (equilibrium). For this reason, the water regime is of great importance, as it determines how long water is in contact with a mineral surface that is dissolving. With a very short residence time in very well-drained soils with high amounts of precipitation, the weathering solution remains highly undersaturated, so that even very poorly soluble minerals are also dissolved on the long term (e.g. quartz in tropical soils). The longer the soil solution is in contact with the solid phase, the more its composition will approach that that is in equilibrium with the dissolving mineral (e.g. orthoclase). However, the solubility product of a less soluble mineral is usually exceeded (e.g. of kaolinite) before this equilibrium is reached. The growth of this new mineral depletes the corresponding elements in the weathering solution, and therefore the solution composition of the seepage water percolating below no longer corresponds to the composition of the weathering primary minerals (see Eq. 2.10 for incongruent dissolution).

2.4.4.3 Weathering Intensity

The weathering intensity can be characterized mineralogically, e.g. using so-called **index minerals**. In humid climates, low weathering is indicated by the dominance of gypsum, calcite and olivine, moderate by biotite, illite and smectite, strong by secondary chlorite and kaolinite, and very strong weathering by gibbsite and anatase. However, deviations are possible depending on local weathering conditions. In addition to changes in the mineral constituents, increasing contents of mineral inclusions, e.g. of goethite and hematite, also indicate increasing weathering intensity.

Chemical indicators are also suitable for the characterization of the weathering intensity. Soils are initially mainly depleted of Na, Ca and Mg, while the K content decreases more slowly. Among the anions, especially chloride and sulfate are rapidly depleted, while even though phosphate is liberated from the apatite, it is then usually relatively strongly bound in another form. Although silicate is also already depleted in the initial phases of weathering, it is only recognizable at an advanced weathering stage. This desilification takes place in stages, because initially Si-rich secondary minerals (illite, smectite) are formed again, and then more Si-poor minerals (kaolinite) are formed, until finally in extreme cases, almost all of the Si is depleted. In this rare state, the elements Al, Fe, Ti etc. relatively accumulate strongly in form of oxides, and associated with them, also several microelements such as Ni and Cr, e.g. in bauxite.

The explained mobility sequence can be derived from the comparison between the mean element contents of the rocks (see Table 2.1) and those of the river water residues (Fig. 2.27). The sequence of decreasing mobility in an oxidative environment is:

$$\mathrm{Cl} > \mathrm{S} > \mathrm{Na} > \mathrm{Ca} > \mathrm{Mg} > \mathrm{K} > \mathrm{Si} > \mathrm{Fe} > \mathrm{Al}$$

The rate at which silicates are weathered in soils can be calculated from the losses of Na, K, Ca and Mg in the soil profile, and from the loads of these elements and of Si in the watercourses. For soils in temperate-humid regions, values between 0.02 and 0.08 mol m^{-2} a^{-1} were obtained.

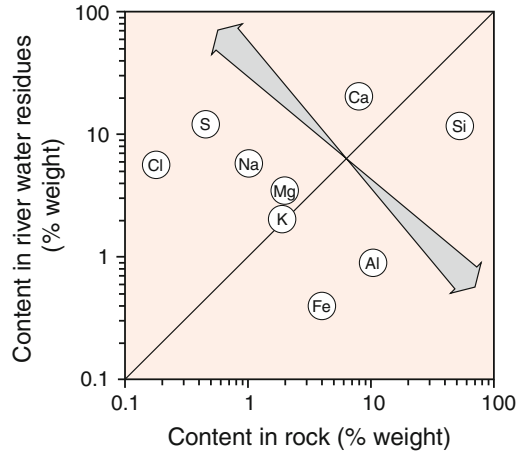

Fig. 2.27 Relationship between the element contents in rocks and in river water residues as a measurement for their mobility (after Hudson 1995). The *arrow* indicates accumulation in the river water or accumulation in the rock

The stability of rocks against physical and chemical weathering also depends on other rock properties in addition to the structural stability of their minerals. As mentioned above, e.g. granite physically weathers more readily and therefore more deeply than fine-grained basalt. It is the opposite for chemical weathering: Here, basic igneous rocks, especially fine-crystalline vulcanites due to their high content of readily weatherable minerals (olivine, pyroxenes, Ca-rich plagioclase), weather more rapidly and more deeply than acidic igneous rocks. As a result, granites in temperate-humid climates form deep soils whose mineral constituents (with the exception of biotite) have changed little compared to the parent rock, while basalts form shallow soils with strongly altered mineral constituents.

2.5 Mineral Constituents of Soils

Just like rocks, soils also consist of a mixture of minerals. During the course of weathering, a portion of the minerals was inherited unchanged

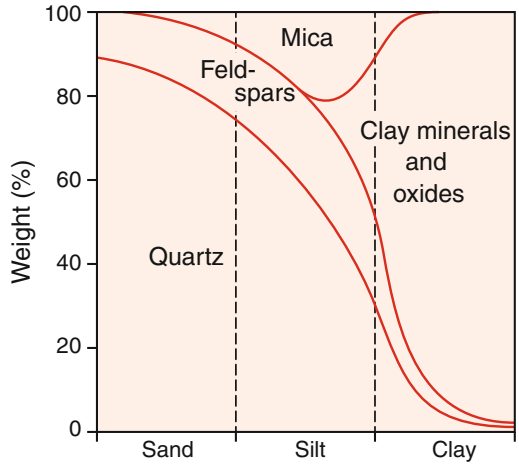

Fig. 2.28 Mineral constituents in the particle fractions sand, silt and clay (example from the glacial landscape of Northern Germany)

from the parent rock, and another portion is pedogenic. Thus, the less weathering and pedogenesis have taken place and the more poorly weatherable the parent materials, the more the mineral constituents of many soils reflect those of their parent materials. In contrast, pedogenic minerals are increasingly dominant in more mature soils. This also influences the distribution of the various minerals in the grain size fractions of the soils. The sand and silt fractions consist mainly of stable igneous and metamorphic minerals such as quartz, potash feldspars, micas (mainly muscovite) and numerous heavy minerals (zircon, rutile, ilmenite, magnetite, tourmaline) that remain after weathering, while in the clay fraction, the clay minerals and oxides from sediments and pedogenesis dominate (Fig. 2.28).

Soils originating from acidic igneous and metamorphic rocks (e.g. granite, gneiss) usually consist of >60 % quartz, those from sandstone, fluvial and eolian sands up to 95 %. In contrast, soils from loess, limestone and claystones are lower in quartz (<50 %), while those from basic igneous rocks hardly contain any quartz, unless it is from eolian input. The quartz content is highest in the sand fraction and decreases towards the finer fractions (see Fig. 2.28). However, quartz can still be found in coarse clay after cryoclastic weathering. Soil development can lead to relative quartz accumulations, if less stable minerals, e.g. silicates, are degraded.

The feldspar content in soils in temperate-humid climate regions often ranges from 5 to 30 %; from which 80 to 90 % can be attributed to alkali feldspars, since Ca-rich feldspars weather more readily. The influence of weathering intensity is demonstrated by the fact that e.g. soils from lower Pleistocene sands usually contain <10 % feldspars, and those from the upper Pleistocene sands on average 15–20 %. Soils from loess, clay and clay schist have feldspar contents of 10–15 %. The feldspar content decreases towards the finer fractions (Fig. 2.28). In soils from parent rocks with a high alkali feldspar content, however, they can also still occur in the clay fraction. In many soils in the humid tropics, in contrast, feldspars are largely transformed into clay minerals.

Plagioclases, pyroxenes, amphiboles and olivines are only present in small amounts in the coarser fractions, since they weather more readily than alkali feldspars. Their proportion generally decreases within the profile from bottom to top, because weathering in the upper horizons is most intensive. They are completely absent in strongly weathered soils of the humid tropics (Ferralsols).

The mica content, consisting mainly of muscovite and bleached (=weathered) biotite, is highest in the silt fraction of soils, since micas are easily mechanically degraded due to their pronounced cleavability (Fig. 2.28).

In many young soils of temperate climate regions, clay minerals and oxides are inherited from sediments, however, they also originate from pedogenesis. Thus, mainly illite and smectite dominate in post-Pleistocene soils originating from loess, calcareous glacial till, fluvial sediments and marshes, but also from claystones and limestones. In contrast, the clay minerals in soils are always pedogenic on parent materials that do not contain any clay minerals, such as igneous rocks. They are determined by the mineral

Table 2.13 Dominating pedogenic clay minerals in orders of the soil taxonomy orders and WRB reference group (Chaps. 7 and 8)

Soil order/Reference group	Clay minerals
Alfisols	Illite, smectite, Al chlorite
Luvisols, Alisols	
Andisols	Allophane, imogolite, halloysite
Andosols	
Aridisols	Palygorskite, sepiolite, smectite
Calcisols, Solonchaks, Solonez	
Entisols	None
Regosols, Leptosols, Anthrosols, Technosols	
Inceptisols	Illite, smectite, Al chlorite
Cambisols, Umbrisols, Gleysols, Stagnosols	
Mollisols	Illite, smectite, vermiculite
Chernozems, Kastanosems, Phaeosem	
Oxisols	Kaolinite, goethite, hematite, gibbsite
Ferralsols, Plinthosols	
Spodosols	Illite, Al chlorite, (smectite), allophane
Podzols	
Ultisols	Kaolinite, muscovite, hematite, goethite
Acrisols, Lixisols	
Vertisols	Smectite
Vertisols	
Gelisols	Illite
Cryosols	

composition of the igneous or metamorphic rocks and the pedoclimate, and change with the degree of soil development.

At low weathering intensity, smectite is often found on basic igneous rocks (basalt etc.), in contrast, illite and vermiculite are found on acidic igneous rocks (granite u. a.), and primary chlorites are often found on metamorphic rocks. With stronger acidification, smectites and vermiculites are transformed into soil chlorites, and primary chlorites are partially dissolved. Local accumulations of goethite, lepidocrocite and ferrihydrite occur in redoximorphic soils. On volcanic ashes, soils with higher Si concentrations contain allophane, and with lower concentrations, imogolite; at later stages of development, in contrast, halloysite and kaolinite dominate. However, allophane and imogolite are also found in the B horizon of Podzols.

Numerous soils in temperate-humid climate regions, e.g. Rendzic Leptosol, calcaric Regosols, young floodplain and tidal Fluvisols, still contain calcite and dolomite in the A horizon, usually in the silt fraction (e.g. in loess). Pedogenic calcite is also found with increasing aridity.

The mineral constituents in strongly developed soils of the perhumid tropics and subtropics are dominated by kaolinite, goethite, hematite, gibbsite and anatase. On acidic igneous and metamorphic rocks, weathering-resistant minerals such as quartz, orthoclase or muscovite are also found, which are largely lacking on basic igneous rocks. Smectite is widespread in neutral to slightly alkaline soils of seasonal wet and dry climatic regions, while under dryer, semiarid conditions and higher Mg concentrations, palygorskite and sepiolite and various salts (sulfates, chlorides, nitrates, borates) are found. In many regions (India, Central Africa) with kaolinitic soils on plateaus and slopes, smectite-rich soils (Vertisols) in plains with high groundwater tables and in hollows are connected by the landscape's water balance. Typical pedogenic minerals in the anaerobic soil zone are iron sulfides, siderite and vivianite.

Almost all soils contain small amounts (<2 %) of heavy minerals, e.g. apatite, magnetite, ilmenite, garnet, rutile, zircon, tourmaline etc. The poorly weatherable heavy minerals accumulate all the more with increasing intensity of soil weathering. In contrast, the apatite content decreases with increasing acidification.

Because the mineral soil orders of *Soil Taxonomy* and the soil reference groups of WRB are broadly defined following a sequence of development, they can be associated with dominant pedogenic minerals (Table 2.13).

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Soil Organic Matter

3

3.1 Origins, Distribution and Dynamics

In most topsoils, the mass of the soil **organic matter** only amounts to a few percent, but has an important influence on all soil functions and plays a central role in the global carbon cycle. For this reason, the **carbon content**, or the dark color value, is a differentiating criterion for soil descriptions in German and international classifications.

About 80 % of the terrestrial organic carbon reserves participating in the active C-cycle are bound in soils, and only about 20 % in the vegetation. Bound C is mainly returned to the atmosphere through soil respiration due to microbial oxidation processes. On the long term, the non-mineralized fraction remaining in the system is stored in the soil organic matter. This carbon is subject to stabilization processes in the soil, which protect it to a large extent against microbial decomposition. Under constant environmental and vegetation conditions, an equilibrium is reached in the soil between the supply and degradation of organic matter, resulting in a characteristic humus or organic matter content.

Due to its large surface area, soil organic matter is an important **sorbent** for organic and inorganic substances in the soil solution. It offers (mainly negative) charges and thus increases the cation exchange capacity, but also contains hydrophobic areas, where the less-soluble hydrophobic organic substances can be bound. At the same time, the organic matter is of central importance for the development of a stable soil structure through formation of soil micro- and macroaggregation. The organic matter content essentially determines the color of the topsoil and, especially in arable soils, has an effect on the soil heat balance. The mineralization of plant residues is a significant source of nutrients for plants and microbial biomass. Last but not least, soil organic matter is a source of C and energy for the soil fauna and microflora. Organic matter is the C and energy source for heterotrophic soil organisms, so that with constant environmental factors, there is a close correlation between organic matter content and biological activity. The maintenance of high biological activity requires constant replenishment of the consumed organic matter by adding plant residues to the soil (see Chap. 4).

The chemical composition of the organic matter is heterogeneous, because it consists of plant and animal residues at different stages of degradation. Soil organic matter comprises all of the dead plant and animal residues and their organic transformation products found on and in the mineral soil. It also includes substances introduced by human activities, e.g. synthetic organic substances (e.g. pesticides, organic wastes). Living organisms (edaphon, consisting of the soil flora and fauna) and living roots do not belong to the organic matter in soils.

The term humus is often used synonymous for the organic matter in soils. Soil organic matter is

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composed of a mixture of plant and microbial residues in different degrees of transformation. Humus is a complex organic material of brown to dark colored amorphous substances, which have originated during the decomposition of plant and animal residues by microorganisms, under aerobic and anaerobic conditions (Waksman 1938). Chemically, humus consists of certain constituents of the original plant material stabilized against decomposition, of substances modified during decomposition, either by processes of hydrolysis or by oxidation and reduction; and of various compounds synthesized by microorganisms.

In this chapter and in the rest of this book, the term **humus** refers to the dead **organic matter** in the soil as a whole. In mineral soils, the organic matter is mixed with the mineral phase, but it also forms the forest floor in many soils (ref. to humus forms). In addition to solid organic substances, the soil water also contains dissolved organic substances ("DOM" = *dissolved organic matter*).

The following components are often differentiated:

Plant litter: These are undecomposed or only weakly transformed plant residues, and the tissue structures are still morphologically recognizable. They include both aboveground dead **plant remains** and dead roots. These materials are found in the litter layer (L horizon) on the forest floor, but can also be isolated from the mineral soil as particulate or light organic fraction. They mainly consist of lipid, protein, polysaccharide and lignin compound classes. Their turnover time in the soil is short.

Partly degraded plant residues are found in the forest floor O horizons or occur inside aggregates. They are called occluded particulate organic matter as they can be isolated after destroying the soil aggregate structure. They have longer intermediate turnover rates.

Stabilized soil organic matter: These are strongly morphologically transformed substances without macroscopically perceptible tissue structures. They are stabilized against mineralization, i.e. they have a low turnover rate or a long residence time in soil. If they exist as organo-mineral compounds, they can be isolated from the mineral soil using particle size and density fractionation, and are then often referred to as heavy or fine organic fraction.

The decomposition of organic matter is also called **degradation**, and their transformation into humic matter is called **humification** or **stabilization**. **Mineralization** refers to complete microbial decomposition to form inorganic substances (CO_2, H_2O), where the plant nutrients (e.g. Mg, Fe, N, S, P) contained in the organic matter are also released. "Humification" is defined as the transformation and binding of organic matter in the soil, which leads to a stabilization against mineralization.

Humic substances can be isolated from soils by strong alkali and then further differentiated into acid soluble (fulvic acid) and acid-insoluble materials (humic acids). They are often used as model compounds for soil organic matter, but their occurrence in soils as defined macromolecular entities is questioned more and more (Piccolo 2001; von Lützow et al. 2006; Schmidt et al. 2011).

3.2 Contents and Quantities of Organic Matter in Soils

The carbon content of organic matter varies within individual substance classes, with polysaccharides containing about 40 % C, and lipids about 70 % C. The average C content is usually around 50 %. In addition to the nonmetals C, H, O, N, S and P, the organic matter in soils also contains metals. These occur either in an exchangeable form (especially Ca, Mg,), or are in the form of complexes, where they are generally firmly bound (e.g. Cu, Mn, Zn, Al and Fe).

The organic matter content in the individual soil horizons and the average organic matter content in different soils vary across wide ranges (Table 3.1, Chap. 7.2), and are also subject to a seasonal variation. The content of carbon in a soil is quantified by the concentration (mass of OC by mass of the soil, e.g. mg g^{-1}), and the amount of carbon by the stock (mass of OC, e.g. based on a

Table 3.1 Contents and stocks of organic matter in different soils of southern Germany; data from Wiesmeier et al. (2012)

Soil type Parent material Land use	Horizon	Depth (cm)	Bulk density (g cm^{-3})	Gravel content (%)	Texture sand/silt/clay (%)	OC content (g kg^{-1})	OC stocks (kg m^{-2})	OC stocks in the solum (kg m^{-2})
Calcaric Hyperskeletic Leptosol Limestone Mixed forest	O	0–3	0.20	0	–	382	2.3	7.3
	Ah	3–10	1.00	10	11/57/32	51	4.6	
	CAh	10–53	1.20	90	15/53/32	27	1.4	
Dystric Hyperskeletic Leptosol Quartzitic schists Coniferous forest	O	0–2	0.20	0	–	455	1.8	8.2
	Ah	2–12	1.00	28	58/38/7	74	5.3	
	AhC	12–37	1.00	60	58/38/7	11	1.1	
Dystric Cambisol Sandstone Deciduous forest	O	0–3	0.10	0	–	428	1.1	7.2
	Ah	3–8	0.48	2	61/32/7	58	1.4	
	AhBw	8–12	1.03	4	60/32/8	17	0.7	
	Bw1	12–43	1.53	8	59/32/9	8	3.5	
	Bw2	43–64	1.60	13	62/23/15	2	0.5	
Eutric Cambisol Loamy-sandy tertiary sediments Cropland	Ap	0–30	1.33	2	38/40/22	17	6.4	12.6
	Bw1	30–65	1.56	2	30/47/23	7	3.6	
	Bw2	65–89	1.57	4	18/55/27	5	1.8	
	C	89–105	1.59	10	30/46/24	3	0.8	
Luvisol Loess Cropland	Ep	0–33	1.33	0	6/66/28	13	5.8	10.2
	Bt1	33–45	1.52	0	2/53/45	7	1.2	
	Bt2	45–57	1.50	0	2/56/42	5	0.9	
	C	57–93	1.54	0	6/61/34	4	2.3	
Podzol Granite Coniferous forest	O	0–7	0.29	0	–	448	9.1	20.5
	Ah	7–10	0.80	20	59/30/11	46	0.9	
	Eh	10–37	0.92	40	65/28/7	30	4.5	
	Bhs	37–67	0.93	60	64/25/11	46	5.1	
	C	67–72	1.00	70	50/35/15	59	0.9	
Gleysol Fluviatile sediments Grassland	Ah	0–21	1.29	0	60/32/8	26	6.8	17.6
	2Ahl	21–29	1.31	0	47/40/13	21	2.7	
	3Alh	29–45	1.22	0	38/43/19	16	3.8	
	4Blr	45–69	1.23	0	42/36/22	13	3.0	
	5Brl1	69–81	1.61	0	67/19/14	3	0.5	
	6Brl2	81–100	1.73	0	75/13/12	2	0.8	
Planosol Deciduous forest	Ah	0–5	0.74	0	7/74/19	57	2.1	8.1
	Eg	5–35	1.18	2	8/73/19	12	4.1	
	2Bg	35–75	1.36	5	8/44/48	3	1.3	
	2C	75–90	1.58	20	12/52/36	3	0.6	

(continued)

Table 3.1 (continued)

Soil type Parent material Land use	Horizon	Depth (cm)	Bulk density (g cm^{-3})	Gravel content (%)	Texture sand/silt/clay (%)	OC content (g kg^{-1})	OC stocks (kg m^{-2})	OC stocks in the solum (kg m^{-2})
Ombric Histosol Raised bog	H1	0–20	0.10	0	–	533	10.7	52.3
	H2	20–40	0.10	0		533	10.7	
	H3	40–60	0.10	0		523	10.5	
	H4	60–90	0.10	0		507	15.2	
	H5	90–100	0.10	0		535	5.4	
Rheic Histosol Grassland	H1	0–6	0.23	0	–	403	5.6	69.2
	H2	6–20	0.16	0		513	11.5	
	H3	20–48	0.13	0		529	19.3	
	H4	48–100	0.12	0		525	32.8	

depth of 1 m over 1 ha). The quantity of organic matter, in turn, depends on the soil type, the bulk density and the content of stones and coarse fragments. Soils with finer textures generally store more organic matter than coarse-grained soils. Litter horizons have organic matter contents close to 100 %; their organic carbon content (OC) usually lies between 400 and 450 g kg^{-1}. The highest concentrations and turnover of organic matter are found in the topsoil. Ah horizons in forest and arable soils have C contents of 7.5–20 g kg^{-1}. In German arable soils, the organic matter stocks average 100–200 t ha^{-1}. They can be higher in colluvial soils, Chernozems, Andosols, Vertisols and Podzols. Higher contents can be found in the topmost horizons of permanent grassland soils (up to about 150 g kg^{-1}). The carbon concentrations in the subsoil, with the exception of colluvial soils, Fluvisols, Podzols, Vertisols and Andosols, are much lower and mostly lie between 1 and 10 g kg^{-1}. Recent inventories demonstrate that large amounts of organic matter, although in low concentrations, are stored in the subsoil (B and C horizons). Redoximorphic soils exhibit particularly high C concentrations, e.g. the A horizons of Gleysols contain up to 200 g kg^{-1}, H horizons of fens and bogs more than 200 g kg^{-1}, whereby raised bogs can contain up to almost 500 g kg^{-1} C. In contrast, the OC contents in soils of arid regions are much lower due to the low litter input, with typical values lying between 2 and 6 g kg^{-1}. The stocks of organic carbon in soils fluctuate across a wide range. They are regulated by, among other factors, the climate, vegetation and thus also the input of organic matter, the groundwater level, the rooting depth, and the soil type (Table 3.1).

Global estimations show that about 1500 Pg of organic carbon (1 Pg = 10^{15} g) are stored in the first meter of terrestrial soils, about 700 Pg of which is found in the top 30 cm (Table 3.2). When considering a soil depth of 0–2 m, Batjes (1996) obtained a total of about 2400 Pg OC. In comparison, the global C reserves in the plant biomass only amounts to about 500 Pg C. Changes or redistributions of the C stocks in the soil are thus very important for the **global C budget**.

Only a small fraction of the soil organic matter is water soluble and mobile, so it usually does not play a role for the C balance. The mobile, dissolved phase is still significant for pedogenic processes, e.g. podzolization, but also for the binding and translocation of contaminants. The soil solution contains between 1 and 100 mg L^{-1} of dissolved organic carbon (DOC).

The **quantitative determination** of the organic matter can be performed using different methods:

1. Oxidation by combustion in oxygen and determination of the liberated CO_2. In soils

Table 3.2 Global stocks[a] of terrestrial organic carbon (Pg C) by IPCC climate region in soil, and in above- and below-ground phytomass carbon pools (from Scharlemann et al. 2014)

Climate region	Soil		Total (%)	Phytomass (%)	Terrestrial carbon pool
	Topsoil	Subsoil			
Tropical wet	62.6	65.4	128.0 (47.7)	140.2 (52.3)	268.1
Tropical moist	78.6	72.3	150.9 (49.9)	151.7 (50.1)	302.6
Tropical dry	67.3	69.0	136.2 (76.2)	42.5 (23.8)	178.7
Tropical montane	29.6	26.5	56.1 (58.1)	40.5 (41.9)	96.6
Warm temperate moist	33.3	29.7	63.0 (68.7)	28.7 (31.3)	91.7
Warm temperate dry	38.9	39.6	78.5 (76.4)	24.2 (23.6)	102.7
Cool temperate moist	104.1	106.2	210.3 (88.1)	28.5 (11.9)	238.8
Cool temperate dry	52.2	50.0	102.2 (91.8)	9.1 (8.2)	111.3
Boreal moist	162.0	194.7	356.7 (93.8)	23.5 (6.2)	380.2
Boreal dry	32.0	37.0	69.1 (93.1)	5.1 (6.9)	74.2
Polar moist	30.6	21.7	52.4 (96.0)	2.2 (4.0)	54.5
Polar dry	8.0	4.3	12.3 (96.2)	0.5 (3.8)	12.8
Total	699.3	716.4	1415.7 (74.0)	496.6 (26.0)	1912.2

[a]Estimates of global soil OC stocks by topsoil (0–30 cm), subsoil (30–100 cm) and the combined layers (0–100 cm or when less to depth of soil layer)

containing carbonate and at combustion temperatures exceeding 650 °C, it is necessary to remove the carbonates prior the analyses, or to determine the concentration of carbonate-C separately (Kalbitz et al. 2013).

2. If the thermal method is not available, the oxidation of the organic matter using Cr(VI) (dichromate) in a sulfuric acid solution and photometric determination of the formed Cr (III) can be used (based on Walkley and Black 1934). Alternatively, the excess dichromate Cr(VI) or the CO_2 released by oxidation can be determined. The Walkley-Black method also requires the removal or separate determination of carbonate-C.
3. In organic soils and in soils where clays are largely absent, the determination of the loss on ignition at 400 °C provides sufficiently accurate values.

The C content is determined using method (1); the organic matter content is then calculated by multiplying this value by 2.0. The factor 1.724 is also sometimes used, which results from an assumed average C content of the organic matter of 58 %. Dichromate oxidation (2) also records other oxidizable substances, e.g. Fe(II) sulfides. The edaphon is also included to some extent in the determination of the organic matter, because it (except for larger animals or roots) hardly can be removed from the sample before

analysis. However, the related error is seldom more than 10 %; it can be roughly estimated by determining the microbial biomass.

3.3 Plant Residues and Their Transformation During Decomposition

3.3.1 Composition and Structure of Organic Residues

3.3.1.1 Litter Type and Quantity

In addition to the **above-ground biomass** produced by green plants during photosynthesis (wood, leaves, needles, twigs) and falling to the ground as litter when they die, **the parent materials** for soil organic matter formation include dead roots, organic root exudates and residues (**rhizodeposition**) as well as dead soil fauna and microorganisms. These plant and edaphon residues are continuously added to the biologically active horizons of the soil. Plant residues and exudates are called primary resources, and those from microorganisms are secondary resources. In addition to the incorporation of crop residues, organic matter is also added to cultivated soils through fertilization and waste disposal (e.g. liquid manure, compost, sewage sludge). Soils in industrial-urban areas are often also contaminated with organic constituents from the petroleum and coal industry, as well as from coal combustion (e.g. tar oil, coal dust, black carbon).

The above-ground litter in forests mainly consists of leaves and/or needles. In deciduous forests of cool temperate climates, the twigs, bark and fruit only account for a fraction of about 20 %, and in coniferous forests of 20–40 % of the total litter falling on the surface. In temperate climate zones, the contribution from herbaceous vegetation to the total aboveground litter in forests amounts to less than 5 %. The fraction of the foliage in the total aboveground litter represents on average about 70 %. In coniferous forests, the total aboveground litter was estimated to be of 200–600 g dry mass m^{-2} a^{-1}. Similar ranges are also found for the aboveground input in deciduous forests, e.g. beech forests with 390–570 g m^{-2} a^{-1}. In coniferous forests, e.g. under spruce, litterfall is not restricted to a specific season. In general, the average quantity of aboveground litterfall in forests increases with decreasing latitude and increasing productivity from boreal coniferous forests (100–400 g m^{-2} a^{-1}) to the tropics (600–1200 g m^{-2} a^{-1}). In intensively managed forests, the proportion of leaf or needle litter is high compared to the woody constituents.

A considerable portion of the organic matter reaches the soil as below-ground input, i.e. as root litter and rhizodeposition. The predominantly low-molecular, usually N-rich organic matter that is secreted by plant roots (rhizodeposition) contributes significantly to the C input to the soil. Most of the root exudates are rapidly metabolized by microorganisms, and due to this constant C source, there is a high population density in the rhizosphere. About 30, 50, and 75 % of the root biomass are found in the topmost 10, 20 and 40 cm of the soil respectively; however, the maximum rooting depth, and thus also the range influenced by root residues and rhizodeposition, is much larger. In this way, root residues and exudates also reach greater depths, and together with translocated organic matter from the topsoil, contribute significantly to organic matter formation in the subsoil. Grassland and steppe soils generally exhibit a greater proportion of root mass in the total carbon input compared to forest ecosystems under comparable climatic conditions. In forests of cool temperate climates, the contribution of root litter to the input of organic matter, depending on the tree species and the life form (evergreen or deciduous), accounts for between 20 and 50 %. Under wheat cultivation, the subsurface input is around 25 % of the total C input, under grassland around 40 %.

3.3.1.2 Chemical Composition of Plant Residues

Essentially, there are two different types of tissues undergoing decomposition: parenchymatic tissues and woody tissues. Parenchymatic plant

cells are found in the living, green tissues of leaves, and in the cortex of young twigs and fine roots. They consist mainly of cellulose and protein. Woody tissues form the woody parts (xylem) and the supporting tissue (sclerenchyma) of the stems, leaf epidermis, leaf veins and bark. Woody plant residues, such as straw or wood, contain mainly cellulose, hemicellulose and lignin (also called lignocellulose).

Cellulose makes up the cell wall and consists of glucose units that are linked to each other in linear chains through hydrolyzable, glycosidic bonds. The regular arrangement of the hydroxyl groups along the cellulose chain leads to the development of H bonds, and thus to the fibrillar structure with crystalline properties that is characteristic for plant organisms, accounting for around 85 % of the cellulose molecule. **Hemicellulose** and **pectin** are also cell wall components and differ from cellulose in their arrangement of various carbohydrate monomer types, namely pentoses, hexoses, hexuronic acids and deoxyhexoses (Fig. 3.1), with side chains and branching. Plant hemicellulose in the soil can hardly be analytically differentiated from microbial polysaccharides. The pentoses arabinose and xylose originate mainly from plant residues, while microorganisms mostly produce the hexoses galactose and mannose, as well as deoxyglucose (rhamnose and fucose). As a storage polysaccharide, **starch** is a component of the cell and consists of glucose monomers.

Lignin is a high molecular, three-dimensional substance made of phenylpropane units (Fig. 3.2a). In woody plants, it fills and strengthens the structure of the cell wall, which mainly consists of linear polysaccharides. The lignin from coniferous trees consists almost exclusively of coniferyl alcohol units, and that from deciduous trees has approximately equal proportions of coniferyl and sinapyl alcohol. The lignin found in grasses is formed from about equal proportions of the three monomers coniferyl, sinapyl and p-coumaryl alcohol. The various proportions of the individual phenylpropane units result in different methoxyl group contents, which are around 15 % for gymnosperm lignin and 21 % for angiosperm lignin.

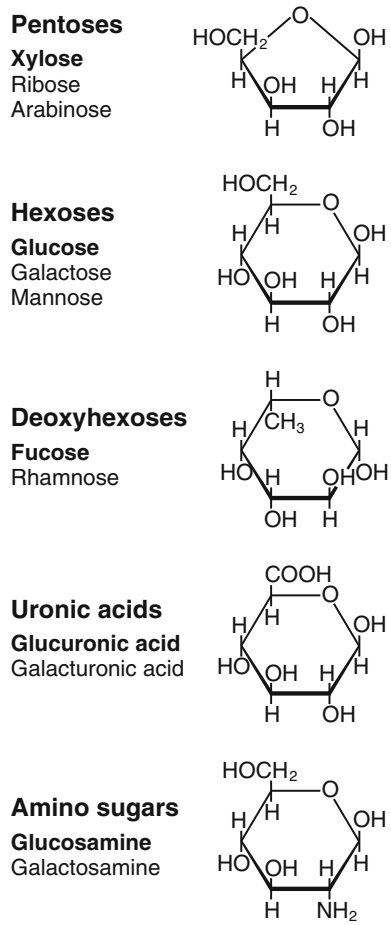

Fig. 3.1 Important sugar monomers in soils

The monomers are linked by a multitude of non-hydrolyzable C–C and C–O bonds.

Tannins are natural polyphenols with a great diversity of compositions. The hydrolizable tannins are esters formed by glucose and gallic acid. The more complex structure of non-hydrolyzable tannins or proanthocyanidins consists of up to 10 polyhydroxy-flavan-3-ol units. Organic compounds with tanning properties are capable of irreversibly linking proteins to one another. It is assumed that this effect also plays a role in the decomposition of litter in the soil, stabilizing proteins against degradation.

Cutin forms the macromolecular frame of the plant cuticle, which covers all of the aerial plant parts and is bound to the epidermis through a pectin layer. The cuticle consists of cutin, an

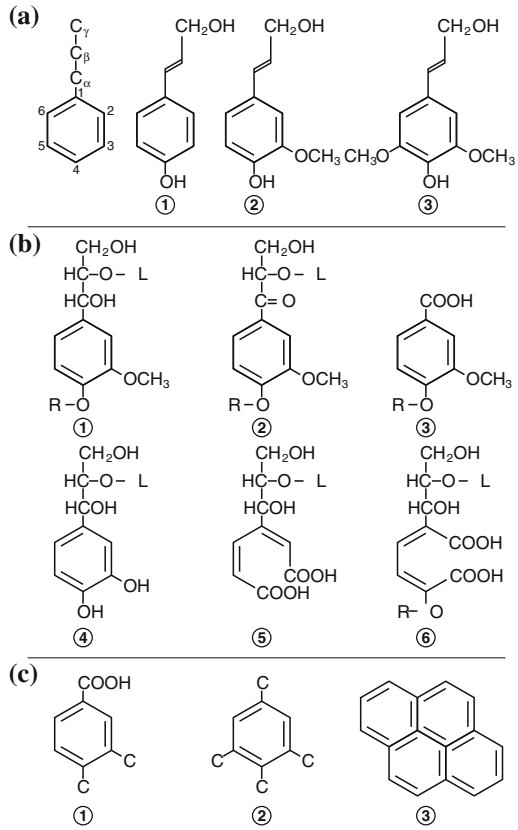

Fig. 3.2 Aromatic building blocks of organic matter. **a** Monomeric precursors of lignin (phenylpropane units): (*1*) p-coumaryl alcohol, (*2*) coniferyl alcohol, (*3*) sinapyl alcohol; **b** fragments of phenylpropane units modified by decomposition. (*1*) Intact phenylpropane unit in the macromolecule, (*2*) α-carbonyl formation, (*3*) splitting off of the side chain and oxidation of the Cα, (*4*) demethylation to o-diphenyl, (*5*, *6*) ortho-ring cleavage; **c** possible basic structures of the aromatic components in humic substances: C substituted (*1*, *2*) and condensed (*3*) aromatic C

insoluble polyester made of various hydroxy and epoxy fatty acids, mostly with chain lengths of C_{16} and C_{18}, in which low-molecular waxes and fats are embedded. These extractable **lipids** consist of a series of different substance classes, e.g. long-chain hydrocarbons, primary and secondary alcohols, ketones, triglycerides and wax esters. Similar to cutin, the *suberin* found in the root cortex and subsurface storage organs also has a polyester structure, however, it is embedded in the cell wall of the peridermal cells. In addition to aliphatic components, consisting of long-chain fatty acids and dicarboxy(lic) fatty acids (about 5–30 %), there is also a multitude of phenolic components, especially cinnamic acid.

Proteins are the most common intracellular compounds. They consist of a group of about 20 different amino acids that are connected with each other through peptide bonds. 99 % of the nitrogen in the remains of plants and animals are bound in organic form, mainly in proteins. Proteins also contain the majority of organically bound sulfur in the form of the amino acids cystine, cysteine and methionine.

N is also found in **DNA** (deoxyribonucleic acid), the carrier of genetic information, and in RNA (ribonucleic acid), responsible for the translation of the information for protein synthesis. The individual building blocks are deoxyribonucleotides, each consisting of one heterocyclic N compound (the purine or pyrimidine bases adenine, thymine, guanine, uracil and cytosine), the monosaccharide deoxyribose and one phosphoric acid molecule. They form the double helix structure of DNA.

P in plant residues occurs mainly in organic compounds as orthophosphate mono- and diesters, mostly in **inositol phosphates**, which are esters with hexahydroxycyclohexane, and **phospholipids**.

Root exudates contain a multitude of generally low-molecular components, whereby sugars and polysaccharides, organic acids, amino acids and peptides dominate.

The proportions of the individual contents in different raw materials are given in Table 3.3. The cell wall constituents cellulose, hemicellulose and lignin, as well as lipids, cutin/suberin and proteins are the most important components, accounting for more than 95 % both in the above-ground plant parts and the roots. In addition, plant residues contain a multitude of secondary constituents such as phenols, free sugars, amino acids, peptides and secondary metabolites, such as phenols and resins.

3.3.1.3 Microbial Residues

Here, the most important secondary resources are the residues from bacteria and fungi, which mainly serve as a source of C and energy

Table 3.3 Common composition of important C and energy sources for decomposition in the soil: plant residues, microorganisms; % dry matter (compiled from Haider 1992; Fengel and Wegener 1989; Swift et al. 1979)

	Cellulose	Hemicellulose[a]	Lignin % DM	Protein	Lipids[b]	C/N
Spruce (*Picea abies*)						
Wood	40	31	28	<2	1.4	100–400
Bark	48	17	38	<2	21	
Needles	15	13	14–20	3–6	7	40–80
Beech (*Fagus sylvatica*)						
Wood	32	43	24	2	0.8	100–400
Bark	38	23	39	2	11	
Leaves	20	17	11–16	6	5	30–50
Root wood	33	18	22	1.6	1.3	190
Fine roots	19	10	33	5.4	3.1	55
Ryegrass (shoot)	19–26	16–23	4–6	12–20		
Alfalfa (shoot)	13–33	8–11	6–16	15–18		
Wheat straw	27–33	21–26	18–21	3		50–100
Bacteria	0	4–32	0	50–60	10–35	5–8
Fungi	8–60 (chitin)	2–15	0	14–52	1–42	10–15
Phytoplankton (lakes)		18 + 50[c]	0	17	1.5	5–12

[a]and other non-cellulosic polysaccharides
[b]and/or other fractions that are extractable with solvents (e.g. waxes, resins, chlorophyll)
[c]non-structural carbohydrates

(Table 3.3). With the exception of lignin, tanning agents and cutin/suberin, all of the above-mentioned plant compound classes are also found in bacteria or fungi. Bacteria cell walls consist of murein, lipids and lipopolysaccharides. Murein is a peptidoglycan, which, in addition to amino acids, contains the bacteria-specific constituents galactosamine, muramic acid and diaminopimelic acid. High proportions of aliphatic biomacromolecules of lipidic nature were detected in the cell walls of various bacteria and algae, the precise structure of which is not yet known. Many bacteria produce extracellular polysaccharides consisting of neutral and acidic sugars. The cell walls of fungi contain proteins, chitin (an amino sugar polymer consisting of glucosamine, similar to cellulose), sometimes cellulose, and other polysaccharides containing a high fraction of mannose and glucose. The exoskeleton of arthropods (Chap. 4) is also made of chitin. Specific components of bacteria or fungi can be used as biomarkers to estimate the proportion of microbial residues in the soil. Glucosamine from fungi and bacteria, and galactosamine and muramic acid from bacteria are particularly well-suited for this purpose.

3.3.2 Decomposition and Transformation Reactions in the Soil

The degradation and mineralization of litter takes place in several closely interacting phases. Numerous organisms of the soil fauna and flora are involved in these decomposition and transformation processes. The first transformation processes take place already shortly before or immediately after plant organs or animals die, consisting of enzymatic reactions of the organ-

ism's own substances (senescence). Here, polymer compounds are broken down into individual components by hydrolysis and oxidation processes inside the cells (e.g. starch into glucose, proteins into amino acids). Chlorophyll is transformed into colorless decomposition products, while yellow carotenoids accumulate and red anthocyanins are formed, resulting in the autumn colors of leaves. Furthermore, a large portion of the mineral nutrients (K, Mg, Ca, u. a.) are liberated and can be leached or absorbed by plants.

When the organic matter is deposited on or in the soil and is broken down by the soil fauna, it is rapidly mineralized to CO_2, while the majority of the mineralized N is incorporated into the microbial biomass. The C/N ratio therefore becomes narrower during the course of decomposition, and can reach values of about 10. The mineralization of organic matter to form CO_2 occurs from all soil organic matter compartments, with the highest rates from the decomposition of fresh litter and the turnover of the microbial biomass. Because of the properties of their chemical structures, certain macromolecular components of plants or microorganisms are not readily decomposable by microorganisms, and are called **recalcitrant**. Especially aromatic plant constituents, particularly lignin, but also long chain aliphatic compounds accumulate selectively in the soil during decomposition compared to other, more readily decomposable substances, such as polysaccharides. The availability of a N source probably plays an important role in the regulation of the decomposition of lignocellulosic substances in the soil. Lignin can only be decomposed under aerobic conditions and its decomposition is inhibited by oxygen deficiency, so that only low-molecular lignin components or lignin precursors are attacked. This causes the accumulation of lignin in anoxic soils or sediments (formation of peat and coal). During the course of the decomposition of litter, phenols can form recalcitrant polyphenol-protein complexes together with proteins and thus reduce N losses in N-poor sites. The condensed aromatic structures (Fig. 3.2c) resulting from vegetation fires are considered to be recalcitrant. In general, the following stability sequence can be derived for organic compounds originating from plants: sugars, starches, proteins < celluloses < lignins, wax, resins, tannins.

A considerable portion of the organic matter in soils can consist of finely distributed charred organic matter (*black carbon*, *charcoal*), originating from vegetation fires. The leads to an incomplete combustion of organic materials that leaves behind a continuum of charred aromatic structures condensed to different degrees. Both the chemical recalcitrance and interactions of the charred structures with minerals protect them from rapid degradation, so that estimates for the residence time of char in soils range from a few hundred to more than 10,000 years.

3.3.2.1 Decomposition Pathways for Various Plant Constituents

The decomposition of sugars, starches, proteins, hemicellulose or cellulose, and non-lignified parts (Fig. 3.3) in general takes place most rapidly. In contrast, lignocellulose is decomposed much more slowly, as well as already decomposed material, e.g. peat, manure or compost. Aquatic plants do not have any supporting tissue, and therefore do not contain lignocellulose. This is why the organic matter in subaquatic soils is generally much more strongly decomposed than peats or bogs in near-shore marine environments. Polysaccharides (cellulose, hemicellulose) and proteins serve as a C and energy source for microorganisms and are fully metabolized in the process. After extracellular enzymatic hydrolysis the resulting monomer or dimer fragments are absorbed by the microorganisms. These substances are oxidized by heterotrophic bacteria as a source of energy ("catabolism"). H_2O and CO_2 are produced as end products in aerobic environments, while the associated mineral salts are taken up by the bacteria or are released in the soil solution. The same products can be produced under anoxic conditions, provided that other oxidizing agents (electron acceptors) such as NO_3^-, SO_4^{2-}, Mn(IV) or Fe(III) are available. However, decomposition is then slower and usually incomplete, and results in low-molecular organic substances such as fatty

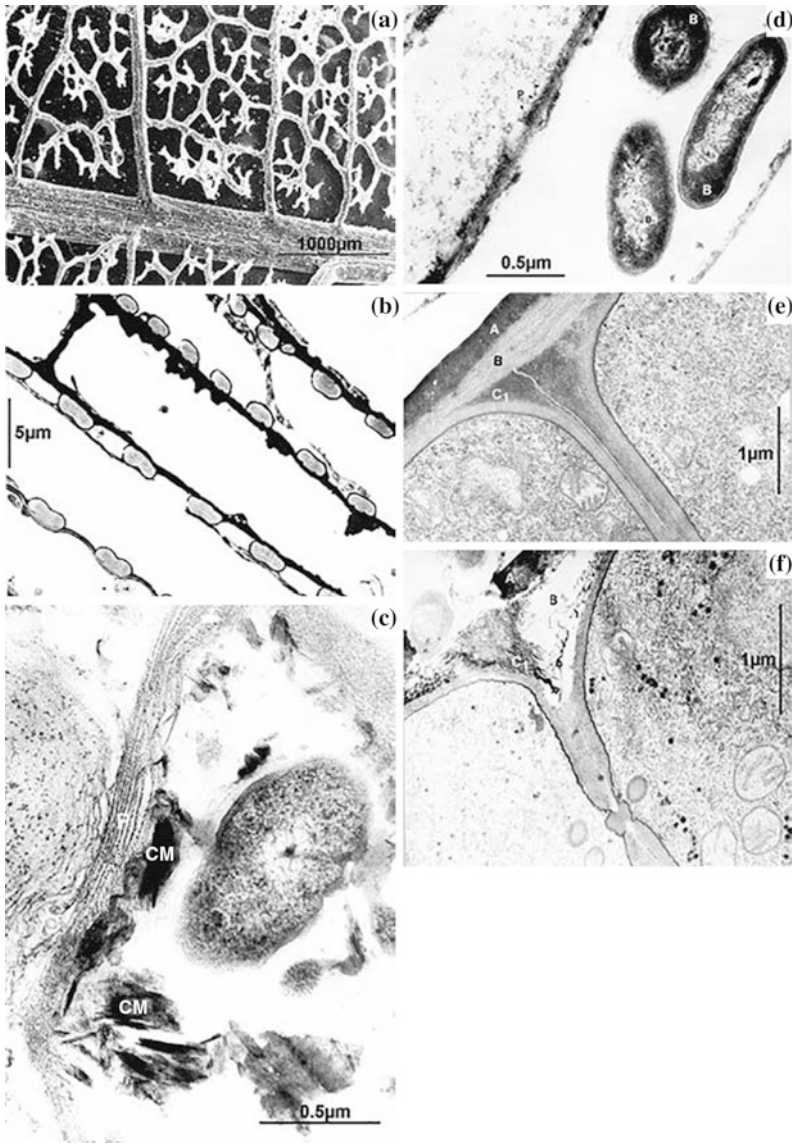

Fig. 3.3 Scanning electron microscope image of an oak leaf 4 weeks after falling off the tree (from Olah et al. 1978): **a** Preferential decomposition of parenchymatic tissues, the ligneous tissues remain behind; **b** fungi can be seen on the surface of the decomposed leaf. **c** Polysaccharide fragments (*P*) of an algae cell in close association with clay minerals (CM); decomposition of secondary resources: **d** invasion of a fungi (*Stropharia cubensis* Earle) by bacteria and decomposition of the cytoplasm after 7 days in the soil; **e/f** fungi cell wall before and after decomposition by bacteria

acids, methane, hydrogen sulfide or also hydrogen, with a lower energy gain for the microbes.

A portion of the easily digestible substrates is directly taken up by the microorganisms and used for the synthesis of their cells ("anabolism"). Labelling with radioactive or stable isotopes (usually ^{14}C, ^{13}C and ^{15}N) showed that the C and N from polysaccharides and proteins added to soils is found in the microbial biomass or their metabolites. Thus, plant polysaccharides and proteins are mainly subject to microbial resynthesis. A small fraction of the polysaccharides can be selectively accumulated due to "impregnation" with recalcitrant plant (lignin, cutin) or microbial constituents (melanin).

In contrast, the decomposition of lignin takes place much more slowly as an extracellular, co-metabolic process, i.e. the lignin does not serve as a C or energy source for microorganisms. For this reason, the decomposition of lignin requires the presence of a C and energy source (e.g. sugar, cellulose), since the lignin-decomposing

microorganisms, mainly white rot and soft rot fungi, cannot grow with lignin as their only source of C. Brown rot fungi cause a modification of the lignin (e.g. demethylation), but no complete decomposition. Thus the fate of C from lignin is different to the fate of C from polysaccharides and proteins. Lignin decomposition takes place through a non-specific radical mechanism, which leads to the cleavage of bonds in the side chains and in the aromatic rings (Fig. 3.2b). On the one hand, a liberation of CO_2 is observed that indicates partial mineralization, and on the other, often only part of the lignin macromolecule is transformed in its structure. These modified lignin components are subject to further direct oxidative transformation. Especially the more easily degradable fractions of lignin, particularly those units that are linked by ether bonds, are strongly transformed. Lignin macromolecules that are modified by degradation consist of aromatic components with a high degree of C substitution, mainly carboxyl groups (Fig. 3.2c). Because of this and because of the opening of the rings during decomposition, the lignin molecule becomes increasingly soluble in bases and also in water. Thus a part of the partly degraded lignin components are leached. The recalcitrant lignin constituents, i.e. the ring units that are linked by C–C bonds, are selectively accumulated. Lignocelluloses in the soil are decomposed by a synergetic microbial community, where cellulose and lignin decomposing organisms work together. The microorganisms use both low-molecular lipids and cutin as a C and energy source, and at the same time, new microbial alkyl-C compounds are formed in the soil. Generally all recognizable plant or microbial components in a soil have turnover times lower than the turnover times of the total organic matter (Amelung et al. 2008).

3.4 Formation of Stable Organic Matter

Plant and microbial residues and their transformation products can be protected from further microbial degradation through various mechanisms. These stabilization processes have an effect on the mixture of fresh and transformed plant residues resulting from the decomposition phase, as well as on newly-formed microbial residues that were in turn transformed (Fig. 3.4). They lead to a significant deceleration of the initial rapid mineralization rate.

Parts of the litter can be protected from further decomposition inside aggregates where they are poorly accessible, and thus enter the moderately stable organic matter fraction. Poorly decomposable components (e.g. lignin or aliphatic compounds) can be selectively accumulated in these plant residues at different states of decomposition. The sorption of dissolved organic matter (DOM), resulting either directly from the

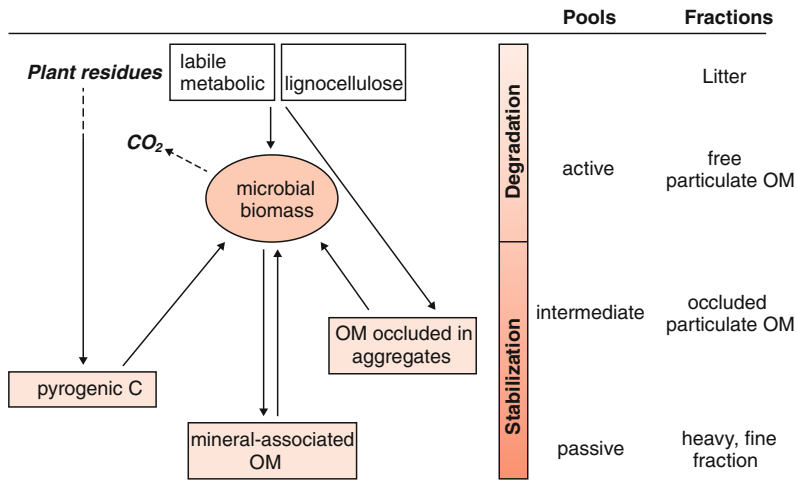

Fig. 3.4 Processes of transformation and stabilization (humification) of organic matter (OM) in the soil

decomposition of litter or from the microbial biomass, can lead to the transfer of carbon into the stable fraction. The development of organo-mineral compounds leads to the formation of stable organic matter products, which are mineralized only very slowly. Especially microbial polysaccharides and proteins are stabilized against further decomposition through binding onto the fine-grained minerals of the silt and clay fraction (Fig. 3.3c).

3.4.1 Stabilization by Interactions with the Mineral Phase

Organic substances can be stabilized and protected from microbial degradation through interactions with minerals. This mainly involves interactions with particles in the clay fraction (clay minerals, iron oxides). This leads to the formation of stable "**clay-organic matter associations**" or **organo-mineral compounds**. The binding between minerals and organic substances can take place through various mechanisms and depends on the one hand on the type of mineral and its surface charge, and on the other, on the type and charge of the functional groups in the organic matter. Therefore, pH value and base saturation are of great importance for the development of organo-mineral compounds. The following mechanisms play a role in binding of organic matter onto the mineral phase (Fig. 3.5):

1. Binding onto singly coordinated hydroxyl groups on the mineral surface, which can be either protonated or dissociated depending on the pH value of the soil. Through **ligand exchange**, inner-sphere complexes are formed between the carboxyl groups of the organic matter and protonated surfaces with positive partial charges. Here, the surfaces of Fe and Al oxides, allophanes and imogolites, and also the edge surfaces of clay minerals are most significant, whereas no ligand exchange reactions take place with silanol groups (SiOH) (Fig. 3.5a, b). Fe and Al oxides, allophanes and imogolites provide a particularly high specific surface area for such interactions. Because ligand exchange reactions only take place with protonated, singly-coordinated hydroxyl groups, they mainly play a role in acidic soils.
2. In soils with slightly acidic or neutral pH values, binding onto the siloxane surface of clay minerals (Chap. 2) with permanent charge increases in significance (Fig. 3.5a). The dominating mechanisms are the ionic bond between organic cations and the negative charges of clay minerals. The main organic cations involved are amines (alkyls etc.), amino sugars and amino acids, which accept a proton below the isoelectric point and thus have a positive charge. They are instead of the exchangeable inorganic cations bound by Coulomb forces. But also metal complexes of organic acids can be adsorbed. A polyvalent, usually hydrated metal cation forms a bridge and simultaneously neutralizes negative charges on the clay mineral and on the dissociated acidic groups of the organic molecule. An outer-sphere complex is formed. The exchangeable cations of clay minerals, especially polyvalent cations such as Ca^{2+} and Al^{3+}, can have an effect on the stability of the organo-mineral compounds. The adsorption of organic acids onto a smectite that is saturated with various cations increases in the sequence $Na^{+} < K^{+} < Ca^{2+} < Al^{3+} < Fe^{3+}$. Extractants, such as sodium pyrophosphate, which transform Fe, Al, and Ca into soluble complexes therefore also extract a relatively large amount of organic matter from the soil.
3. Weak interactions occur between the uncharged, nonpolar groups of the organic matter and the uncharged, neutral mineral surfaces (e.g. Si–O–Si groups) (Fig. 3.5c). Hydrogen bonds play a role in the binding of larger organic molecules. H bonds form preferentially via H_2O molecules of the exchangeable cations, or between molecules that are sorbed and those that are not yet sorbed. In contrast, they occur less frequently between these directly with the mineral

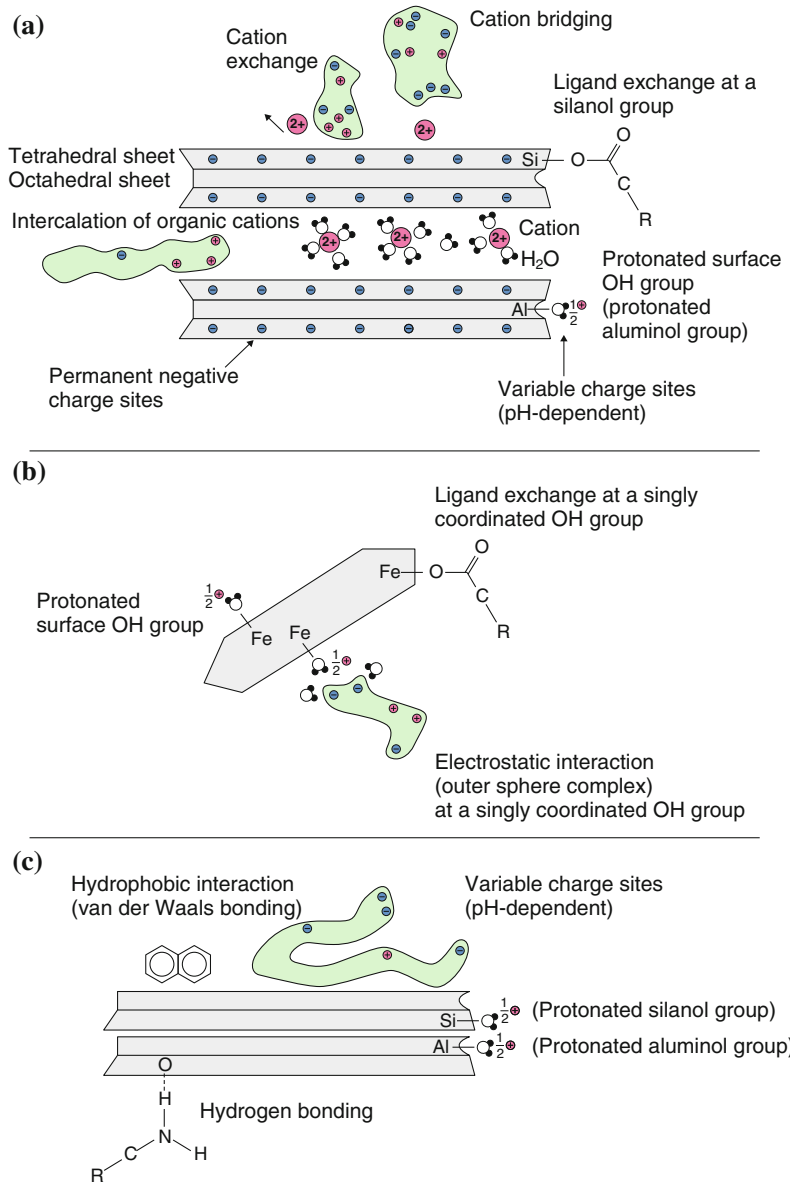

Fig. 3.5 Binding mechanisms of clay-humus coupling in the soil. **a** On phyllosilicates with permanent charge, **b** on (hydr)oxide surfaces with variable charge, **c** on minerals with neutral surfaces

surface. Despite the weaker and short-ranging individual bonds compared to the interactions mentioned above, Van der Waals interactions are probably mainly responsible for the binding of larger molecules onto the uncharged surfaces of clay minerals, e.g. kaolinite, pyrophyllite, or quartz. Hydrophobic interactions can then lead to additional binding of organic substances onto already sorbed molecules. They are most significant at low pH values, because the hydroxyl and carboxyl groups are then protonated.

4. The decomposability of organic matter can also be strongly reduced by complex formation with metal cations. In this case, the bonding of metal cations (Ca, Al, Fe, heavy metals) onto the organic matter inhibits attack by enzymes.

This strong association between organic and mineral matter in soils is evidenced by the fact

Table 3.4 Properties and composition of organic matter in the particle size fractions of the A horizon of a Cambisol (Guggenberger et al. 1994)

Characteristic	2000–63 µm	63–2 µm	<2 µm
Composition (%)	Plant residues		
Alkyl C (e.g. lipids)	40–46	31–44	46–50
O Alkyl C (mainly polysaccharides)	35	26–30	22–25
Aryl C (aromatic C)	24–26	16–27	13–14
C/N ratio	Wide	Medium	Narrow
Degree of transformation of lignin	Low	Medium	Strong
Origin of polysaccharides	Mainly plant	Plant/microbial	Mainly microbial

that it is impossible to fully separate the organic matter from the mineral phase. It is possible to use an alkaline solution (0.1 N NaOH, humic substance extraction) to partially extract the organic matter from the soil, but a non-extractable fraction (the so-called humic fraction) always remains in all soils. A further portion can be extracted when the minerals are previously dissolved using hydrofluoric acid. Even through oxidation with H_2O_2 or NaOCl, it is not possible to completely destroy the bound organic matter.

There are many simple organic compounds that can be bound onto minerals of the clay fraction. These include alcohols, sugars, amino acids and amines, as well as simple aromatic compounds such as benzene, phenols etc. If the clay fraction is isolated from the soil and its composition is investigated, mainly alkyl compounds and polysaccharides are found, however, only low concentrations of aromatic compounds, such as strongly transformed lignin fragments (Table 3.4). Bound organic matter is also rich in carboxyl and amide groups.

The stabilization in organo-mineral compounds is also highly significant for the organic nitrogen, the majority of which is bound in the clay fraction in the form of slowly mineralizable peptide structures. Some of these compounds are also enzymes. Their activity and the decay rate are reduced by binding onto the minerals of the clay. For this reason, the C/N ratio in the clay fraction is often between 8 and 12. However, it must also be considered that this also includes the NH_4^+ that is bound to the clay minerals. The association of organic substances and clay minerals becomes visible under the electron microscope (Fig. 3.6). The high stability of organo-mineral compounds is reflected by the fact that the temperature of thermal decomposition of organic matter increases after binding onto the mineral phase, and at the same time, the **decomposition rates** of these bound organic substances decline strongly.

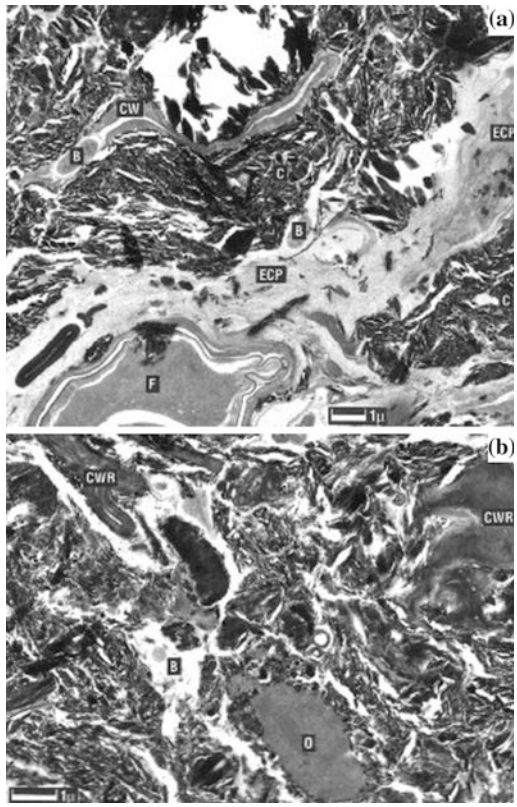

Fig. 3.6 Scanning electron microscope images of the association between organic matter and mineral particles in the soil; *B* bacteria cells, *C* clay minerals, *ECP* extracellular polysaccharides, *F* fungi, *CW* cell wall of a collapsed cells, *CWR* cell wall remains, *O* amorphous, humified organic matter (after Ladd et al. 1996)

The cation exchange properties of clay minerals apparently hardly change through bonding/binding with humic substances. In contrast, organic substances can effectively compete with the sorption of inorganic anions onto clay minerals and oxides. Furthermore, the crystallization ("aging") of pedogenic Al and Fe oxides can be delayed or inhibited, if adsorbed organic substances combine in very stable complexes with Al and Fe ions. The polarization of the adsorbed organic molecules and the high charge density of the clay minerals may promote catalytic reactions (protonation, oxidation, polymerization).

3.4.2 Stabilization by Spatial Separation

Stabilization of otherwise readily decomposable substrates in the soil can result from the spatial separation of the substrate from the decomposers, which thus prevents degradation. The spatial localisation of organic matter in aggregates hinders access by microbes and enzymes. Inaccessibility is mainly caused by occlusion of OM in aggregates and entrapment of OM in pore spaces. This usually involves partially decomposed plant residues that are occluded inside the aggregates and are inaccessible to microorganisms. It was observed that the plant residues occluded inside aggregates are enriched in lignin, while the polysaccharides had already been degraded.

Soil aggregation has a strong effect on the physical separation between substrate and decomposers. The distribution and composition of organic matter is regulated by the aggregation, which in turn is determined by, among other things, the soil type, the pedogenesis and the activity of the soil fauna. The aggregation of mineral soil particles by organic matter is a complex series of interactions, taking place at various spatial scales (Fig. 3.7). Particles in the clay fraction are aggregated into packages of <20 μm, which are then in turn bound to form stable microaggregates with a size of 20–250 μm. These are bound together to form macroaggregates (>250 μm). Mainly polysaccharides, secreted by roots and microorganisms, are responsible for the formation and stabilization of microaggregates. Microaggregates are stable over decades. Macroaggregates result from the effects of roots, fungal hyphae and other plant residues, which link the microaggregates together to form larger aggregates. For this reason, stable macroaggregates have a high proportion of relatively young particulate organic matter. The stabilizing effect of these organic constituents in the macroaggregates only lasts for a few years. The composition and properties of the macroaggregate surface therefore differs significantly from those inside the aggregates.

The formation of organo-mineral compounds in soils as well as aggregation are promoted by high biological activity, because microorganisms

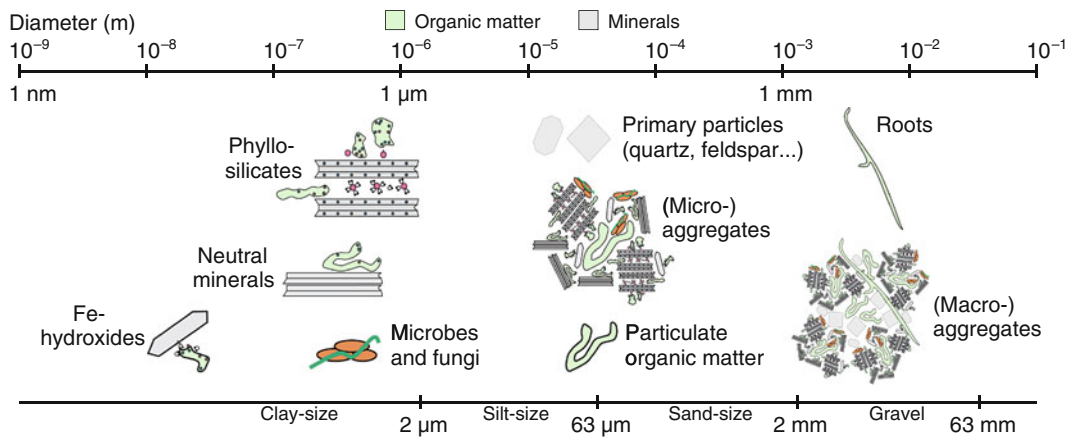

Fig. 3.7 Diagram of the association of organic matter in micro- and macroaggregates in soils of temperate climates

constantly form reactive organic substances (e.g. mucus) and soil fauna mixes organic matter closely with mineral particles (see bioturbation). Here, the formation of organo-mineral compounds in the intestines of earthworms is of special importance. The combination of poorly degradable organic substances (e.g. peat) with clay minerals under sterile conditions, in contrast, does not result in any stable organo-mineral compounds, even after a longer period of exposure. The significance of organo-mineral compounds for soils lies mainly in the fact that the organic matter binds mineral particles together and thus makes a considerable contribution to the structure formation. Accordingly, the formation of stable aggregates is closely linked to the development of organo-mineral compounds. If the supply of organic residues is reduced or even totally eliminated, the structure formation is strongly impaired. This is associated with an initial depletion of the organic matter, especially in the fraction of the occluded plant residues.

3.4.3 Organic Matter in Functional Soil Fractions

Physical fractionation, based on a separation resulting from differences in density or particle size, is used to separate the plant residues from organo-mineral compounds. It is generally performed following pre-treatment consisting of agitation or ultrasound to destroy the aggregates. The obtained fractions are then separated using sieves, sedimentation and/or density fractionation (Christensen 2001). With **density fractionation**, the sample is suspended in a liquid with a density between 1.6 and 2.4 g cm^{-3} (organic solvent mixtures or inorganic salts), so that the light, floating organic material can be separated. For **particle size fractionation**, the material in the >63 μm fraction (sand fraction) is separated, which can be further fractionated by sieving. The organo-mineral compounds <63 μm are separated using sedimentation in water, and the <2 μm fraction can be further separated via centrifugation. Fractionation according to the particle size and the density are often combined. Using such combined particle size and density fractionation, it is possible to separate specific organic matter fraction from mineral soils. The particulate organic matter can be found in the light or coarse fraction, which mainly consists of partly decomposed plant residues. The heavy and fine fractions mainly contain organo-mineral compounds. If the aggregation is selectively destroyed by ultrasound, the occluded particulate organic matter, mainly plant residues with a higher degree of decomposition, can be isolated.

The OC fraction in organo-mineral compounds, which cannot be separated from the clay by ultrasonic treatment (to destroy the aggregates) and subsequent density separation, lies between 10 and 95 % in various soils. In general, organo-mineral compounds account for high proportions of the total carbon especially in the subsoil, while in the topsoil, a larger fraction of plant residues can be found in a form that is free and/or occluded in aggregates. The content of this particulate organic matter is higher in topsoils under forest or grassland than under cultivated land. Plant residues are mainly added to the topsoil; this is why their proportion in the organic matter here is also the highest, while organo-mineral compounds dominate in the B horizon. For this reason, the degree of decomposition generally increases from top to bottom. However, it must be considered that root litter and leaching of particulate and dissolved organic matter have an influence on the composition of the organic matter in the subsoil.

3.5 Composition and Properties of Soil Organic Matter

3.5.1 Binding Forms of C, N, P and S in Soil Organic Matter

Characteristic changes in the composition of the organic matter take place during the course of decomposition and stabilization processes. The relative proportion of aromatic compounds

generally remains constant or decreases, the polysaccharides or O/N-alkyl C fraction decreases, and the alkyl C (long-chain aliphatic C compounds) fraction increases. These conversion processes lead to an increase in the alkyl C to O/N-alkyl C ratio, a parameter often used for the degree of decomposition of organic matter. These typical changes can be observed both in the organic layers of forest soils and in the particle size fractions of mineral soils (Table 3.4). The proportion of carboxyl groups also increases considerably during the course of humification. This higher oxidation state is responsible for the high, pH-dependent cation exchange capacity of organic matter.

Vegetation and forest fires are observed on about 530×10^6 ha of land annually worldwide. These fires convert approximately 90 % of the biomass to CO_2 and NO_x; however, charcoal is also formed due to the incomplete combustion, which represents a relevant C and N sink when entering the soil. It is assumed that charcoal is mainly formed in steppe and savanna soils through (natural) fires, but it also plays a role in soils of temperate and boreal zones. This *black carbon,* the decomposition product of charcoal resulting from vegetation fires, is stored in the soil and remains stable over long periods of time. For this reason, in addition to the morphologically identifiable pieces of charcoal often found in soils, high proportions of aromatic C and N compounds can also be found in the finely distributed soil organic matter. This pyrogenic carbon probably mainly contributes to the organic matter in particularly dark humic soils. High proportions of black carbon have been documented in Chernozems and Chernozem-like soils, and in anthropogenic soils (Terra preta). The charcoal residues are most probably responsible for the condensed aromatic structures (Fig. 3.2c) observed in many soils. Their formation from the lignin of plant residues or other precursors during biochemical conversion processes has not been documented. Condensed aromatic structures in the soil organic matter are increasingly used as an indicator for vegetation fires. Soils at the periphery of industrial areas often also contain organic components originating from industrial sources, such as coal dusts, ashes and soot.

Nitrogen is an important constituent of soil organic matter. While most of the C is liberated as CO_2 over the course of decomposition, N is initially mainly stored in the microbial biomass, more than 95 % of which is stabilized in organic matter on the long term. The C/N ratio of the organic matter therefore becomes increasingly narrow during the course of degradation and associated soil organic matter formation, reaching values of 10–12 in soils or soil fractions which have been intensively processed. The major part of the organically bound nitrogen is probably stabilized in the form of amide structures. The majority of the nitrogen is found in the form of peptide groups, a smaller portion in the form of free amino groups. Wet chemical analyses demonstrate that amino acids and amino sugars, together accounting for about 30–70 % of the total organic nitrogen, represent the majority of the molecular units containing N. However, because the hydrolysis is not complete, the total content of peptide structures cannot be determined. Proteins and enzymes are sorbed onto the clay fraction of soils, and are probably responsible for the narrow C/N ratio of the organic matter in this fraction. Contrary to former beliefs, the proportion of nitrogen in heterocyclic aromatic compounds is considered to be low with a maximum of 5–10 %. However, soils affected by vegetation fires exhibit higher proportions of heterocyclic N compounds, especially pyrrole and indole structures.

Sulfur is also always a component of soil organic matter. The C/S ratio is of about 200 in grassland and forest soils, and about 130 in cultivated soils. Up to 90 % of the sulfur is bound in organic form, about 30–75 % of which as sulfate ester. Another important binding form that is found is C-bound sulfur at various oxidation levels. Reduced organic S (oxidation level < +1) includes organic mono- and disulfides as well as thiols, e.g. as a component of proteins and peptides; intermediate organic S (oxidation level +2 to +5) includes sulfoxides; sulfones and sulfonates; oxidized organic S (oxidation level +6) includes ester sulfates and sulfamates. According

to Prietzel et al. (2007), the distribution of the S binding forms depends on the land use and the O_2 availability in the soil. The proportion of reduced organic S binding forms increases in the sequence: Arable land < forest soil < moor.

Phosphorus is also found in soils with more than 60 % in organic form. Although a portion of the organically bound phosphorus could not yet be identified, more than 50 % of the total P in soils has been found to be in the form of phosphate esters. Analysis using nuclear resonance spectroscopy (^{31}P) demonstrated that the most important chemical forms are orthophosphate monoester R–OPO_3^{2-} (inositol phosphates, mononucleotides, sugar phosphates), orthophosphate diester R_1–OR_2–OPO^{2-} (phospholipids, DNA and RNA, teichon acids) and phosphonate (C–P binding).

3.5.2 Properties of Soil Organic Matter

The properties of the humic substances determine the soil's characteristics in many ways. Of course, the influence of organic matter on the properties of mineral soils is highest in the A horizons.

The **adsorption capacity** of humic substances is significant for the binding of many nutrients that are present as cations in the soil. During the course of the humification process, the CEC increases through oxidation and the formation of carboxyl groups. In general, a sufficient humus supply is particularly important for maintaining the CEC in clay-poor soils, or soils where the clay fraction mainly consists of clay minerals with low CEC, e.g. kaolinite. This is particularly true for organic layers and moors, where the CEC is almost exclusively attributed to the organic matter, as well as sandy soils, which owe about 75 % of their cation exchange capacity to organic matter. The CEC of isolated humic substances lies between 300 and 1400 $cmol_c\ kg^{-1}$, but it is strongly pH-dependent. The CEC of soil organic matter is much lower at 60–300 $cmol_c\ kg^{-1}$, because the less transformed litter substances only have a low CEC. In addition, part of the charges can be protonated or is not available for the CEC due to interactions with the mineral phase or complex formation.

Table 3.5 Sorption capacity of the mineral and organic components of an Ah horizon with different organic matter contents for heavy metals (Lair et al. 2007)

	Sorption capacity ($mmol^2\ kg^{-1}\ L^{-1}$)		
	Cu	Cd	Zn
Mineral phase	10.7	2.5	3.5
Soil organic matter			
Bare fallow 10.0 mg C g^{-1}	65.2	21.4	25.4
Grassland 26.0 mg C g^{-1}	87.5	33.0	37.7

Metal ions, especially Cu^{2+}, Mn^{2+} and Zn^{2+}, but also other polyvalent cations (e.g. Fe^{3+}, Al^{3+}), can also be found in stable complexes with organic compounds. In water-soluble form, these chelates can be transported downwards through the soil with seepage water (e.g. within the scope of podzolization). They also increase the availability of chelated micronutrients for plants.

Organic matter also has a great significance for the **binding of inorganic and organic pollutants** in soils. The binding of pollutants onto organic matter regulates their bioavailability and thus also their persistence. On the one hand, this prevents direct harm to organisms, and on the other, it also reduces or retards their translocation to deeper soil layers or to the groundwater. Investigations in soils with different humus contents show that the organic matter is mainly responsible for the binding of heavy metals. Depending on the humus content, the organic matter in the Ah horizon of a Cambisol provides 6–16 times more sorption capacity for Cu, Cd and Zn than the mineral phase (Table 3.5).

Soils with higher organic matter contents are characterized by a higher **porosity** and lower **bulk density**. This results in a linear relationship over a wide range, only small changes are observed at high OC contents, which are attributed to the organic matter's low density.

Organic matter has considerable effects on the soil's wettability. Plant residues and strongly transformed humic substances have hydrophobic properties. The binding of organic molecules to the surface of (hydr)oxides and clay minerals

generally causes these surfaces to be more water repellent. This has an effect on the development of flow paths in the soil.

Organic matter has a positive effect on the structural stability of soils. It favors the formation of a **stable aggregate structure**, particularly in Cambisols, Luvisols and Chernozems. The binding of organic matter onto the surfaces of (hydr)oxides and clay minerals leads to the development of very stable microaggregates (<250 μm), which serve as building blocks for the less stable macroaggregates (>250 μm) (aggregate hierarchy). The development of macroaggregates is particularly characteristic for clayey soils and requires the continuous input of organic residues. This promotes microbial activity and thus the production of microbial polysaccharides, which are mainly responsible for the stabilization of macroaggregates.

This effect is less pronounced in Ferralsols and Andosols, because here mainly oxides and hydroxides have a stabilizing effect in primary organo-mineral compounds, while macroaggregation is largely lacking. Increased aggregate stability counters the effects of erosion, since there is less tendency towards soil surface sealing. Furthermore, the stability towards heavy loads is improved.

Humus has a high **water storage capacity**; it can store about 3–5 times its own weight in water. Through the aggregating effect, organic matter also has an indirect effect on the pore size distribution and water balance. This is why the humus content determines the field capacity in sandy soils. By adding large amounts of barn manure, it was possible to increase the humus content in such soils from 0.93 to 1.38 % within a period of 18 years, whereby the pore volume increased from 38.4 to 41.4 %. Mulch covers also decrease evaporation and increase the infiltration of water. A high soil organic matter content shifts the soils' **consistency limits** towards higher water contents, so that soil tillage can be performed at a wider soil moisture range without structural damage.

Humic substances are the source of the dark color of the topsoil, and thus promote the warming of the soil in the spring in cool climate regions (longer vegetation period). On the other hand, an organic layer or mulch can lead to insulation of the mineral soil against temperature fluctuations.

3.6 Soil Organic Matter Dynamics

3.6.1 Turnover Rates and Turnover Time of Organic Matter in Soils

The **turnover time** is defined as the quotient of the humus in the soil with the annual input of organic matter:

Turnover time (a) = amount of OM (kg m^{-2})/annual net input (kg m^{-2} a^{-1})

Under the assumption of steady state conditions, one obtains information on the turnover time of organic matter in the soil, i.e. the period of time that is required to completely transform the organic matter one time. The annual input of organic matter represents about 3–5 % of the stocks; about the same amount of C is liberated back into the atmosphere. This results in estimated average turnover times of several decades. Depending on the data used, it is estimated to be of 26–40 a, but large differences are observed in different climate and vegetation zones. Estimated turnover times are of 18 a for soils under grassland, 16 a for deciduous forests, 6 a for tropical forests, 7 a for agricultural soils, and more than 2000 a for tundra soils.

The inverse of the turnover time delivers the **decomposition rate** k (a^{-1}) = annual net input (kg m^{-2} a^{-1})/amount of OM (kg m^{-2}).

Depending on the composition and site conditions, decomposition rates can vary across a wide range. They fluctuate between 0.03 a^{-1} in tundra soils and 6 a^{-1} in tropical rainforests. Decomposition rates of up to 2–3 % d^{-1} are known to exist for readily degradable crop residues on field sites. In forest soils of temperate zones, rates of approx. 0.1 % d^{-1} are given for readily decomposable substances, and up to 10^{-5} % d^{-1} for poorly decomposable substances, which then represent an (almost) inert fraction.

3.6.2 Estimation of the Turnover Time

3.6.2.1 ^{14}C Content of Organic Matter

The **radiocarbon age** of the soil organic matter is derived from the natural ^{14}C activity. The radiocarbon method is based on the measurement of the ratio of the quantity of the carbon isotope ^{14}C to ^{12}C in a sample. The average turnover time of OC in the soil or in soil fractions can then be calculated from the decay constant or the half-life of ^{14}C. The ^{14}C content of a sample can be either determined by counting the decaying ^{14}C nuclei with a Geiger counter or by counting the still existing ^{14}C nuclei using accelerator mass spectrometry. The latter method requires less material, but is more complex and expensive. The results are given in pmC (percentage of the modern C fraction) or as ^{14}C age in years before present, and are based on a standard from the year 1950. The determination the ^{14}C/radiocarbon age enables an estimate of the average turnover time of the organic matter in soils or individual fractions. Meanwhile, it is possible to determine the ^{14}C contents for individual components of the organic matter, e.g. for the microbial biomass and also for the mineralized CO_2 (Fig. 3.8). The use and atmospheric testing of nuclear weapons between 1945 and 1963 strongly increased amount of ^{14}C in the atmosphere. Still today, the $^{14}C/^{12}C$ ratio has not yet dropped back to levels from before 1945. This bomb (radio)carbon can be detected in soils and generally changes the ^{14}C signature of the organic matter to "younger" values, however, due to its penetration behavior into deeper soil horizons and in various organic matter classes, it can be considered as a tracer enabling conclusions about current pedogenic processes, e.g. bioturbation in Chernozems, pedoturbation in Vertisols, cryoturbation in Cryosols, and percolation into the aquifer.

The organic/litter layers of forest soils are recent, as is also the topmost layer of Ah horizons, with a ^{14}C age of less than 500 years, because the organic matter in the topmost profile section is continuously being renewed by the addition of fresh plant litter. The impact of C losses through the cultivation of native soils became obvious in the Great Plains, where the average ^{14}C age was increased by 900 years. This demonstrates that cultivation mainly liberates C from fractions with a low ^{14}C age.

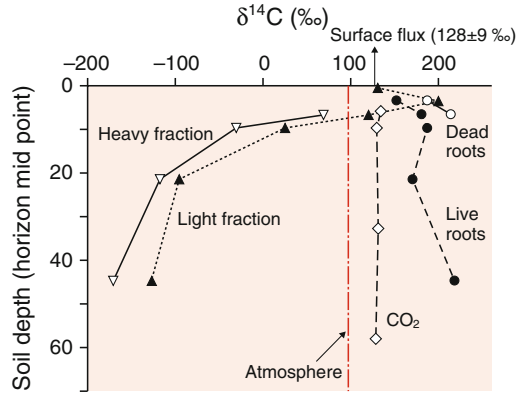

Fig. 3.8 $\delta^{14}C$ contents (‰) of various organic matter fractions in a forest soil in temperate climates (after Trumbore 2000)

With increasing depth, the radiocarbon age achieves values between 2500 and 4000 years before present. Both in cultivated and in native Phaeozems, the organic matter at a depth of 10–20 cm demonstrates a 1200-year higher ^{14}C age than at a depth of 0–10 cm. This is coupled with a lower mineralization rate of the organic matter from deeper soil horizons. ^{14}C ages of up to 5000–6000 years BP were observed in the subsoils of Chernozems and Luvisols, while the Bh horizons in Podzols have a younger ^{14}C age due to constant additions of recent OC.

In general, the ^{14}C age of the individual organic matter fractions increases with increasing profile depth (Table 3.6). As expected, smaller, still poorly decomposed fragments of lignin and polysaccharides are usually only 10–100 years old. Organic matter that is bound in organo-mineral associations is particularly well stabilized against decomposition. The oldest organic matter is found in the fine silt and clay fractions, e.g. in the illuvial horizon of Luvisols.

Table 3.6 Characteristic parameters for various organic matter fractions in soils: organic C contents and stocks

Horizon	Depth (cm)	OC concentration (g kg^{-1})	OC stock (kg m^{-2})	Fraction < 1.6 g cm^{-3}.[a)]	Fraction > 1.6 g cm^{-3}	Fine soil		Fraction < 1.6 g cm^{-3}.[a)]		Fraction > 1.6 g cm^{-3}	
				(g kg^{-1} OC)		^{14}C activity (pmC)	^{14}C age (years BP)	^{14}C activity (pmC)	^{14}C age (years BP)	^{14}C activity (pmC)	^{14}C age (years BP)
Steinkreuz (*Cambisol*)											
Ah	0–5	82.6	4.29	770	230	112.3	Modern	112.4	Modern	111.9	Modern
Bv1	5–24	9.8	2.41	500	500	101.3	Modern	104.8	Modern	98.0	160 ± 25
SdBv2	24–50	3.0	0.79	230	770	92.1	655 ± 25	119.0	Modern	84.2	1375 ± 30
IISd Bv3	50–80	1.4	0.40	190	810	80.9	1700 ± 30	122.8	Modern	69.8	2890 ± 30
IIICv	85–115	1.1	0.14	160	840	80.6	1758 ± 56	117.2	Modern	70.8	2780 ± 45
IVC1	115–140	0.5	0.07	150	850	76.3	2165 ± 30	116.4	Modern	69.1	2960 ± 30
Waldstein (*Podzol*)											
Ae	0–10	38.1	2.90	750	250	93.6	525 ± 30	92.0	655	98.5	120 ± 25
Bh	10–12	92.8	1.04	270	730	98.5	120 ± 25	95.8	435	99.5	30 ± 20
Bs	12–30	52.0	5.47	210	790	91.1	745 ± 40	87.0	1010	92.2	700 ± 25
Bv	30–55	7.7	2.09	120	880	82.2	1570 ± 25	87.3	980	81.5	1640 ± 20
C1	55–70	1.7	0.25	100	900	62.0	3840 ± 70	90.8	730	58.8	4265 ± 30
C2	70–80	1.9	0.19	80	920	62.0	3840 ± 70	112.8	Modern	56.5	4580 ± 30
Rotthalmünster (*Luvisol*)											
Maize Ap	0–30	12.9	5.35	186[a]	814	102.7	Modern 54[b] (±4)	nd	nd	106.5 ± 0.3	Modern 58[b] (+9/-8)
	30–45	6.7	1.55	232[a]	768	nb	144[b] (+9/-8)	nd	nd	97.5 ± 0.3	205 ± 22 151[b] (+23/-18)
Forest	0–7	40.5	2.57	563[a]	437	108.3	Modern	nd	nd	nd	nd

Radiocarbon content and the resulting calculated mean ^{14}C age in different humus fractions (from Eusterhues et al. 2003, 2005; Kaiser and Guggenberger, unpublished; Rethemeyer 2004)
[a]Difference calculation
[b]^{13}C turnover time (John et al. 2005)
nd not determined

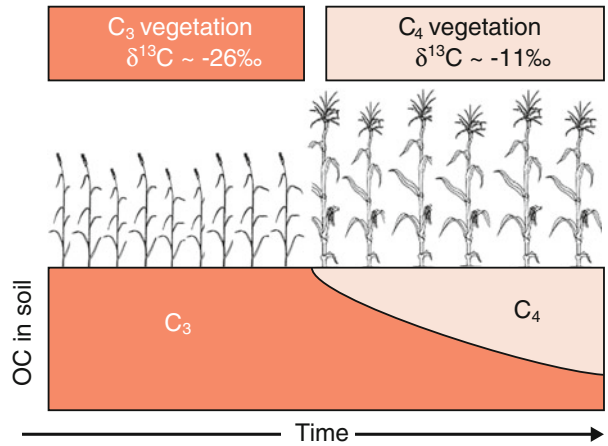

Fig. 3.9 Recording of the turnover time of organic soil carbon based on the change in the $\delta^{13}C$ signature after the change from C3 to C4 vegetation, as well as the quantity and mean turnover time of OC in density fractions of a Luvisol from loess, 24 years after the conversion from wheat cultivation to grain maize cultivation (after John et al. 2005)

OC fraction	Amount (g C kg^{-1})	Proportion maize-derived OC (%)	Turnover time* (years)
Total OC	13.0	35.7	54
OC bound to mineral surfaces (heavy fraction, > 2 g cm^{-3})	11.3	31.4	63
OC in free particulate organic matter (light fraction, < 1.6 g cm^{-3})	0.5	64.8	22
OC in occluded particulate organic matter (light fraction in aggregates, 1.6 ... 2 g cm^{-3})	1.1	38.3	49

*mean turnover time assuming homogeneous C pools and first oder decomposition kinetcs

3.6.2.2 ^{13}C Isotope Signature of Organic Matter

The transformation and turnover time of organic matter can also be determined through the measurement of the **^{13}C isotope signal** in the soil (Fig. 3.9). This method takes advantage of the fact that the **^{13}C signature** of plants with C4 photosynthetic metabolism (C4 plants, e.g. maize) is significantly different from that of C3 plants. The average $\delta^{13}C$ difference between C3 and C4 vegetation is about 15 $^{o}/_{oo}$. For example, after many years of maize cultivation, the fraction of maize C in a soil can be determined where the soil organic matter previously had a C3 signature. This method makes it possible to measure the C turnover in situ over longer periods of time. In a Luvisol, the fraction of maize OC in the soil organic matter was of 36 % after 24 years of maize cultivation, corresponding to a turnover time for the soil organic matter of 54 years. This also then enables the detection of the carbon fixed in different fractions. While mainly maize C was found in the light fraction, only 31 % of the carbon in the mineral-bound fraction came from the maize residues with a turnover time of 63 years. The light fraction occluded in the aggregates has substantially longer turnover times. This confirms that the turnover times of carbon in the clay and fine silt fraction are much longer than in the coarse or light fractions.

The use of tracers (model substances or plant residues) labeled with ^{13}C or ^{15}N, which differ from the natural background in terms of their isotope composition, enables tracing of the development of specific components in the soil, both in laboratory experiments and in field trials. A special advantage of this method is that the use of stable isotopes enables the recording of long-term processes, and in combination with thermal or chemolytic degradation, also enables a component-specific isotope analysis on a molecular basis.

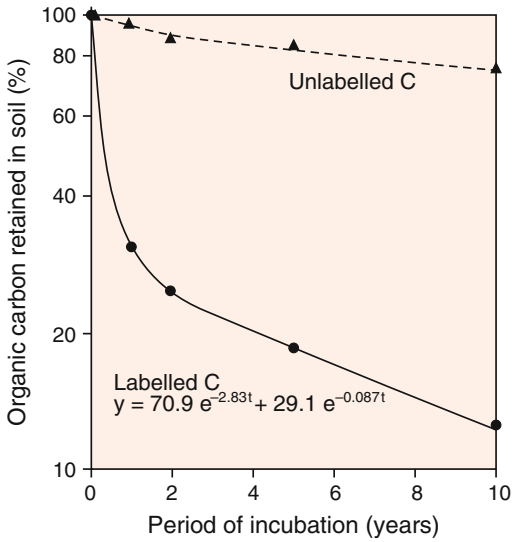

Fig. 3.10 Loss of soil C and C from ^{14}C labelled rye straw over the course of a 10-year open field incubation (after Jenkinson 1977)

3.6.3 C Turnover Modeling

The turnover of fresh organic matter added to the soil can be described with an equation, where the turnover rate is proportional to the amount of existing substrate:

$$A_t = A_0 e^{-kt}$$

Here, A_t and A_0 are the quantities of organic C in plant residues at the time 0 and at the time t, and k is the reaction constant per unit of time. In this 1st order equation, the quantity of added organic matter is reduced respectively by half (half-life) within a specific period of time. This enables a good description of the decomposition of plant residues during the first years (Fig. 3.10).

To describe and predict **C storage** and dynamics in the soil, one must take account of the varying stability of the different SOM pools, which results from the turnover times described above. For this reason, the organic matter in most turnover models is found in a finite number of compartments or pools. Current **carbon turnover models** (Fig. 3.11) use three or more functional pools that are characterized by different carbon turnover rates. In addition, the turnover rates are often described using relationships with the soil moisture, temperature, clay content, pH value and the N availability. The organic matter is generally differentiated into three pools: rapid turnover (labile), slower turnover (intermediate), and very slow turnover rate (passive). The quantitative description of the turnover behavior in the different pools is based on the empirically obtained turnover rates described above.

The labile **pool** is transformed very rapidly, within a few months or years, but only accounts for about 1–5 % of total soil organic matter. The labile fraction of soil organic matter consists of undecomposed, readily available residues from plants and microorganisms, and is mainly significant for the short-term nutrient supply in soils. In soils used for arable farming, about half of the organic matter has an average turnover time of 10–50 a, i.e. it corresponds to the intermediate pool. The intermediate pool mainly consists of partially decomposed plant residues, where the lignin accumulated compared to the

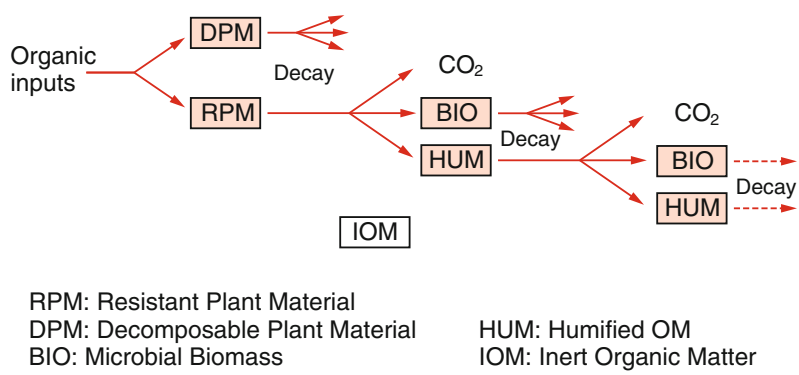

Fig. 3.11 The Roth C model, example for a multi-component model to simulate the C turnover in soils (after Coleman and Jenkinson 1999)

more readily degradable polysaccharides. This fraction is probably protected against decomposition through aggregation, and is therefore strongly influenced by various management and soil tillage methods (Fig. 3.4). This fraction can be successfully isolated using the above-mentioned combined fractionation according to the particle size and density.

The passive pool has average turnover times in the range of hundreds to thousands of years. Some model approaches also contain an inert pool, which is considered to be non-decomposable and is therefore included as a constant. The stable humus fraction accounts for the passive pool in the models and is most significant in terms of quantity. The very stable fractions of soil organic matter probably mainly consist of charred organic matter and organic substances in organo-mineral compounds. Organo-mineral compounds are dominated by polysaccharides and alkyl-C compounds, whereas aromatic constituents are of secondary importance.

The multitude of processes that lead to very long-term stabilization of organic matter in the passive pool has made the prediction of the magnitude and degradation behavior of the passive carbon pool difficult until now. For this reason, it has not yet been possible to establish a satisfactory relationship between the conceptual pools of the model and the measurable fractions of the soil organic matter, and to selectively isolate them from soil. In addition to insufficient fractionation and characterization methods, this is mainly due to the fact that organic matter in the soil exists as a continuum, and not in discrete fractions. Nevertheless, the fundamental components of the individual pools are meanwhile described in such widely used models.

3.6.4 Soils as a Carbon Reservoir and Source

Within the framework of climate protection, the soil's function as a carbon reservoir has gained major interest, because building up the **soil carbon pool** leads to a sequestration of atmospheric CO_2. At the same time, CO_2 storage as well as all biogenic greenhouse gases, i.e. also nitrous oxide (N_2O) and methane (CH_4) must also be considered (Lal 2004). Figure 3.12 shows the C pools and fluxes of the soil C cycle. In every soil under natural vegetation or with long-term unchanging use, a steady-state is established between the supply and decomposition of organic matter according to the climatic conditions (Table 3.7). The production of CO_2 in soils is almost entirely from root respiration and microbial decomposition of organic matter. Like all chemical and biochemical reactions, these processes are temperature-dependent (Fig. 3.13). The question as to

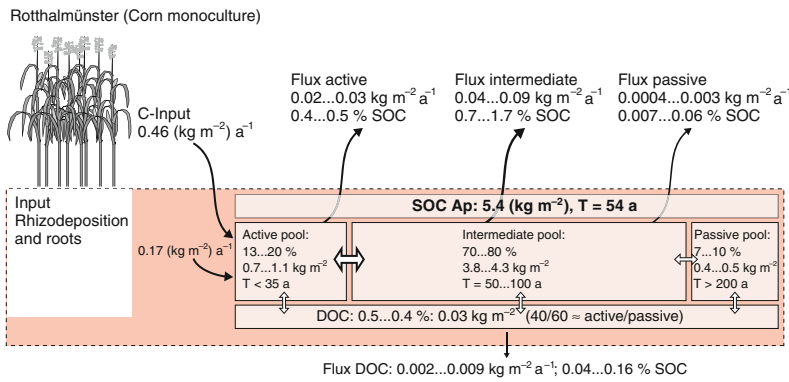

Fig. 3.12 Mineralization rates in different soil organic matter pools. Active, intermediate, passive pool: determined using the particle and density fractionation. Calculation of the turnover times (*T*) using $\delta^{13}C$ measurements in C3/C4 conversion soils (Flessa et al. 2008), C stocks and C input from maize straw (Kögel-Knabner et al. 2008a, b), C input underground (roots and rhizodeposition) (Ludwig 2005), DOC: guideline values from Haynes (2005), von Lützow et al. (2007)

Table 3.7 Turnover time for soil organic matter in different climatic zones

Climatic zone	Ecosystem	Turnover time (a)	References	Method
Boreal	Boreal coniferous forest	220[b]	Trumbore (2000)	Calculation[b]
Temperate	Mean value 31 sites	63 ± 7	Six et al. (2002)	^{13}C method
	Temperate forests	12[b]	Trumbore (2000)	Calculation[b]
	Temperate forests	11–31[c]	Garten et al. (2006)	Calculation[c]
	Cool temperate forests	30[a]	Jenkinson (1981)	Calculation[a]
Humid	Subhumid savanna	34[a]	Jenkinson (1981)	Calculation[a]
	Humid savanna	37[a]	Jenkinson (1981)	Calculation[a]
Maritime (Rothamsted UK)	Wheat, unfertilized	22[a]	Jenkinson (1981)	Calculation[a]
	Wheat, NPK	30[a]	Jenkinson (1981)	Calculation[a]
	Grassland, unfertilized	77[a]	Jenkinson (1981)	Calculation[a]
Tropical	Mean value, 23 sites	36 ± 5	Six et al. (2002)	^{13}C method
	Tropical rainforest	9	Jenkinson (1981)	Calculation[a]
	Tropical rainforest	2.5[b]	Trumbore (2000)	Calculation[b]

[a]Estimated from the ratio of the net primary production to the OC content of the soil
[b]Calculated from OC stocks and soil respiration
[c]Calculation based on measured OC stocks and estimated C input

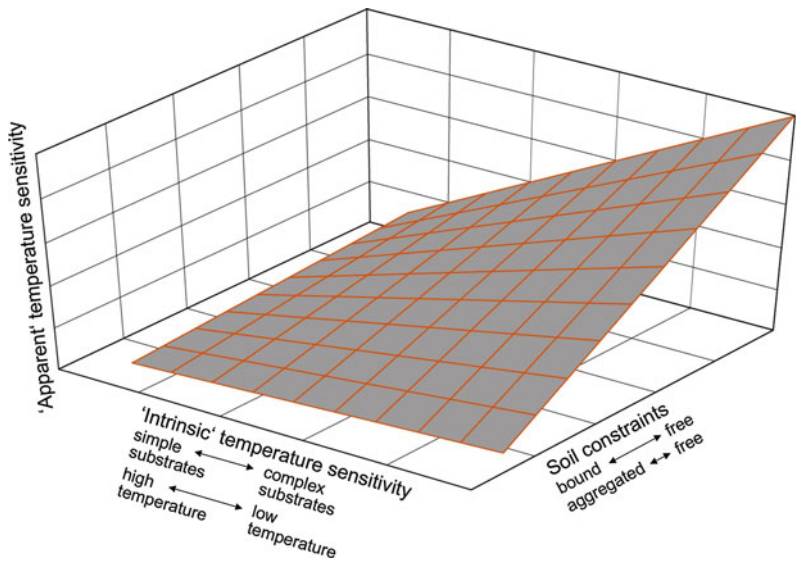

Fig. 3.13 The intrinsic temperature sensitivity of decomposition of an organic-C substrate is a function of the decomposability of the molecule and the ambient temperature. In general, more complex molecular structures have higher activation energies and, hence, higher temperature sensitivity. Environmental and soil constraints on decomposition will dampen or obscure the intrinsic temperature sensitivity by reducing substrate availability, often causing the measured (or 'apparent') temperature sensitivity to be less than expected. Modified from Davidson and Janssens (2006)

whether the build up of soil organic matter (e.g. through higher organic matter input or changes in land use) would ultimately lead to a net CO_2 fixation can only be assessed on an ecosystem level, in conjunction with the net primary production (NPP) (net biome productivity =

NPP − respiration losses). The role of soils as a source or sink for greenhouse gases can thus only be evaluated through simultaneous consideration of the losses through heterotrophic respiration and gains through biomass production and litter incorporation. If carbon stored belowground is transferred to the atmosphere by a warming-induced acceleration of its decomposition, a positive feedback to climate change would occur. Conversely, if increases of plant-derived carbon inputs to soils exceed increases in decomposition, the feedback would be negative (Davidson and Janssens 2006). Soil moisture, temperature and soil texture, as well as the quantity and quality of the supplied litter as a substrate for soil organisms, are important site factors for the intensity of biological turnover processes, which produce CO_2, N_2O and CH_4 (see Chap. 4.2).

Under the same climatic conditions and with the same C supply, clay-rich soils often have higher humus contents than sandy or silty soils. This is probably due to a combination of stabilizing processes through direct interactions with the solid phase and aggregation. The higher humus contents in fine-grained soils are explained by (a) the capacity of clay minerals, aluminum and iron oxides to adsorb organic substances and thus reduce microbial decomposition; (b) the higher content of aggregates, where the enclosed carbon compounds are protected from decomposition by microorganisms, and (c) the resulting more frequently occurring anoxic conditions. Therefore, a smaller fraction of the organic matter is mineralized in clay-rich soils than in clay-poor soils (Fig. 3.14). Here, the significance of the clay fraction is particularly high when the clay contents are low. As shown in Fig. 3.15, the accumulation of C and N in the fine fractions decreases with increasing clay and silt content. Long-term field experiments demonstrate the dependence of the soil organic matter content on the organic matter inputs (Table 3.8; Fig. 3.16). Inorganic fertilization has a direct influence on the organic matter content in soils through the yield quantities and thus the crop residue supply. Under comparable crop rotations, the soil organic

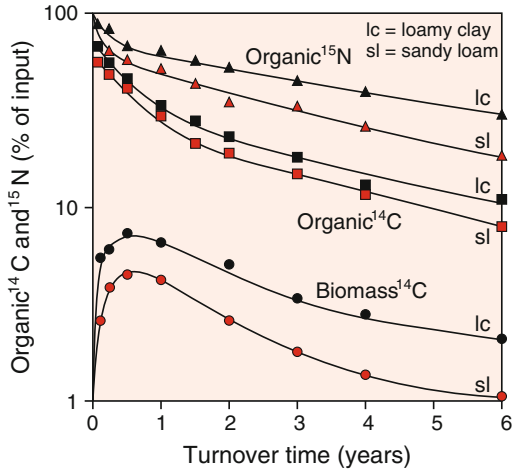

Fig. 3.14 Residual ^{14}C and residual ^{15}N and biomass ^{14}C in a clay (Cl) and a sandy loam (Ls) during the decomposition of labelled legumes under field conditions (after Ladd et al. 1996)

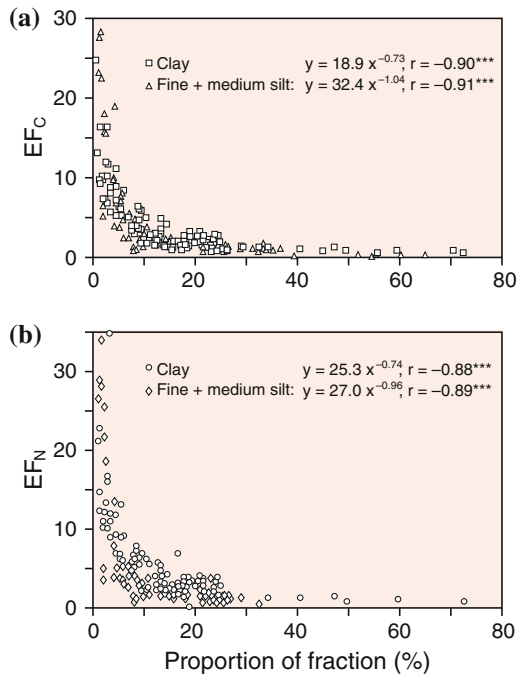

Fig. 3.15 Enrichment factors (Anreicherungsfaktoren) for **a** organic carbon (AF_C) and **b** nitrogen (AF_N) in the clay, fine silt and medium silt fractions of soils with various clay and silt contents. AF_C = % C in fraction/C in the bulk soil, AF_N = % N in fraction/N in the bulk soil (from Schulten and Leinweber 2000)

Table 3.8 Long-term effects of farmyard manure (FYM) application, mineral fertilization (N, NP, PK, NPK) and bare fallow on OC concentrations (mg g^{-1}) of agricultural topsoils

Site	Germany Bad Lauchstädt	Spain Madrid	Sweden Ultuna	UK Rothamsted	India Ranchi	China Yangling/ Shaanxi
Climate	Cool temperate	Mediterranean	Cool temperate	Temperate maritime	Sub-tropical	Semi-arid
Duration (years)	108	26	53	155	30	20
Crop rotation	Sugar beet/ spring barley/ potato/winter wheat	Sugar beet/ potato/cereals	Spring cereals/ fodder crops	Winter wheat	Soybean/ winter wheat	Winter wheat/ maize
Clay content (%)	21	27	37	25	25	na
pH	7.0	na	6.6	6.3	5.3	na
Unfertilized control	15.7	5.5	15.0	10.3	3.5	7.4
FYM	20.6	9.5	22.1	27.3	na	na
Application FYM (t ha^{-1} $year^{-1}$)	10	10	8	35	na	21
N	19.4	–	–	–	3.4	8.5
NP	20.4	–	–	–	4.2	10.2
PK	18.5	–	–	–	–	8.4
NPK	20.9	6.1	–	10.3–12.4	4.5	10.0
FYM + NPK	22.9	10.0	–	26.3	4.7	13.9
Bare fallow	–	–	9.7	–	–	7.9

From Blair et al. (2006), Börjesson et al. (2012), Körschens et al. (2013), Manna et al. (2007), and Yang et al. (2012)
na Not available

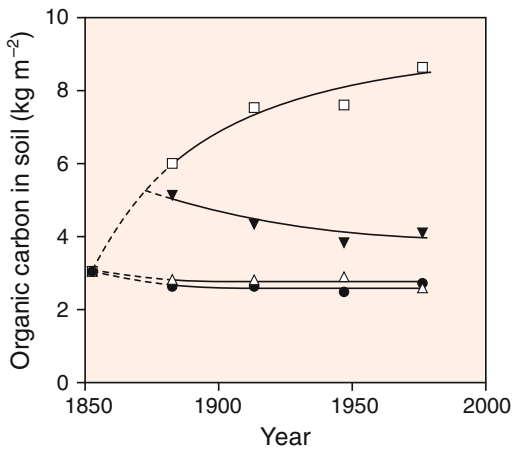

Fig. 3.16 Temporal change in the humus content in loamy Cambisols from the long-term trials in Rothamsted under different management since 1852; *Square box* (□) barn manure, *filled circle* (●) unfertilized, *triangle* (Δ) NPK, *black down pointing triangle* (▼) barn manure, unfertilized since 1871 (after Jenkinson 1988)

matter content of the soil increases with increasing yields through fertilization. In wet soils (peat) and soils with thick forest floor layers, the strongly retarded biological decomposition of organic matter in these soils results in carbon storage (Figs. 3.12 and 3.13).

Although they are difficult to predict, boreal thawing processes are an important influencing factor on the global soil C balance. The top 3 m of all permafrost-zone soils within the northern circumpolar permafrost zone contain about 1024 Pg C. This C accumulated over thousands of years under cold and sometimes waterlogged conditions, but becomes partly susceptible to thawing as the climate changes to warmer conditions. If these soils thaw, the ancient C stored in the permanently frozen layer is available for decomposition by soil organisms and is released to the atmosphere. The progressive mineralization of previously conserved organic matter stocks in the soil could

affect one quarter to one third of the global soil C resources. However, the extent to which these changes have an effect on the soil C stocks mainly depends on the soil moisture conditions. Some of this C is easily metabolized and will be consumed quickly by microorganisms while other fractions are more difficult to break down because the stabilization processes described above also take effect here and will thus remain within the soil for much longer. How much greenhouse gas is released will depend on the balance between the release of carbon dioxide (CO_2) or methane (CH_4), i.e. the prevalence of aerobic or anaerobic conditions after thawing and the subsequent decomposition (Schuur et al. 2013). The greenhouse effect of methane is 20–30-fold higher than that of CO_2. Where the tundra is transformed into active moors, they can continue to grow. While the humus body continues to grow, so do the methane emissions.

Changes in land use disturb the steady state between the supply of organic matter and decomposition. Deforestation and the cultivation of previously forested areas, or the conversion of steppe or grassland into arable land as well as inverse measures have a strong effect on the organic matter dynamics, with changes preferentially in the topsoil. The temporal changes in the organic carbon occurring here follow the same course as those of organically bound nitrogen. The global soil C stocks have been continuously reduced since the beginning of soil cultivation about 10,000 years ago. About 20 % of the current atmospheric CO_2 concentration can probably be attributed to the cultivation of natural sites, 24–32 % of which to the decomposition of soil organic C. The most important factors are, as shown in the following examples, deforestation and the conversion of grassland or forest to cropland, soil tillage, and drainage. Conversion of native grassland or forest to cropland, resulted in losses of 20–40 % of the soil organic matter stocks, mainly from the topsoil (Scharlemann et al. 2014). The reduction of the OC content in the topsoil after the conversion of steppe or grassland into arable land is due to the combined effect of erosion losses, biochemical decomposition of the organic matter, and dilution effects through tillage (deepening of the ploughed A horizon). Soils under permanent grassland or forest often contain more organic matter than neighboring arable land, because litter input is higher and the topsoil is not tilled. When land has been taken into cultivation, the subsequent loss of organic matter does not take place uniformly, but rather preferentially from the particulate organic matter fraction, which mainly contains younger, poorly decomposed plant residues.

If the natural aggregation state of a soil is disturbed, e.g. due to soil tillage and the cultivation of natural soils, the turnover rate of the physically protected fraction increases, and there are particularly high C losses from the coarse fraction. The more often the soil is tilled during the course of the season, and the more ploughings are used, the more the humus content decreases. In doing so, the mineralization of previously physically protected organic matter from aggregates is stimulated. This degradation, caused by intensive aeration and destruction of the aggregates, can be reduced if loosening, non-inversion tillage is used instead of ploughing.

Managing soil carbon is considered to produce multiple benefits and improve soil properties as well as soil fertility. Actual management concepts suggest to increase soil carbon contents by appropriate management and at the same time enhance a range of ecosystem services (Table 3.9). Increasing the soil OC of degraded soils could simultaneously ensure high agricultural productivity, sequester CO_2 whose emissions might otherwise exacerbate climate change, and enhance water capture. Based on the discoveries of long-lasting fertility of the Terra preta, application of biochar to soils is considered a strategy that would increase stable soil organic matter, increase bioavailable water, lower bulk density, act as a liming agent, and reduce leaching of pesticides and nutrients to surface and ground water. Biochar is a carbon-rich product resulting from pyrolyzing biomass. When applied to the soil it is considered to be resistant to decomposition, effectively

Table 3.9 Management options to promote C sequestration in agricultural topsoils

Management option	Potential C sequestration ($t\ ha^{-1}\ year^{-1}$)
Conservation/zero tillage	0–0.8
Incorporation of crop residues	0.2–0.7
Application of manure/slurry	0.2–1.5
Improved rotations/intermediate crops	0.1–0.6
Organic farming	0–0.5
Bioenergy crops	0–0.6
Improved grazing management	0.2–0.7
Conversion cropland to grassland	0.3–1.9
Conversion cropland to forest	0.5–1.9

Based on data from Smith (2004), Vleeshouwers and Verhagen (2002), Dendoncker et al. (2004), Freibauer et al. (2004)

sequestering the applied carbon and mitigating anthropogenic CO_2 emissions. Other promoted benefits of biochar application to soil include increased plant productivity and reduced nutrient leaching. However, the effects of biochar are variable and it remains unclear if recent enthusiasm can be justified (Gurwick et al. 2013). Although biochar application to soil has been considered to be long-lasting carbon capture strategy, only few data are available to date to evaluate the stability of biochar in situ and show variable and uncertain results. But despite the variability introduced by soil and climate, the addition of biochar to soils resulted, on average, in increased aboveground productivity, crop yield, soil microbial biomass, rhizobia nodulation, plant K tissue concentration, soil phosphorus (P), soil potassium (K), total soil nitrogen (N), and total soil carbon (C) compared with control conditions. Soil pH also tended to increase, becoming less acidic, following the addition of biochar. Thus, although there remain many uncertainties biochar addition to soils holds promise in being a win-win-win solution to energy, carbon storage, and ecosystem function (Biederman and Harpole 2013).

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4 Soil Organisms and Their Habitat

The **edaphon** comprises all organisms living in the soil. Based on the body diameter of the organisms, the edaphon is divided into the classifications microflora, microfauna, mesofauna and macrofauna. The body width of soil organisms largely determines their microhabitats (Fig. 4.1). Microflora (bacteria, archaea, fungi, algae) and microfauna (protozoa, nematodes) form the community of microorganisms in soils. Soil organisms influence soil formation (pedogenesis) directly (e.g. through burrowing activity and decomposition of organic matter) and indirectly (e.g. by feeding on plant roots). Soil microorganisms and soil fauna whose life cycle stages all take place in the soil, belong to the permanent soil organisms. Temporary soil fauna spend only part of their life cycle in the soil (e.g. insect larvae), while periodical fauna often leave the soil and then return. Alternating soil fauna alternate between aboveground and underground generations (Fig. 4.2). However, permanent soil organisms can also be spread through the atmosphere in resistant dormant forms (cysts, spores), or sorbed onto dust particles. Active or passive transport of soil organisms within the soil profile can take place as well.

The first sections introduce individual groups of organisms living in the soil; subsequent sections describe ways in which soil organisms have adapted to their habitats and explain their functions in the soil, including their ability to serve as very good bioindicators for natural and anthropogenic changes in soils. The last section explains important classic and molecular approaches in soil biology.

4.1 Soil Organisms

4.1.1 Microflora and Viruses in Soils

Soil organisms can be classified into three domains according to the different structures of their ribosomal RNA (rRNA): bacteria (Bacteria), archaea (Archaea) and eukaryotes (Eukaryota) (Fig. 4.3). Bacteria and archaea, collectively termed prokaryotes, do not have a cell nucleus. Eukaryotes are organisms with a cell nucleus and cell membrane and are generally much larger than prokaryotes. **Viruses, viroids** (infectious molecules consisting of ribonucleic acid) and **prions** (potentially pathogenic proteins in animals and human beings) have their own taxonomic classification. Viruses in the soil often use bacteria as hosts. However, plant, animal, and human pathogenic viruses have also been found in soils. Current knowledge of the ecology of viruses in the soil is limited. Viruses do not have their own metabolism; they are dependent on that of the host cell. Because viruses can destroy their host cell during infection, their presence is likely to affect the microbial foodweb.

Soil bacteria (Bacteria) are small (0.2–2.0 μm) unicellular organisms. Parasitic

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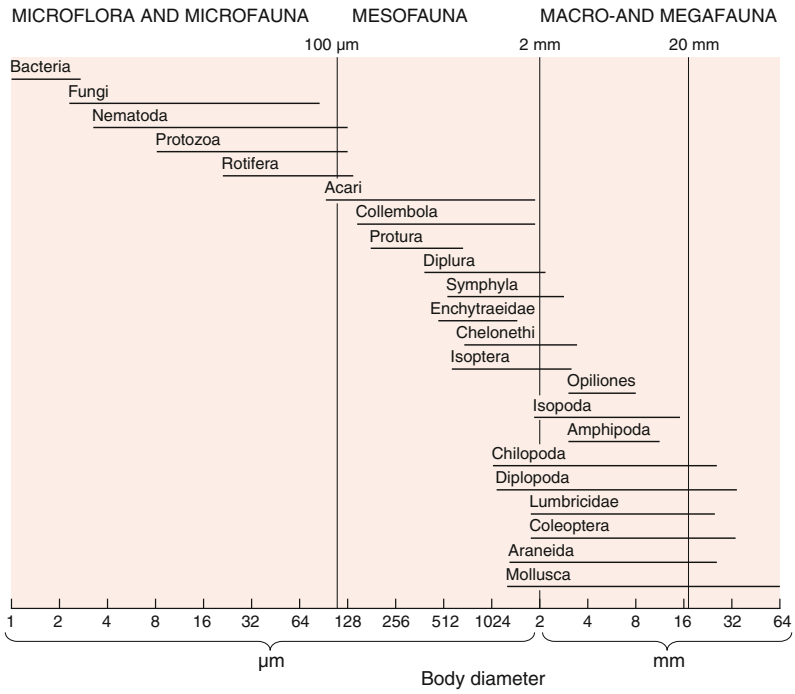

Fig. 4.1 Size classification of soil organisms according to their body diameter (after Paul 2015)

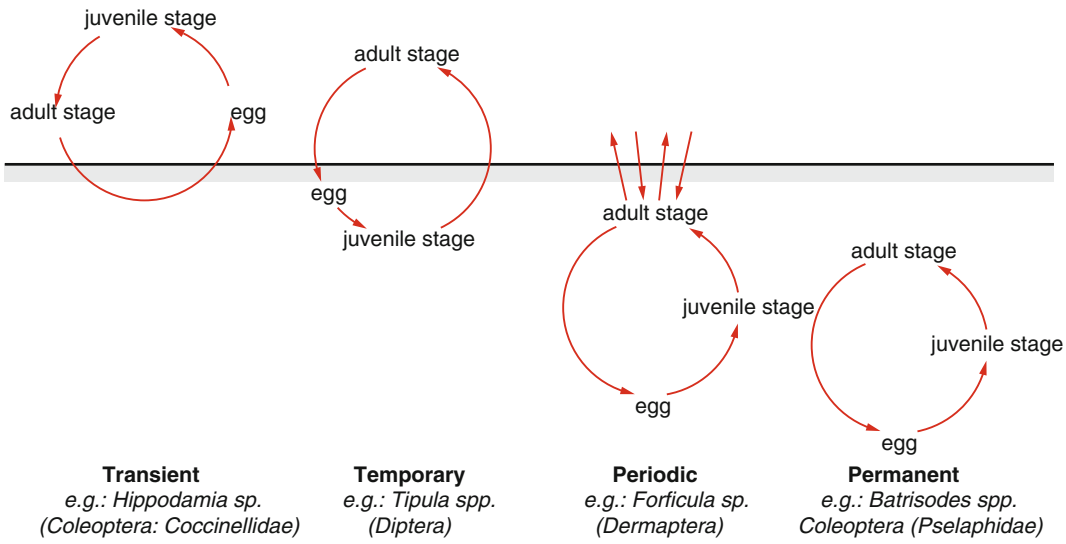

Fig. 4.2 Different soil organisms either spend their entire life or only certain stages of their life in the soil. The various behaviors are represented using different insects (after Coleman and Crossley 1995)

bacteria (e.g. Rickettsia in ticks, fleas, mites and lice) range in size from 500 to 200 nm (Fig. 4.4). Soil bacteria cannot easily be distinguished based on their shape. A classical method of differentiating soil bacteria is named after the Danish scientist Hans Christian Gram, based on differential staining of the bacterial cell walls. **Gram-negative** bacteria have an outer cell

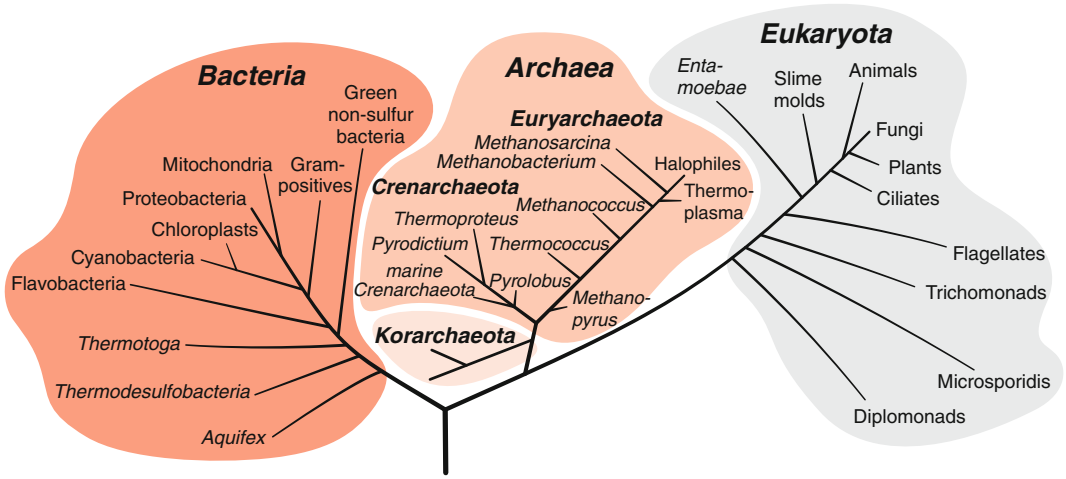

Fig. 4.3 The universal tree of life constructed by analysis of sequences of small subunit rRNA genes (after Fuchs and Schlegel 2007)

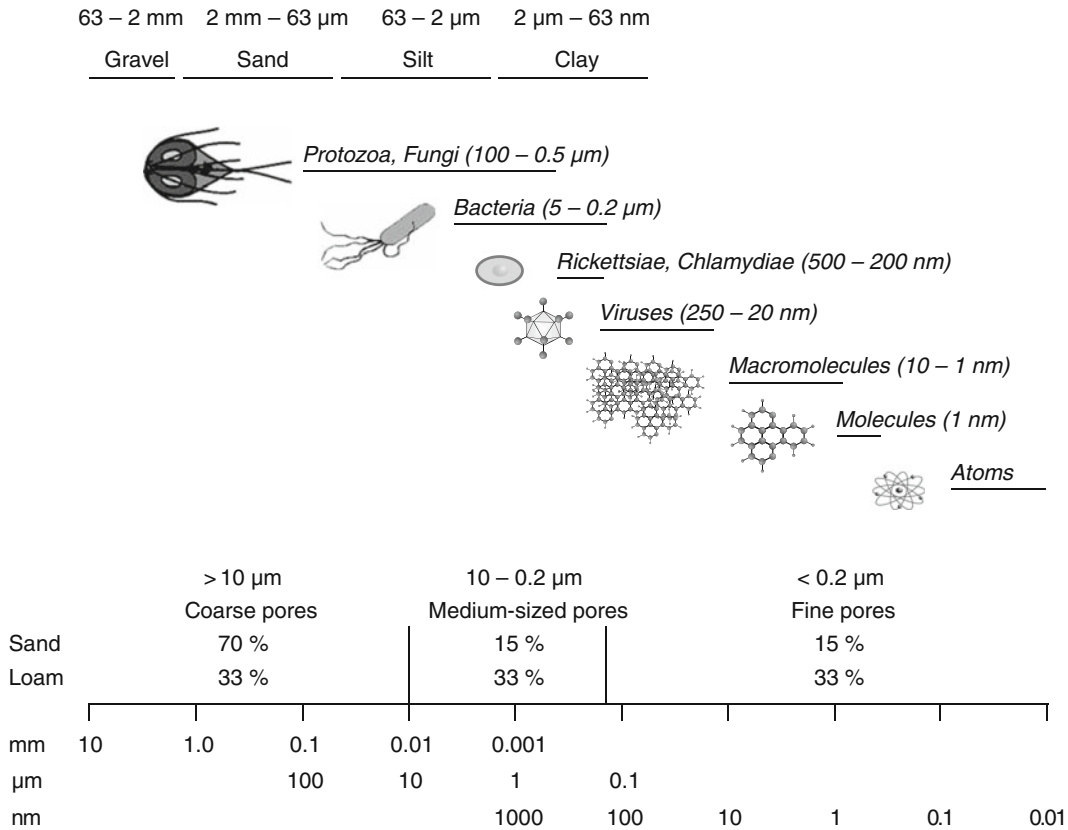

Fig. 4.4 Size comparison of microorganisms, soil pores and particle sizes (after Maier et al. 2000)

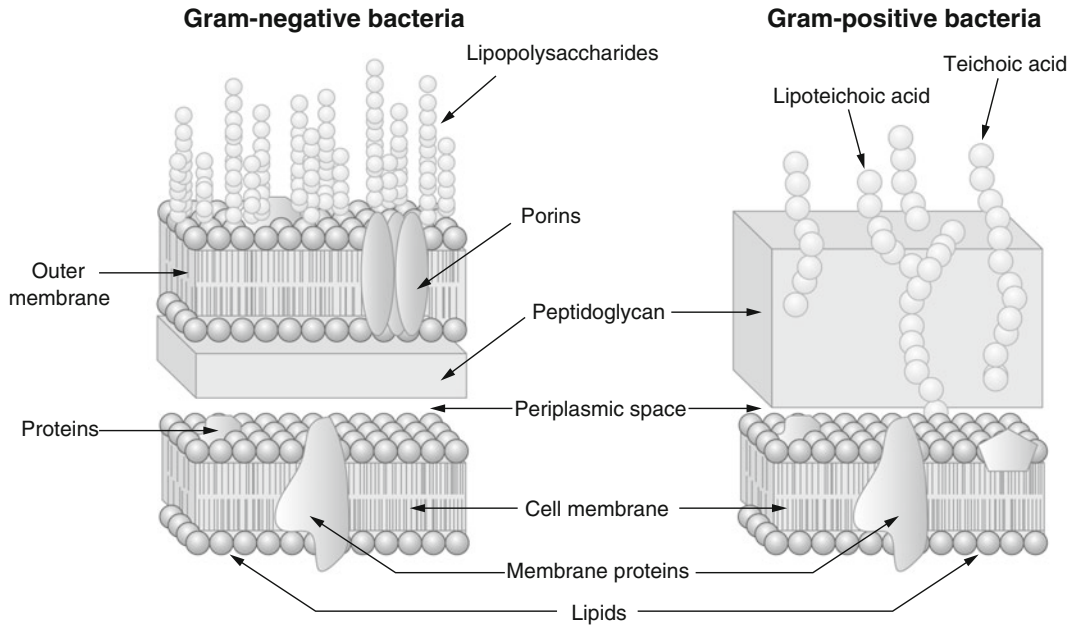

Fig. 4.5 Comparison of the cell wall structure of Gram-negative and Gram-positive microorganisms (after Maier et al. 2000)

membrane consisting of lipopolysaccharides, porins (pore-forming transmembrane proteins) and other mac- romolecules (Fig. 4.5). In contrast, **gram-positive** bacteria do not have an outer cell membrane; their cell walls mainly consist of peptidoglycan. However, some soil bacteria, e.g. cyanobacteria, cannot be clearly classified according to the staining method. Soil bacteria are characterized by high functional diversity: at least 150 different metabolic pathways and 900 different reactions performed by bacteria have been described. Proteobacteria (subclasses: α, β, γ, δ and ε proteobacteria) and representatives of the firmicutes, actinobacteria and bacteroidetes have often been isolated from the soil using culturing methods. Details on the phylogeny of these microorganisms can be found in *Bergey's Manual of Bacteriology*. The α proteobacteria have developed various feeding strategies, including feeding on dead organic matter, symbiotically or parasitically. The α proteobacteria also include rhizobia, which can fix nitrogen in symbiosis with legumes. β and γ proteobacteria (e.g. *Burkholderia* and *Azoarcus*) use readily available plant exudates found in the plant rhizosphere. The β proteobacteria also include various nitrifiers, denitrifiers and xenobiotic-decomposing microorganisms. Many sulfate-reducing microorganisms belong to the subclass of the δ proteobacteria. Firmicutes are Gram-positive bacteria characterized by low levels of the nucleotides guanine and cytosine. They form endospores and can therefore persist in soils for long periods. Actinobacteria (e.g. *Streptomyces*) grow very slowly in the soil and exploit a diversity of hard-to-decompose organic compounds as food sources. Cyanobacteria are photoautotrophic, Gram-negative, uni- to multicellular Eubacteria. Cyanobacteria use a larger range of the light spectrum than plants for their photosynthesis, and can therefore also successfully colonize areas of low light intensity (e.g. the underside of rocks). In addition to chlorophyll, they use various phycobilins as accessory pigments for photosynthesis. Many cyanobacteria transform molecular nitrogen into ammonium (nitrogen fixation) in special cells (heterocysts). Molecular methods furthered the discovery of additional soil microorganisms; however, many of these have remained unculturable until now.

Representatives of the Acidobacteria group are probably of special ecological significance and are found in almost all terrestrial habitats.

Archaea differ from the two other domains particularly through the structure of their cell walls and plasma membranes. The cell walls of archaea do not contain murein (peptidoglycan) and the plasma membranes do not have ester-bound lipids; in contrast, they contain ether-coupled lipids as well as complex RNA polymerases. Archaea are resistant to antibiotics that target cell walls. The significance of archaea in terrestrial ecosystems is much greater than was earlier assumed. Initially, archaea were found mostly in extreme environments (e.g. in hot springs, in highly concentrated saline solutions, in very acidic or very alkaline environments). In recent years, however, archaea have been found in most soils and it is thought that they may play an important role in the nitrogen cycle. Some archaea produce the enzyme ammonia monooxygenase, which is required for the transformation of nitrate to nitrite during nitrification. Meanwhile, due to their special surface structures (*S-layer*), archaea are used in bio- and nanotechnology for microbial ore leaching, biogas production and for ultrafiltration.

Fungi spread through the soil with their cylindrical, thread-like cells (hyphae, diameter 1–10 μm). The hyphae of a fungus, are referred to collectively as its mycelium. All fungi are eukaryotes and, with few exceptions, their cells have a cell wall. Until recently, fungi had been classified into five different phyla: Chytridiomycota, Zygomycota, Glomeromycota, Ascomycota and Basidiomycota. However, the taxonomy of fungi is currently being revised, e.g. representatives of the Zygomycota will be classified with the Glomeromycota and various subphyla. Chytridiomycota form mobile zoospores and are not very common in soils. Zygomycota use readily available carbon sources very rapidly and are therefore also called sugar fungi. They produce thick-walled zygospores, which are formed after the fusion of two different hyphae. Zygomycota have thermophilic representatives that can grow at temperatures of up to 60 °C. The phylum Glomeromycota includes all fungi that form arbuscular mycorrhiza (see Sect. 4.1.4) as well as those that can interact symbiotically with cyanobacteria. The Ascomycota (sac fungi) get their name from their reproductive structure (ascus = special cell of sexual fruiting bodies). Haploid ascospores are formed in the asci after meiosis (reduction division). This group includes many yeast and mould fungi, edible mushrooms (e.g. morels, truffles), as well as a multitude of fungi without sexual stages in their life cycles (Deuteromycota). Ascomycota (e.g. *Mucor, Penicillium, Trichoderma* and *Aspergillus*) play an important role in the decomposition of litter in soils. The Basidiomycota form a large group, whose hyphae are septate and divided into individual compartments. Several Basidiomycota (white-rot fungi) completely decompose lignin from dead plant material and lead to white-rot of wood, where the cellulose remains behind as a white mass. Brown-rot fungi only decompose cellulose and hemicellulose, and leave various brown-colored oxidation products of lignin behind. Certain fungi also live on protozoa and nematodes; others are plant pathogens (e.g. species from the genera *Phytophtora*, *Fusarium*, *Gaeumannomyces*) or hyperparasites of plant pathogenic fungi (e.g. *Trichoderma*) and are therefore of biotechnological interest. The Peronosporomycetes (formerly Oomycota) are much more closely related to algae than to the higher fungi. The Oomycota include the pathogens of numerous plant diseases, such as late blight in potatoes and downy mildew (Peronosporaceae). The taxonomical position of the Myxomycota (slime molds) is also disputed. As heterotrophic organisms, they form plasmodia (plasma masses with many cell nuclei or ameboid cells). Plasmodia can move like large amoebae and feed through phagocytosis, but can also form mushroom-like fruiting bodies. Most species are found on various substrates (dead wood, grass, dead plant parts and moss).

Soil algae are mainly active in the upper centimeters of the soil. In the continental Antarctic, they play an important role in humus formation after the snow has melted. Soil algae are eukaryotic organisms containing chlorophyll in their cells, and as phototrophic organisms, they can use light as an energy source. The range of species of soil algae consists of euterrestrial

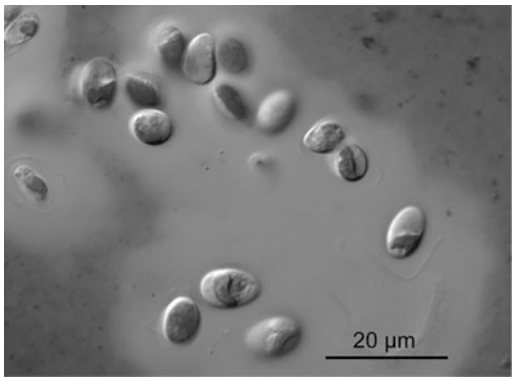

Fig. 4.6 Single-cell green algae (Radiococcaceae), a member of the Trebouxiophyceae (Chlorophyta), in culture. The cells excrete extracellular polymer substances (EPS), which become visible through the addition of ink particles. Scale: 20 µm. *Image* Collection of algae cultures, University of Göttingen

and facultative terrestrial representatives. Facultative terrestrial algae are constituents of aeroplankton in the atmosphere; they temporarily enter the top soil layer, but cannot establish themselves permanently in the soil. Euterrestrial algae, in contrast, are optimally adapted to the soil environment and exhibit site specificity. Most soil algae belong to the green algae (Chlorophyta, Streptophyta), yellow-green algae (Heterokontophyta: Xanthophyceae) or diatoms (Heterokontophyta: Bacillariophyceae). Green algae and cyanobacteria, the latter classified among the bacteria, enter symbioses with certain Ascomycetes; the product of these symbioses are called lichens. Soil algae often excrete extracellular polymer substances (EPS), which contribute to the physical stabilization of soils. Figure 4.6 shows the wide zone of EPS excretion, which is differentiated from the surrounding medium through dye particles. Environmental changes can be detected by monitoring soil algae.

4.1.2 Soil Fauna (Micro-, Meso-, Macro- and Megafauna)

As single-celled eukaryotes, **protozoa** are the smallest soil fauna and are important members of the microfauna. Protozoa have adapted to life in the soil through the formation of cysts, dormant stages (anabiosis [from the Greek *anabiōsis* = resuscitation]), and tolerance to high CO_2 concentrations. Protozoa generally reproduce through asexual division of the mother cell into two daughter cells; sexual propagation is rare among protozoa. Three groups of protozoa are found in the soil, classified according to their motility as follows: **flagellates** (**Mastigophora**), **amoebae** (**Sarcodina**) and **ciliates** (**Ciliophora**) (Fig. 4.7). Flagellates can move in the soil water by means of one or several flagella. Phytoflagellates contain chlorophyll and live photoautotrophically in the topmost soil layers. Flagellates mainly feed on bacteria. A smaller number of flagellates live exclusively as parasites or pathogens. *Trichomonas* species live in the guts of termites and other insects. Naked amoebae (Amoebina) and testate amoebae (Testacea) develop cytoplasmic appendages (pseudopods). Amoebae feed by absorbing particulate substances (bacteria, fungi, algae or small organic particles) (**phagocytosis**). Ciliates have cirri, which assist in motility and food intake. Site-specific ciliates are found in organic layers (e.g. mull and moder). Ciliates often feed on bacteria; however, some are also predators on other protozoa.

Because their body diameter is smaller than 0.2 mm, **nematodes** (**Nematoda**) are members of the microfauna. With their cylindrical body shape tapering at the end, they are very well adapted to conditions in the soil. They live in the thin water films, around soil aggregates, and in the rhizosphere. Nematodes absorb oxygen directly through their body surface. The shapes of the animals' heads are important taxonomical characteristics in nematodes (Fig. 4.8): Nematodes use their stylets to pierce plant roots or fungal hyphae. Predators have teeth and ridges to break down their food. Bacteria feeders have an oral cavity opening into a muscular, sucking pharynx; they suck in their food by contracting their pharynx. A distinction is made between free-living and parasitic nematodes. Ectoparasites pierce root hairs and cells with a short or long stylet, migratory endoparasites move within the root tissues, and sedentary endoparasites reside in galls or cysts. Free-living nematodes mostly feed on bacteria or fungi. By grazing on

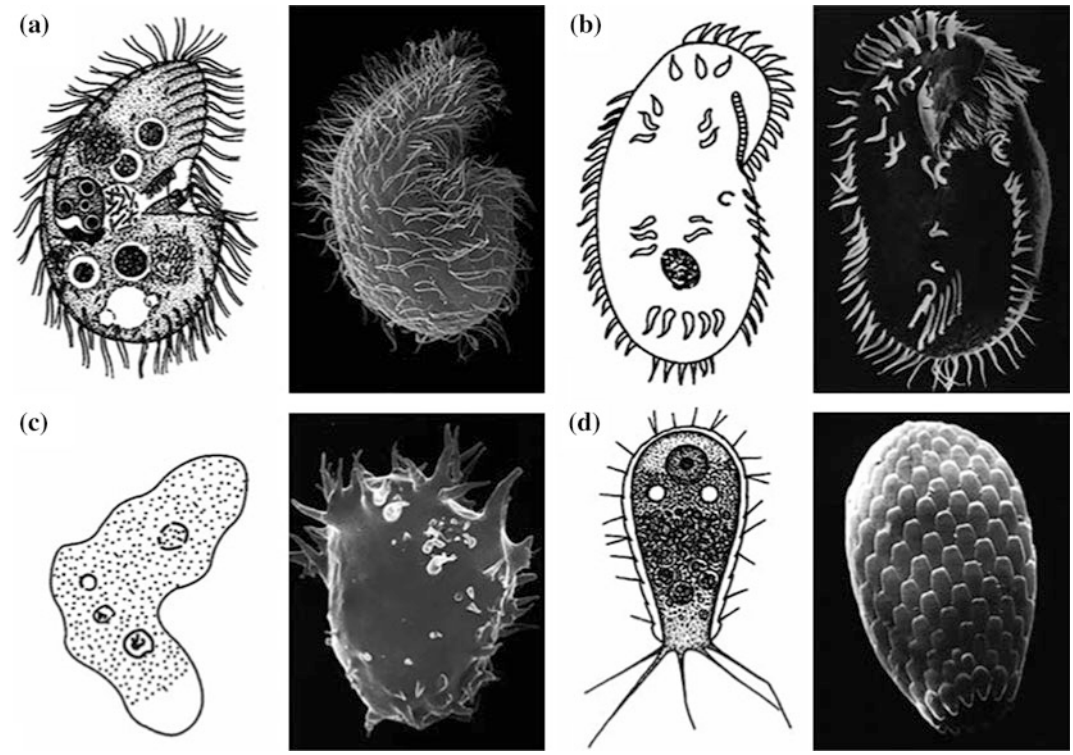

Fig. 4.7 (**a**–**b**) Ciliophora (photos **a** *Colpoda inflata*, length ca. 50 μm; **b** *Pattersoniella vitiphila*, length ca. 200 μm); **c** Amoebina (naked amoeba, *Mayorella* sp., size about 40 μm); **d** Testacea (testate amoebae), *Euglypha* sp., length ca. 50 μm); (drawings **b** and **c** after Paul 2015; drawings **a** and **d** and photos **a**–**d** from W. Foissner, University of Salzburg, Austria)

soil microorganisms, nematodes mobilize nutrients and accelerate mineralization processes in the soil.

Arthropods (**Arthropoda**) are members of the mesofauna (Fig. 4.1). **Arachnids (Arachnida), crustaceans (Crustacea), centipedes and millipedes** (**Myriapoda**), and **insects (Hexapoda**) have a chitin cuticle, protecting them from desiccation and mechanical injury. Collembola (springtails) and Acari (mites) are particularly common representatives of the microarthropods in soils.

Springtails (**Collembola**) are wingless animals that are unable to dig, using the voids in the soil as habitat. Epedaphic forms live on the surfaces of soil and snow. They are protected from UV radiation by their strong pigmentation and hair coat. Their long antennae serve, among other functions, to detect odors, and their well-developed furcula (an abdominal, tail-like appendage) helps them to escape from predators. Hemiedaphic species colonize the litter and the topmost soil layer. Euedaphic-living species are found in deeper soil layers. This life strategy is characterized by size reduction, shortening of the extremities, reduction of the eyes and lack of pigmentation. Collembola mostly feed on fungi and bacteria or on dead plant parts, carrion and feces from larger animals. With their scouring mouthparts, predatory Collembola feed on rotifers, water bears, nematodes, and even on eggs from other springtails.

The species- and individual-rich group of mites **(Acari)** also uses—like Collembola—the pore space as habitat. Because they are unable to dig, they cannot expand their living environment. As arachnids, mites have four pairs of walking legs and use their mouthparts to break down their food or to pierce and suck plant sap. In soft-bodied mites, respiration takes place through the skin and,

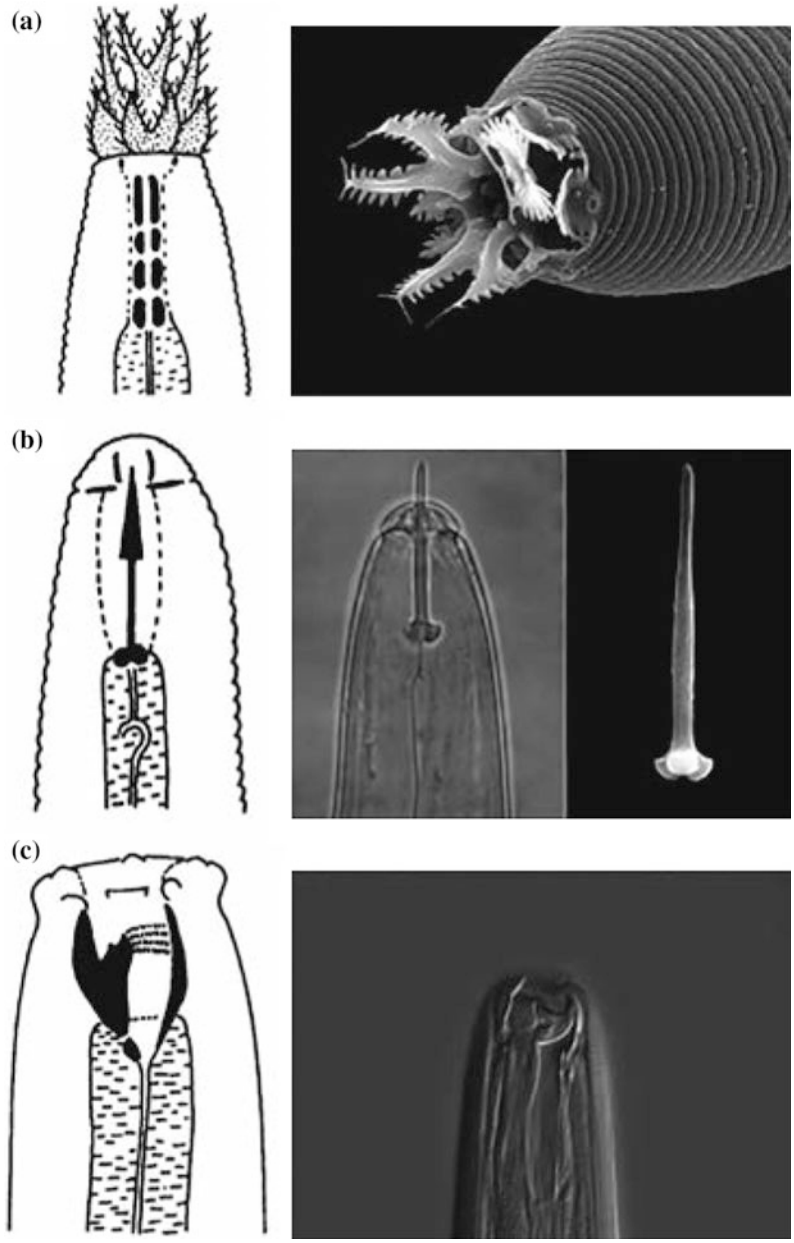

Fig. 4.8 The head structure of different nematodes gives an indication of their feeding habits: **a** Bacteria feeders suck their food into their mouths with appendages on their heads (e.g. *Acrobeles* sp.), **b** Stylets are used by phytophagous and mycophagous nematodes to pierce roots and fungal hyphae (e.g. *Tylenchid* sp.), **c** Ridges enable predatory species to break down their food (e.g. *Mononchus* sp.) (drawings after Coleman and Crossley 1996, photos after Eisenback and Zunke 2000)

in species with a cuticle, through tracheal tubes. **Tracheae** are air channels that are distributed throughout the body, emerging outside at several points called stigmata. The position of the stigmata (respiration openings) is an important taxonomical characteristic (Fig. 4.9): The soft-bodied **astigmatid mites (Astigmata)** breathe through their skin and have no stigmata. **Prostigmatid mites (Prostigmata)** have one pair of stigmata close to their heads, and predatory mites **(Mesostigmata)** above the hips of their walking legs. **Oribatid mites (Cryptostigmata)** have several concealed stigmata that are distributed all over the body. Oribatid mites live in the litter and the topmost soil layers. Mites feed on living plant parts (**macrophytophagous**), microorganisms (**microphytophagous**), nematodes (**zoophagous**), feces of other animals (**coprophagous**), or carrion (**necrophagous**).

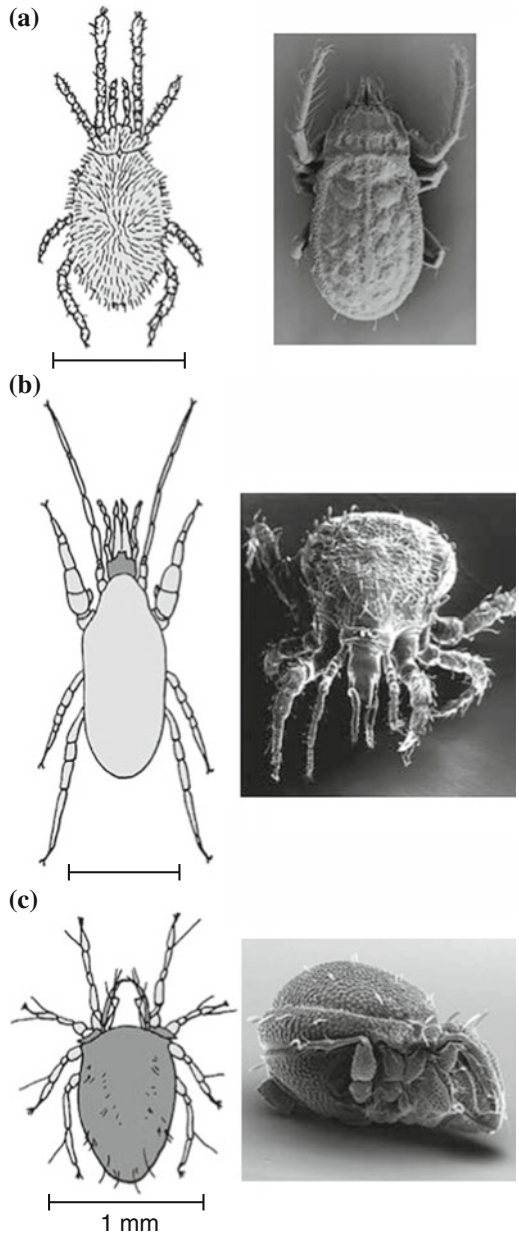

Fig. 4.9 Typical representatives of the Acari (mites), which are characterized by different locations of their breathing openings (stigma): **a** Prostigmate mites (Labidostommatidae, Prostigmata), **b** Mesostigmate mites (Mesostigmata) and **c** Cryptostigmate mites (*Carabodes ornatus,* Orbatida); [scanning electron micrograph images from: Sue Lindsay **a**, Valerie Behan-Pelletier **b** and Katja Domes and Mark Maraun **c**]; (drawings modified after Gisi et al. 1997)

Spiders (Araneae) are members of the macrofauna, and are the most species-rich order of the arachnid**s** after the mites. They live on the soil surface and feed on e.g. mites, springtails, or ants, which they first inject with digestive fluids and then suck dry. The **harvestmen (Opiliones)** are mostly nocturnal predators; they can be easily recognized by their four pairs of legs, which are much longer than their body diameter.

Woodlice (Isopoda) are the only crustaceans adapted to terrestrial life. The occurrence of gills in various terrestrial woodlice is a reminder of their aquatic origins. Other woodlice (e.g. common woodlouse, *Oniscus asellus*) breathe through trachea-like lungs in their paddle-shaped hind legs (pleopods), called pleopodal lungs. Woodlice prefer moist sites; they are usually nocturnal and contribute to the primary decomposition of litter by feeding on dead plant material.

Enchytraeida represent a small family of the Oligochaeta; together with the earthworms, they belong to the phylum Annelida (segmented worms). Enchytraeidae are found globally in subarctic to tropical regions. Particularly high population densities can be found in soils with low pH values, where earthworms cannot live. Enchytraeidae are colorless and almost transparent worms with a length of 1–50 mm. The diversity of the Enchytraeidae is much lower than that of mites or Collembola. Enchytraeidae mainly feed on bacteria and fungi, which they absorb together with particulate organic matter. It is assumed that Enchytraeidae can influence the community composition of soil microorganisms through selective feeding. The feces of Enchytraeidae contribute to stabilization of the soil structure.

Earthworms (Lumbricida) are important members of the macro- and megafauna, and are found on all continents with the exception of Antarctica. Earthworm abundance is high in forest and grassland soils of temperate and tropical regions. Extremely cold or arid regions (e.g. deserts, tundra, polar regions) are sparsely populated by earthworms. A distinction is made

between three different types according to their life strategies (Table 4.1): Epigeic species (e.g. *Lumbricus rubellus*) live predominantly in the humus layer and in accumulations of organic matter (compost, decomposing wood). These comparatively small earthworms are protected from the UV radiation of light by strong pigmentation. **Anecic** species (e.g. *Lumbricus terrestris*) exploit both the surface litter as a food source and the mineral soil as refuge (e.g. during periods of drought). **Endogeic** species (e.g. *Aporrectodea caliginosa*) live in mineral soils and dig burrows to a depth of 50 cm. They feed on organic particles that they consume together with soil. Under conditions of desiccation, they roll themselves up to minimize water loss. Like deep-burrowing worms, they are not found in medium and coarse sand or in gravelly soils.

The smallest earthworm species is less than 20 mm long; giant earthworms, living in Australia (e.g. *Megascolides australis*), can grow to 3 m in length. Earthworms have up to 160 segments, each of which is equipped with small bristle-like structures called **setae**. The setae consist of chitin and proteins, and serve as anchors to the surface of the burrows during locomotion. As burrowing animals, earthworms make use of the peristaltic movement of the two layers of muscles, a thin outer layer of circular muscle, and a much thicker inner layer of longitudinal muscle, to expand their habitat. Earthworms do not have skeletons; they maintain their structure with fluid-filled chambers functioning as hydrostatic skeletons. Earthworms breathe through their skin, which must be kept moist by the mucus-producing cells. Earthworms have hemoglobin for the transport of oxygen throughout the organisms. Earthworms are hermaphroditic animals that reproduce by exchanging semen between two partners. The larvae develop in fertilized eggs inside a cocoon in soils, and become adult animals within a few weeks. Earthworms survive the winter in a dormant state (**quiescence**) that is triggered by low temperatures.

Ants (Formicidae) are important members of the macrofauna which can be found all over the world and include more than 12,000 species; there are about 180 species found in Europe. No ants have yet been found in Iceland, Antarctica, and in parts of Polynesia. Ants belong to the insects that form colonies, having strong local effects on soil structure through their burrows, and warming the soil significantly through intense bioturbation. Many ants are predators (e.g. the red wood ants of the genus *Formica*) and feed on other insects.

Termites (Isoptera) are particularly numerous in Africa and America. In the rainforests of the Amazon, the biomass of ants and termites account for one third of the overall animal

Table 4.1 Life forms and characteristics of earthworms living in Central Europe (after Stahr et al. 2012)

Life form/characteristic	Litter forms Epigeic species	Deep-burrowing worms Anecic species	Mineral soil forms Endogeic species
Pigmentation	Uniformly brownish red	Brown (the back is blackish-reddish brown)	Without pigmentation
Body length	20–120 mm	150–450 mm	20–150 mm
Digging muscles	Reduced	Strongly developed	Developed
Food intake	At the soil surface	At the soil surface	In the soil
Intestinal passage	Slow	Variable	Fast
Respiration	Intensive	Medium	Weak
Light sensitivity	Weak	Moderate	Strong
Threat from predators	Very high	Low (retreat in tunnels possible)	Weak
Survival of unfavorable periods	Encysting in cocoon	Diapause or no dormant stages	Often quiescence

biomass. They are not found in Central Europe beside a few exceptions (introduced species). Termites are insects that build colonies in most cases. They change the soil structure through their various structures (e.g. termite hills and subterranean nests). The function of termites in the subtropics (savanna) is similar to that of earthworms in temperate climates. Lower termites decompose wood in symbiosis with microorganisms that live in their gut. Microsymbionts (flagellates and bacteria) in the gut of termites produce enzymes that decompose wood components. Carbon dioxide, hydrogen and methane are liberated as decomposition products. Higher termites feed on humus or fungi, which they cultivate on substrates (e.g. wood, cellulose) in their underground structures. Some termites (e.g. *Mastotermes*) have symbiotic bacteria in their guts that can fix N_2.

Mammals (Mammalia) live in the soil either periodically (e.g. mice, hamsters, rabbits, badgers, foxes, as well as ground squirrels and gophers in steppe soils) or permanently (e.g. moles), and mix the soil with their burrowing activities. The **European mole** (*Talpa europaea)* lives mainly in meadows, forests and cultivated landscapes of temperate regions; they are not found in the cooler regions of Eurasia or in the Mediterranean area. In continental and maritime Antarctica, penguins strongly contribute to soil formation through the building of ground burrows using rocks and excrement.

4.1.3 Numbers and Biomass of Soil Organisms

4.1.3.1 Abundance of Organisms

Soil organisms from various size classes are represented in the soil in different numbers. As a general rule, the numbers of soil microorganisms dominate those of larger soil animals. An overview of the abundance (number of individuals of a species related to a specific area or volume unit) and biomass of the most important soil organisms in soils of Central and Northern Europe can be found in Table 4.2. However, a site does not simultaneously provide optimal living conditions for all groups of organisms. Minimum values for microorganisms are several orders of magnitude lower than the given average values, while individual groups of the macro- and megafauna are completely absent. The importance of the individual animal groups for ecosystem function can be compared using their respiration rates (Fig. 4.10). Soil microorganisms account for the highest fraction of the total respiration of an ecosystem at 91 %. Among the soil fauna, the smallest soil animals (protozoa) contribute the most to total respiration.

An important criterion for the characterization of the quantity of soil microorganisms is their carbon content. Using the fumigation-extraction method (see Sect. 4.5.1), approx. 100–1,000 μg C g^{-1} of soil is given for agricultural soils and approx. 500–10,000 μg C g^{-1} of soil for forest soils (Table 4.3). Microbial biomass decreases within the soil profile. The highest quantity of carbon, which is stored by microorganisms, is found in litter layers of forest soils and in the topmost centimeters of grassland soils. The percent fraction of microbial carbon in the total quantity of organic matter of a soil is similar for all soils: 0.9–6.0 % (mean values 2–3 %). For a forest soil, Raubuch and Joergensen (2002) calculated that the carbon flux through the microbial biomass is of approx. 540 kg C ha^{-1} a^{-1}.

4.1.3.2 Spatial and Temporal Variability of Soil Organisms

Food supply, temperature and soil moisture are important factors determining the spatial and temporal variability of soil organisms and their functions. Studies of soil microbial properties in a depth profile revealed, for example, that N-mineralization showed a more pronounced depth gradient than invertase and phosphatase activities (Fig. 4.11). The distribution of roots in the soil profile provides an initial indication of the main activity zones of the soil organisms. If organic substances are transported as dissolved organic matter (DOM), colloids or particles to deeper soil layers, they are used by heterotrophic soil microorganisms as sources of carbon and energy under aerobic or anoxic conditions. The microbial

Table 4.2 Mean (m) and high (h) numbers as well as the live mass of the most important soil organisms in soils of Central and Northern Europe (after Dunger 1983)

Group	Number of individuals per m^2		Mass (g m^{-2})	
	m	h	m	h
Microflora				
Bacteria	10^{14}	10^{16}	100	700
Actinobacteria	10^{13}	10^{15}	100	500
Fungi	10^{11}	10^{14}	100	10^3
Algae	10^8	10^{11}	20	150
Microfauna (0.002–0.2 mm)				
Flagellates	10^8	10^{10}		
Rhizopods	10^7	10^{10}	5	150
Ciliates	10^6	10^8		
Nematodes	10^6	10^8	5	50
Mesofauna (0.2–2 mm)				
Rotifers	10^4	10^6	0.01	0.3
Water bears	10^3	10^5	0.01	0.5
Mites	7×10^4	4×10^5	0.6	4
Springtails (Collembola)	5×10^4	4×10^5	0.5	4
Macrofauna (2–20 mm)				
Enchytraeids	3×10^4	3×10^5	5	50
Snails	50	10^3	1	30
Spiders	50	200	0.2	1
Woodlice	30	200	0.4	1.5
Millipedes	100	500	4	10
Other polypods	130	2×10^3	0.5	3
Beetles with larvae	100	600	1.5	20
Dipteran larvae	100	10^3	1	15
Other insects	150	15×10^3	1	15
Megafauna (20–200 mm)				
Earthworms	100	500	30	200
Vertebrates	0.01	0.1	0.1	10

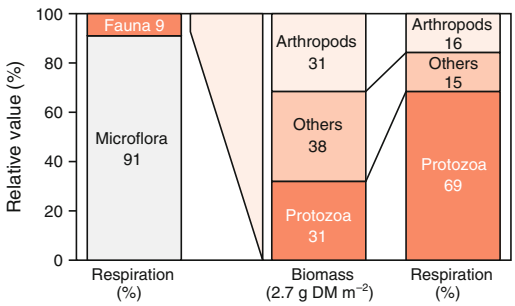

Fig. 4.10 Mean biomass and respiration of soil organisms. *DM* dry matter (after Weaver et al. 1994)

colonization of deeper soil layers takes place either through active or passive transport of the organisms (Fig. 4.12). Mobile soil microorganisms use their flagella to reach their food sources; soil microorganisms without flagella are transported passively within the soil profile through diffusion and convection. Deeper soil layers also provide soil fauna an opportunity to retreat in case of poor weather conditions (dryness, cold).

The spatial distribution of soil organisms within an area is also determined by the food

Table 4.3 Microbial biomass and organic matter of soils from different ecosystems. The determination is performed using the fumigation extraction method or substrate-induced respiration (after different sources)

Ecosystem	Horizon (cm)	C_{mic} (µg g^{-1})	C_{org} (%)
Arable soil	0–5	250–1,080	1.0–3.0
	0–20	70–720[a]	0.8–2.5
Grassland	Litter layer	9,650	2.0–20
	0–10	2,670	2.9–15
	10–20	1,120	1.9–10
Forests, temperate climate	Litter layer	10,830	20–45
	0–10	1,670	3.4–40
	10–20	730	1.8–6.7

[a]Determination of the microbial biomass using substrate-induced respiration

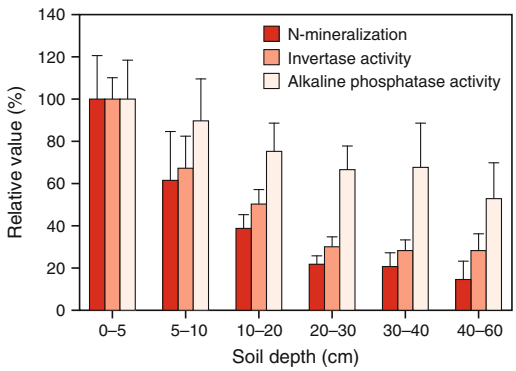

Fig. 4.11 N mineralization, invertase and alkaline phosphatase activities at various soil depths of a grassland (Chernozem, Colorado). The results from deeper soil layers were given as a percent deviation from the results from the topmost soil layer (0–5 cm). (30.2 µg NH_4^+–N g^{-1} 7 d^{-1}: 100 % of the N mineralization; 3.8 mg glucose g^{-1} 3 h^{-1}: 100 % invertase activity, 0.7 mg phenol g^{-1} 3 h^{-1}: 100 % alkaline phosphatase activity; the pH value (H_2O) of the surface soil is 7.2 and the organic matter content is 0.89 %) (after Kandeler et al. 2006)

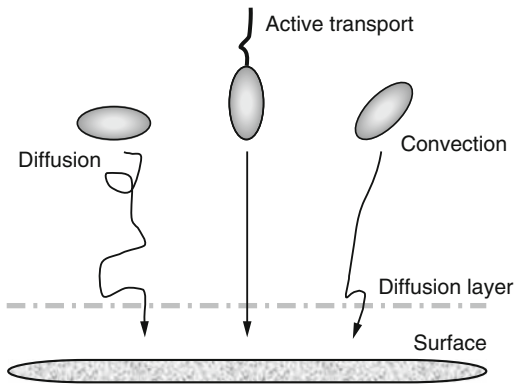

Fig. 4.12 Active and passive transport of bacteria to an organo-mineral surface (after Maier et al. 2000)

supply and microclimatic conditions. Geostatistical methods have shown that the distance between two plants in agricultural and forested soils influences the occurrence of soil microorganisms. Biogeography investigates the distribution patterns of soil organisms on a regional and global scale. Until now, according to an idea from the microbiologist Martinus Beijerink, it was assumed that many soil microorganisms are ubiquitous and that environmental conditions determine which microorganisms can establish themselves (*everything is everywhere, the environment selects*). The global distribution of soil microorganisms takes place through various transport mechanisms (water transport through rivers, groundwater and oceans; transport through the atmosphere by dust particles and aerosols; transport through animals and human beings). Even in very remote areas (such as Antarctica), mainly microorganisms are found that are already known from other regions. However, new molecular methods have shown that there are soil microorganisms that only occur locally (endemic soil microorganisms). Intraspecific requirements for growth temperature, pH value and substrate concentration (NH_4^+), for example, determine the dominance of nitrifiers in various ecosystems. *Penicillium* is often found in temperate and cold regions, while *Aspergillus* dominates in warmer regions.

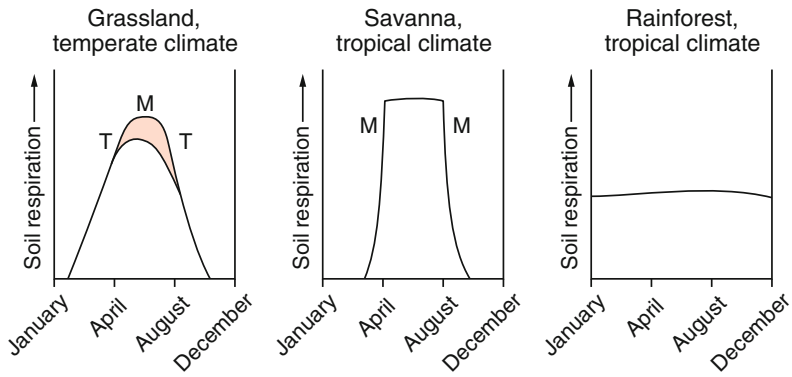

Fig. 4.13 The effect of seasons in the northern hemisphere on the respiration of soils in different ecological zones. (*T* temperature as a limiting factor, *M* soil moisture as a limiting factor) (after Wood 1995)

The temporal variability of the abundance and activity of soil microorganism differs regionally (Fig. 4.13). In grasslands in temperate zones, the low temperatures in the winter and phases of low soil moisture in the summer limit the activity of soil microorganisms. Dryness is the cause for the low activity of soil organisms in tropical savannas in the winter. In tropical rainforests, constant temperature and moisture conditions lead to a constant rapid decomposition of organic compounds during the whole year. Therefore, ecosystem functions vary among different biomes (biomes are defined by similar climatic and geographic conditions). Tundra and desert soils contain only few organisms, because there is a lack of food, heat or water. The composition of species also depends on the climate: In the tropics and subtropics, for example, large earthworm species (e.g. Lumbricidae) are lacking. For this reason, despite the higher abundance of smaller earthworm species, the biomass in rainforest soils is low.

4.1.4 Soil Organisms as a Biocoenosis

4.1.4.1 Interactions Between Soil Organisms

All of the soil organisms living in a site form a biocoenosis, consisting of individual populations of different species. The ecological living and habitat conditions determine the composition of the biocoenosis. Quantity and quality of the biocoenosis differs depending on the climate, relief, vegetation, soil form, soil depth and season. Within a biocoenosis, the **diversity** (number of different species), **abundance,** and **trophic level** (diet) determine which organisms dominate or are displaced, as well as the extent of the interactions between two populations. In a loose biocoenosis, both partners use the same food resources without having direct contact; in doing so, they can behave indifferently towards one another (**neutralism**) or compete with one another (**competitive exclusion**). The inhibition of a partner can take place through the excretion of inhibitors (**amensalism**); **antibiotic** inhibition takes place between microorganisms, and **allelopathic** inhibition between plants. Soil organisms can also mutually promote one another by decomposing substrates that can then be used by other organisms (**metabiosis**, e.g. litter decomposition or nitrification). For this reason, the loss of individual animal species or organisms groups can significantly disturb various metabolic pathways of an ecosystem.

A higher intensity of interaction is found in organisms that colonize plant and animal surfaces (**epibiosis**), and thus make use of the partner's exudates. **Parasites** damage their partner, e.g. through the removal of nutrients (e.g. plant parasitic nematodes). With symbiosis, both partners are involved in intensive spatial

and physiological interactions. Symbioses (nitrogen-fixing bacteria, mycorrhiza-forming fungi) are discussed in more detail in Sect. 9.6.1.1; several symbioses between microorganisms and animals have been described in Sect. 4.1.2.

4.1.4.2 Interactions Between Soil Microorganisms and Plants in the Rhizosphere

The rhizosphere is the narrow region of soil that is directly influenced by root secretions and associated soil microorganisms (Fig. 4.14). The direct surroundings of plant roots are a preferred microhabitat for soil microorganisms and various soil animals. Soil organisms can live in the rhizosphere, on the surface of roots (rhizoplane), and/or inside the root tissues (endophytic habitat). Microorganisms in the rhizoplane are attached by adsorption and/or through the development of short hair-like fimbriae more or less strongly to the root's surface. Rhizobacteria, which form the strongest associations with plants and live inside the plant roots, are called **endophytes**.

Roots exude, both actively and passively, various volatile, soluble, and particulate materials as root **exudates** (Fig. 4.14). The release of sugars, amino acids, and organic acids stimulates the growth of soil microorganisms, which react by growing rapidly on the readily available nutritive medium. However, plants also release growth factors and signal compounds into the rhizosphere, which serve to facilitate cell communication. Organic compounds are added to the soil not only as root exudates, but also as mucilages (high-molecular weight compounds like polar glycoprotein, and an exopolysaccharide produced by nearly all plants) and lysates (higher-molecular weight substances that are released through autolysis or microbial decomposition of old root cells). The composition of the microbial community in the rhizosphere is determined by the plant species, their root morphology and their root exudates. Figure 4.14 shows various microbial interactions. On the one hand, rhizosphere microorganisms compete with the plant for nutrients and oxygen, and on the other, they can also liberate nutrients and make them available to the plants. Pathogenic microorganisms first have to establish themselves in the rhizosphere before they are able to penetrate the roots. They can be either inhibited or promoted by the organisms living there. The cell walls of pathogenic fungi, for example, can be dissolved by chitinase that is excreted by rhizobia (example of parasitism). Various pseudomonads can repress less competitive pathogenic microorganisms through better nutrient acquisition.

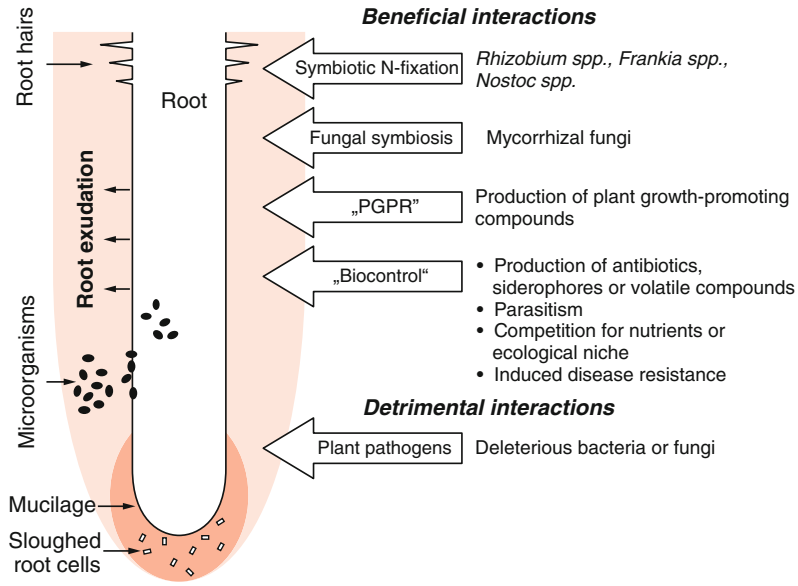

Fig. 4.14 Microbial interactions in the rhizosphere. PGPR (plant-growth promoting rhizobacteria) (Brimecombe et al. 2007)

In general, plant growth promoting rhizobacteria (PGPR) living in the rhizosphere are bacteria that directly or indirectly stimulate plant growth. PGPR's produce compounds such as growth-stimulating phytohormones or those (siderophores), which improve plant nutrient uptake. These microorganisms increase the plant's resistance towards pathogens or abiotic stress factors (e.g. frost) and modulate the concentration of plant signals (e.g. ethylene). The rhizosphere also provides an ideal habitat for various soil animals (e.g. protozoa, nematodes).

4.1.4.3 Symbioses Between Microorganisms and Plants

Various mutualistic symbioses describe interactions between two organisms where both partners gain benefits (Table 4.4). Several **nitrogen-fixing bacteria** form symbiotic biocoenoses with plants, whereby the plants supply the bacteria with carbon and energy sources and the bacteria provide the plants with nitrogen. The symbiosis between root nodule bacteria and legumes is particularly well investigated, since nitrogen fixation has practical importance for plants such as soybean, clover, alfalfa, and peas. According to the host specificity and the development of the nodules, a distinction is made between *Rhizobium, Bradyrhizobium, Sinorhizobium, Mesorhizobium* and *Azorhizobium.* Nodules are formed in the following manner: free-living rhizobia are attracted to species- or genus-specific signal substances from the plant (e.g. certain flavonoids such as luteolin and genistin) and grow on the root surface. The rhizobia cells enter through a deformed root hair and cause the plant to form an intracellular tube (infection thread). Infection threads enter the central root tissue and release the rhizobia in these cells, where they differentiate morphologically into **bacteroids** (swollen vesicles with a peribacteroid membrane). The plant supplies various organic acids as energy sources for nitrogen fixation. Nitrogen fixation and excretion of ammonium take place in the bacteroids and are catalyzed by the enzyme **nitrogenase**. Ammonium is transported from the bacteroid to the plant cells, converted to glutamine or other nitrogen-containing compounds, and transported into the plant tissues (see Sect. 9.6.1.1 for more information on symbiotic N_2 fixation).

Soil fungi develop close interactions with higher plants. The fine roots of more than 90 % of flowering plants live in symbiosis with fungi (**mycorrhizae**). The fungal hyphae radiating out of the mycorrhizae increase the contact area with the soil. With their small diameter (2–12 μm),

Table 4.4 Important mutualistic symbioses (after Fuchs and Schlegel 2007)

Contribution from the microbial partner	Microorganisms	Eukaryotic partner
CO_2 fixation	Cyanobacteria	Fungi (lichen)
N_2 fixation	Rhizobia and others	Legumes, alder, sea buckthorn, white dryas
	Frankia	Kallar grass
	Azoarcus	Sugar cane
	Acetobacter	Livermosses, mosses, Azolla
Nutrient supply	Fungi mycorrhiza	Most terrestrial plants, many trees
Synthesis of essential amino acids and cofactors	Bacteria	Many insects (mycetome), Protozoa
Removal of metabolic products (hydrogen)	Methanogenic archaea	Protozoa
Decomposition of polysaccharides (celluloses)	Eubacteria, archaea, protozoa	Termites (guts), cockroaches
Movement	Spirochaetes	Protozoa
Synthesis of antibiotics	Eubacteria	Nematodes, insects

fungal hyphae can absorb nutrients and water from pores that are not accessible to the roots. The advantage of mycorrhization for plants is mainly in improved phosphate absorption from mineral and organic phosphorus sources in the soil. In alkaline soils, mycorrhizae can prevent iron chlorosis and manganese deficiency symptoms. Mycorrhizae act as an "anti-stress factor" for higher plants, which creates a positive effect particularly in sites with low water and mineral nutrient availability. Many forest trees (beech, oak, spruce, pine, fir) cannot survive without **ectomycorrhizae** completely coating their roots, because they not only absorb nutrients and water for the host, but also protect from soil-borne pathogens. Most higher fungi in forests (basidiomycetes), such as boletus, russula, and milk-caps, are ectomycorrhiza fungi. **Endomycorrhizae** are widespread in cultivated soils. Fungi in the Glomales family colonize root cells intracellularly by forming arbuscles (dichotomously branched hyphae). Arbuscular mycorrhizae facilitate phosphorus absorption in phosphate-poor and in strongly phosphate-fixing soils of the tropics and subtropics. Ericoid mycorrhizae play an important role in the P supply for Ericaceae plants in moors and heathlands.

In most mycorrhizae, the heterotrophic fungal partner is dependent on organic substances from its host plant and obtains carbohydrates from the roots. However, this loss of assimilates for the host plant is low compared to the benefit gained from the mycorrhizae for the absorption of nutrients and water. Still, some mycorrhizal species undergo a direct transition to a parasitic mode of life, where the fungus or the host damages or kills its partner.

4.1.4.4 Interactions Between Soil Microorganisms and Soil Animals

Soil animals are characterized by different feeding behaviors and preferences. They influence the abundance and activity of soil microorganisms through selective feeding. Figure 4.15 shows that smaller soil animals (nematodes and protozoa) graze on soil microorganisms in the rhizosphere and thus liberate nitrogen, which is then used by plants for their growth. Improved plant growth, in turn, promotes root exudates and microbial growth. This cycle was named the *microbial loop* by the Swedish scientist, Marianne Clarholm (1981).

Soil animals are responsible for the passive distribution of microorganisms in the soil. Soil microorganisms can be transported on the surface of the bodies or inside soil animals, or are consumed as food by larger soil animals (e.g. earthworms) and excreted after passing through their digestive systems, becoming active again somewhere else. Some soil animals (e.g. ants and termites) require microorganisms in their guts for the digestion of poorly degradable organic substances.

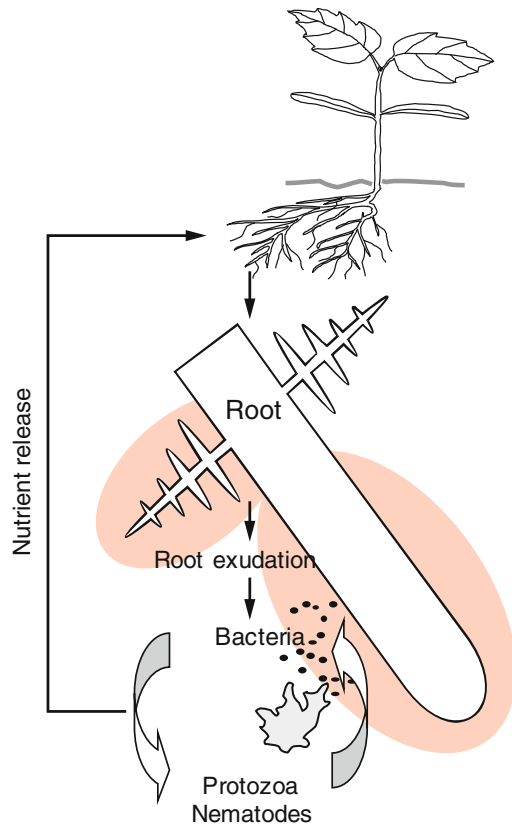

Fig. 4.15 Interactions between soil animals (protozoa, nematodes), rhizosphere microorganisms and plants. By feeding on rhizosphere microorganisms, soil animals liberate nutrients that stimulate plant growth (see text: microbial loop)

4.2 Environmental Conditions

4.2.1 The Soil as a Source of Nutrients and Energy for Soil Organisms

Nutrient and energy sources are distributed heterogeneously in the soil, and therefore their accessibility by soil organisms varies (Fig. 4.16). Soil bacteria depend more strongly on the transport of substrates with soil water than soil fungi, which grow towards the food source with their hyphae. The rhizosphere, drilosphere and detritusphere are preferred microhabitats for soil microorganisms. These microhabitats are also called *hot spots* and are characterized by high nutrient and energy source availability. Plant roots exude different low-molecular organic compounds that attract soil microorganisms chemotactically. Soil microorganisms that use readily available food sources aggregate in the **rhizosphere**. The **drilosphere** is defined as the direct zone of influence by earthworms. This microhabitat includes the earthworm burrows in the soil (the first 1–2 mm of the wall of the earthworm burrows) and the excretion products from earthworms (intestinal contents, feces). Earthworms stabilize the surfaces of the burrows with mucilage secretions. The walls of earthworm burrows are preferentially colonized by soil microorganisms, protozoa, nematodes and fine roots. The detritusphere, the layer that includes the litter and the adjacent soil influenced by the litter, is a very thin but microbiologically highly active zone in soil.

In all habitats, soil organisms use nutrients and energy sources for tissue formation and to maintain their life processes. In order to describe the role of individual soil organisms in matter cycling, they are assigned to individual trophic levels. Microorganisms use oxidizable chemical compounds (**chemotrophy**) or light energy (**phototrophy**) for energy conversion (Fig. 4.17). Chemoorganotrophic and chemolithotrophic microorganisms either use organic (e.g. sugar) or inorganic (e.g. sulfur) compounds as electron donors. Soil microorganisms incorporate carbon from numerous organic compounds into their body substance. Microorganisms that use litter and dead or alive soil organic matter as carbon sources are called **heterotrophic**. Only a few soil organisms can use CO_2 and H_2O to build organic compounds **(C autotrophs)**. **Photoautotrophic** microorganisms (e.g. algae, cyanobacteria, and

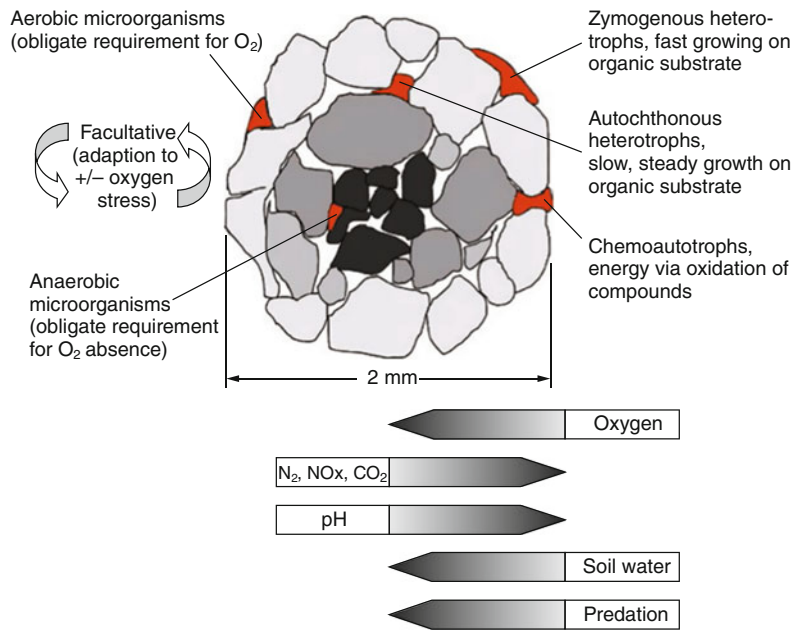

Fig. 4.16 Biotic and abiotic factors determine the presence of various microorganisms in an aggregate. The *arrows* under the figure show the direction of diffusion for individual elements or processes (after van Elsas et al. 2006)

some flagellates) obtain the required energy from sunlight and use CO_2 as a carbon source to build their cell substance. **Chemolithoautotrophic** bacteria (e.g. nitrifying bacteria) obtain their energy from the oxidation of inorganic compounds, and their cell carbon from CO_2 and H_2O: *Nitrosomonas* oxidize NH_4^+ to NO_2^-, *Nitrobacter* NO_2^- to NO_3^-, *Thiobacillus* H_2S and S to SO_4^{2-}, and *Leptothrix* and *Thiobacillus* Fe^{2+} to Fe^{3+}. The energy that is bound in this way is liberated again by other organisms through a reversal of the above-mentioned processes (respiration). The classification of soil microorganisms based on their energy and carbon requirements contributes to understanding the roles of individual soil microorganism groups in an ecosystem. In recent years, however, it has become increasingly clear that there are exceptions to this general rule. Nitrifiers that live heterotrophically, for example, cannot be classified according to the scheme.

Soil animals are generally heterotrophic organisms that feed on alive or dead organic matter. They are separated into three groups according to their contribution to different soil processes (see Fig. 4.18):

- **Ecosystem engineers** (e.g. earthworms, termites, ants) change the physical structure of the soil, and influence the nutrient and energy flux in the soil.
- **Litter transformers** (e.g. arthropods) break down the litter and thus make it more accessible for soil microorganisms.
- The **micro-foodweb** includes soil microorganisms and their direct predators (nematodes and protozoa).

Soil organisms are also classified according to their food source. **Saprotrophic organisms** live from dead organic matter, **phytophagous** from live plant material, **mycophagous** from fungi, **coprophagous** from digestive products of other animals, and **zoophagous** organisms live as predators on other soil fauna.

Soil organisms have mineral nutrient requirements similar to those of higher plants: N, P, K, Ca, Mg, S, Mn, Fe, Cu and Zn are essential, sometimes also B, Co, Mo and V. Earthworms (e.g. *Lumbricus terrestris*) and land snails (*Helix pomatia*) require Ca-rich sites, while Enchytraeidae and arthropods thrive in more nutrient-poor soils.

4.2.2 Water and Atmosphere

Water is vital to all soil organisms. Soil microorganisms require water to maintain the osmotic

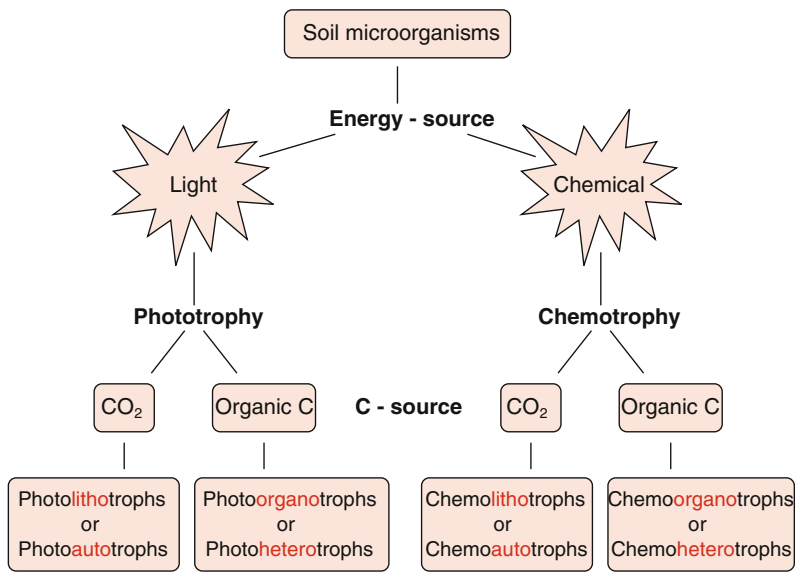

Fig. 4.17 Physiological classification of soil organisms according to their use of carbon and energy sources (after van Elsas et al. 2006)

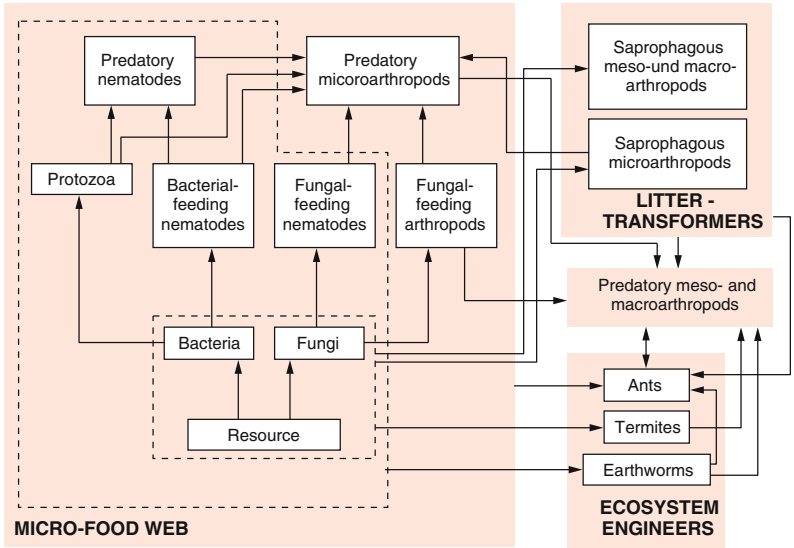

Fig. 4.18 Organization of the foodweb into three categories: Ecosystem engineers, litter transformers, micro-food web (after Paul 2015)

potential of their cells, for the transport of substrates to the cells, for the removal of excretion products from cells, and for locomotion (mobile stages such as flagellated spores), etc. Soil microorganisms live mainly in the thin film of water surrounding all organic and mineral particles. This water film does not freeze at temperatures below 0 °C, and thus provides good living conditions over a broad temperature range. Biofilms with a thickness of approx. 0.1 mm, consisting of hydrophobic organic molecules, develop inside individual pores at the boundary surface between the soil water and the soil atmosphere, and can be rapidly colonized by soil microorganisms.

Soil microorganisms have adapted to the varying water potentials found in soil. A water potential of −50 kPa is optimal for aerobic soil microorganisms. Under arid or wet conditions, the activity of aerobic soil microorganisms is reduced. With low soil moisture, the activity of soil microorganisms decreases due to the limited diffusion of organic substrates and reduced mobility of the microorganisms. Bacteria react more sensitively to desiccation than fungi. Considerable differences in the reactions towards water stress can also be observed within the bacteria: nitrifiers are more sensitive than ammonifiers. Therefore, under severely arid conditions, the NH_4^+ formed by ammonifiers is no longer converted and accumulates in the soil. Bacteria that can survive in highly arid environments are called **xerophilic** microorganisms. Resistance to desiccation is often coupled with resistance to temperature extremes. The various dormant forms of soil organisms are described in Sect. 4.1.

The dependence of soil microorganisms on the presence of oxygen in the soil varies. Because oxygen only dissolves to a limited extent (0.031 cm^3 O_2 l^{-1} at 20 °C) in soil water, oxygen can rapidly become a limiting factor for microbial growth in microhabitats. **Aerobes** are species that live under full oxygen tension (the atmosphere has 21 % O_2). The oxygen reaches the inside of the cells of aerobic soil microorganisms through diffusion. In loose sandy soils, the O_2 supply for soil microorganisms is ensured on average at field capacity, and in dense clayey soils, at 50 % field capacity. Anaerobic organisms can live without oxygen, either intermittently (**facultative anaerobes**) or completely (**obligate anaerobes**). These groups include the soil bacteria *Clostridium pectinovorum* (pectin decomposer), *C. cellulolyticus* (cellulose decomposer), *C. sporogenes* (protein decomposer) as well as yeasts, which can live anaerobically but require oxygen for the formation and germination of their spores. Obligate anaerobic microorganisms are inhibited or even killed by the presence of oxygen. They do not have any catalases and peroxidases to detoxify the toxic

intermediate products from aerobic metabolism (e.g. H_2O_2). **Obligate anaerobiosis** is observed only in Bacteria and Archaea, and in a few fungi and protozoa.

The larger members of the soil fauna require oxygen and cannot live under stagnant moisture conditions in soils. Heavy rainfall can force some soil animals to the surface due to lack of oxygen. Soil animals absorb oxygen either through their skin, through gills or tracheae. **Cutaneous respiration** represents a primitive form of respiration, yet is very effective due to the positive ratio of body surface to body volume. Earthworms dissolve atmospheric oxygen through the moist mucilage film on their skin; oxygen penetrates the epidermis into the blood vessels and is loosely bound to hemoglobin. Other soil animals, such as insects, centipedes, millipedes, and spiders, cannot breathe through their skins because of their chitin exoskeletons. They absorb oxygen through tracheae. Woodlice breathe through trachea-like lungs in their paddle-shaped hind legs (pleopods), called pleopodal lungs.

4.2.3 pH Value and Redox Potential

Soil acidity is a chemical property of soils that has a decisive effect on the species composition and function of soil organisms. The pH value can affect soil organisms directly (e.g. by changing the enzyme activities of soil microorganisms) or indirectly (e.g. by changing the solubility of ions). While bacteria prefer soils in a pH range of 5–7, fungi dominate in acidic soils. Soil microorganisms can be classified into the following groups according to their preferred pH range: extremely acidophilic (pH 1–3), acidophilic (pH 1–6), alkaliphilic (7–12) and extremely alkaliphilic (pH 13) microorganisms. The obligate acidophiles include several *Acidithiobacillus* species as well as several archaea genera (e.g. *Sulfolobus, Thermoplasma*). Acidophilic soil microorganisms have adapted to low pH values in the soil through mechanisms such as modification of their cell membranes. Particularly long-chained fatty acids (32–36 carbon atoms) protect the membranes from acid hydrolysis. In addition, acidophilic soil microorganisms can control ion transport through their cell membranes very effectively. In this way, they maintain the pH value inside their cells between 5 and 7, although the pH of their environment is approx. 2. Alkaliphilic organisms are found in strongly alkaline habitats (natron lakes and soils with high carbonate content). A preference for alkaline sites is often coupled with a tolerance to high salt concentrations.

Soil animals tolerate different soil acidities. Most earthworm species prefer soils with neutral to slightly acidic pH values. In strongly acidic soils, in contrast, only few and mostly epigeic earthworms (pure litter-dwellers) are found, which make only a small contribution to bioturbation. Earthworms are not found in strongly acidic peaty soils. Enchytraeidae tolerate lower soil pH values than earthworms. The optimal pH is hard to determine for many members of the mesofauna, because other factors such as food supply and soil moisture play a more important role for them. Protozoa and nematodes, however, react very sensitively to changes in soil pH.

Soil fauna can change the soil pH through the excretion of urea and other compounds. In acidic forest soils, for example, earthworms excrete feces with a pH that is at least one pH value unit higher than the surrounding soil.

In addition to pH value, the soil's redox potential also plays a significant role in the function and species composition of soil organisms. However, soil microorganisms themselves also influence the soil's redox potential (e.g. through respiration processes of aerobic soil organisms and reduction processes of anaerobic microorganisms).

4.2.4 Temperature

Soil temperature affects physical, chemical and biological processes. The relationship between an increase in temperature and the rate of

microbiological processes was described by Svante Arrhenius using the following equation:

$$k = A\,e^{-Ea/RT}$$

A is the pre-exponential factor, Ea is the activation energy, R is the universal gas constant (8.314×10^{-3} kJ mol^{-1} K^{-1}), e is the base of the natural logarithm, T is the temperature in Kelvin, and k is the specific reaction rate (per unit time). The **Q_{10} temperature coefficient** is the factor by which the reaction rate increases with an increase in temperature of 10 °C. The Q_{10} value depends on the quality of the organic matter, on the microbial reaction, and on the temperature range. On average, the Q_{10} value is 2.0 for carbon mineralization at a temperature range of 10–30 °C, and 1.7 for N mineralization.

Soil microorganisms can be classified into the following groups according to their preferred temperature range: psychrophilic (−5 to 28 °C), mesophilic (18–45 °C), thermophilic (42–70 °C), extremely thermophilic (65–90 °C), and hyperthermophilic (85–110 °C) microorganisms. Most well known soil bacteria are either psychrophilic or mesophilic. Psychrophilic soil microorganisms maintain their membrane function at low temperatures through the production of unsaturated fatty acids, and thermophilic soil microorganisms protect themselves from the denaturation of enzymes at high temperatures through the production of thermally stable proteins. Thermophilic microorganisms are found, e.g., in composts.

Soil organisms have developed different strategies to survive periods of unfavorable temperature and moisture conditions. Several organisms can survive cold periods as spores (bacteria, fungi), cysts (protozoa, nematodes) or as eggs encased in a cocoon (earthworms). Nematodes, rotifers and water bears strongly decrease the water content of their cells and reduce their life processes to a minimum (**anabiosis**: *anabiōsis* = to return to life). Many arthropods lower their freezing point in the winter by maintaining a high glycerin content in their tissues and can thus survive in frozen soil horizons. In Central Europe, earthworms spend the cold season in a type of cold rigor at a soil depth of 40–80 cm. Vertebrates seek out deeper, frost-free horizons.

4.3 Functions of Soil Organisms

Soil organisms are significantly involved in different soil functions: 1. Decomposition and transformation of organic matter, 2. Formation of humic substances, 3. Structure formation and bioturbation, 4. Redox reactions, and 5. Detoxification of contaminants. Soil microorganisms are considered **omnipotent**, because together they are able to decompose or transform virtually all organic compounds that are added to the soil. Xenobiotic substances (**xenobiotica**) represent an exception; they can be decomposed only slowly by soil microorganisms or not at all. Microorganisms play an important role in the reduction/oxidation reactions in soils, since numerous microbial processes are coupled with the liberation or consumption of electrons or protons. Soil fauna contribute to the decomposition of litter substances and to structure formation (bioturbation). They influence the species composition of the microbial and animal biocoenoses through their food selection. The individual functions of soil organisms will be briefly explained subsequently. The focus of this chapter is on the role of soil organisms in the decomposition of litter. Sections 9.6 and 9.7 explain the function of soil microorganisms in the mineralization and immobilization of nutrients and micronutrients in more detail.

4.3.1 Function of Soil Organisms in Matter Cycles

4.3.1.1 Foodwebs

The different animal and microorganism groups in an ecosystem are classified according to trophic levels, which reflect their feeding behavior. Autotrophic green plants are called primary producers, and all other organisms are consumers.

Primary consumers are herbivores; in contrast, secondary consumers are carnivores. Reducers are heterotrophic bacteria and fungi who take their food from all of the other trophic levels. Figure 4.19 shows a foodweb representing the mutual interactions of the organisms during the decomposition of organic materials in a grassland soil. Primary consumers and primary reducers first make use of rhizodeposits and litter substances. In doing so, both groups of primary decomposers modify the organic matter in various ways. As primary decomposers, soil animals (earthworms, Enchytraeidae, millipedes, macrophytophagous snails) break down and transport organic substances, and bacteria and fungi as reducers are responsible for the enzymatic cleavage of organic compounds. Secondary decomposers (mites, springtails, some nematodes and protozoa) and predators include groups of organisms with microphytophagous or saprophagous feeding habits (feeding on dead organic matter). Because many soil organisms cannot be observed in the soil during their quest for food, their position in the foodweb is insufficiently understood. A new method has been established to follow food selection activities of different soil organisms, based on the theory that consumers incorporate neutral lipids from their prey into their own bodies without modification (Fig. 4.20).

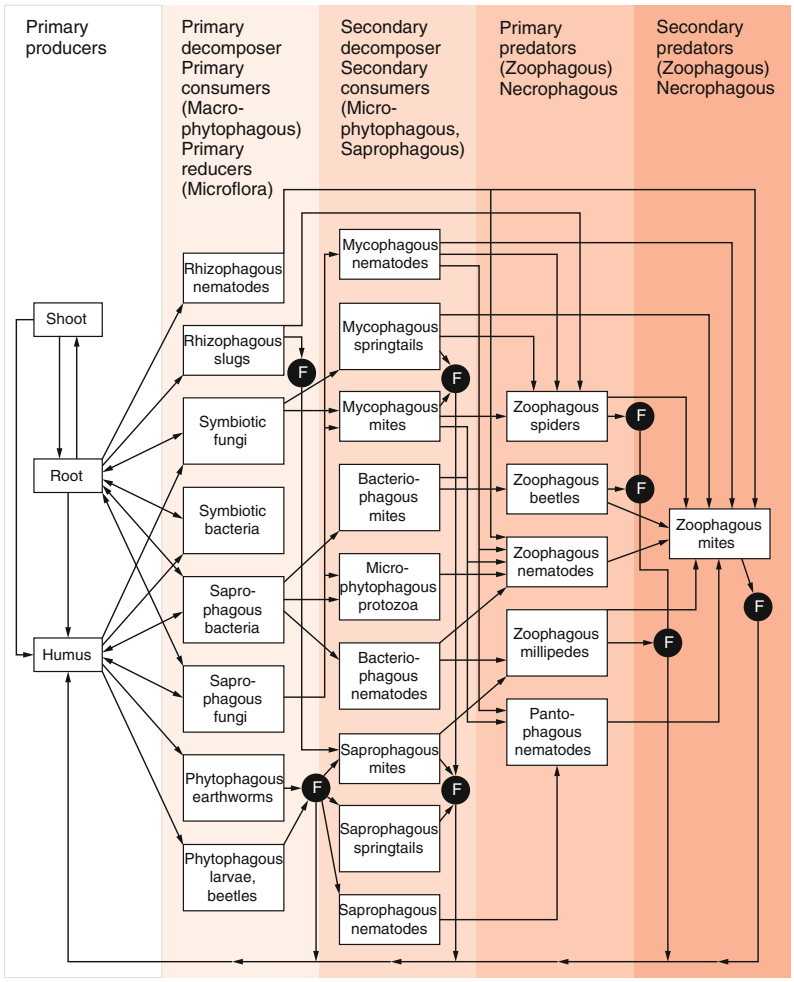

Fig. 4.19 Foodweb established during the decomposition of organic matter on a meadow site. *F* = feces (detritus, excrement) (after Gisi et al. 1997)

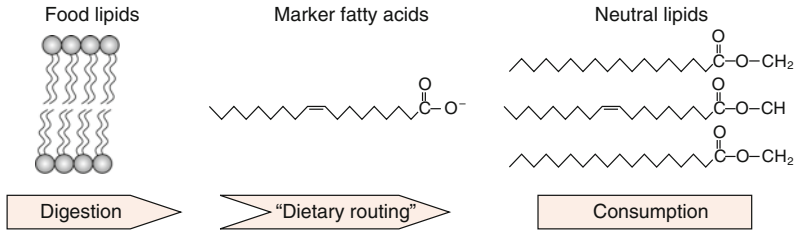

Fig. 4.20 Consumers absorb marker fatty acids with their food and store them unchanged in their own neutral fats. The determination of the neutral fats can therefore enable conclusions on the food preference of the soil fauna (after Ruess et al. 2005)

4.3.1.2 Carbon Cycle

Cyanobacteria, purple bacteria, nitrifiers, and sulfur-oxidizing bacteria contribute to carbon fixation and thus to primary production. However, the greater portion of primary production is transformed by plant photosynthesis into organic compounds. Figure 4.21 shows important processes through which soil organisms participate in the carbon cycle. During the decomposition of organic residues, soil microorganisms and fauna incorporate part of the carbon into their own bodies (**assimilation**). Compared to bacteria, fungi incorporate more carbon into their bodies. A complete mineralization to CO_2 and water can only occur under aerobic conditions; under anoxic conditions, organic compounds are decomposed progressively through nitrate reduction, sulfate reduction, fermentation, methanogenesis and acetogenesis. Methanogens living in soil use fermentation products (e.g. organic acids, alcohols) as substrates for methane formation. **Methanotrophic** microorganisms oxidize methane in aerobic microhabitats. The decomposition pathways for individual constituents of litter are described in Sect. 3.5. This section describes only the decomposition of high molecular weight substrates using cellulose as an example. Soil microorganisms excrete extracellular enzymes (endo-1,4-β glucanase and exo-1,4-β glucanase) that catalyze the decomposition of polymers to cellobiose. Cellobiose is split by the enzyme 1,4-β glucosidase to form glucose, which is then absorbed by the cells and used as a source of carbon and energy. According to a very similar principle, all other high molecular organic substrates are initially reduced to smaller fragments by extracellular enzymes outside of the microorganisms, before the individual monomers (sugar, amino acids etc.) are transported into the cells and used in cell ana-

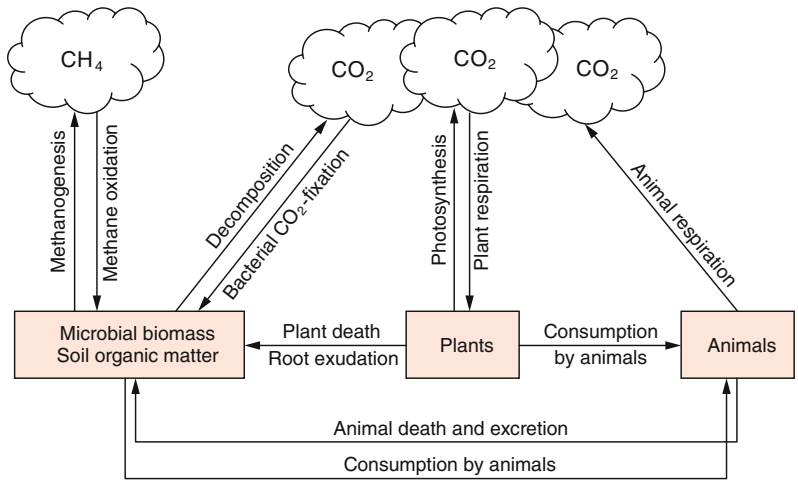

Fig. 4.21 The role of soil microorganisms in the carbon cycle (after van Elsas et al. 2006)

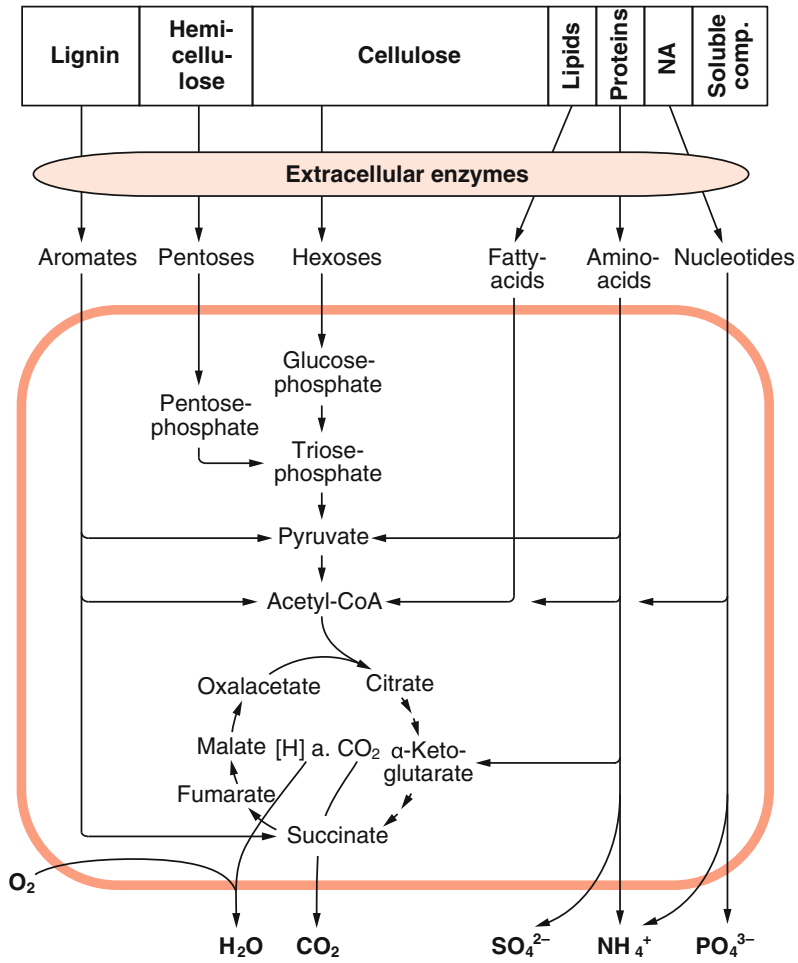

Fig. 4.22 Decomposition of high molecular substrates by soil microorganisms. *NA* (nucleic acids) (after Fritsche 1998)

and metabolism (Fig. 4.22). Soil organisms are not only responsible for the decomposition of organic matter, but also for progressive humification (see Chap. 3).

4.3.1.3 Nitrogen Cycle

Figure 4.23 indicates the role of soil microorganisms in the nitrogen cycle. Free-living and symbiotic N-fixing bacteria are responsible for the fixation of atmospheric nitrogen. The enzyme nitrogenase catalyzes the formation of ammonia. During ammonia assimilation, nitrogen is incorporated by soil microorganisms into organic compounds such as glutamine and glutamic acids. Both N-fixation and the incorporation of nitrogen into organic compounds are processes with high energy demands. Bacterial nitrifiers and nitrifying

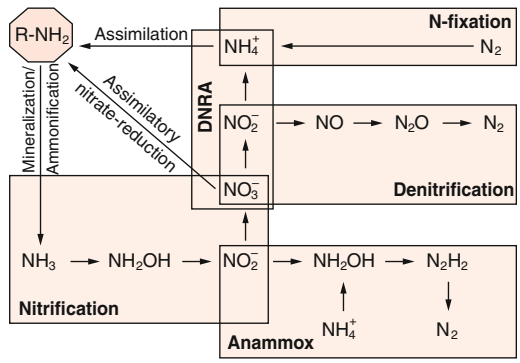

Fig. 4.23 Soil microorganisms catalyze important processes in the nitrogen cycle. *Anammox*: anoxic ammonia oxidation, *DNRA*: dissimilatory nitrate reduction to ammonium, *R-NH₂*: pool of organic N compounds (after Philippot et al. 2007)

archaea are able to use a 2-step process to transform ammonia into nitrite and then into nitrate, and to gain energy from this process. Archaea play an important role not only in extreme sites, but also in many other terrestrial ecosystems. Bacteria nitrify ammonia only in alkaline and slightly acidic environments. It is thought that archaea can operate across a broader pH range. Nitrate is absorbed by soil organisms and plants. During assimilatory nitrate reduction, nitrogen is converted back to an organic form. Under anoxic conditions, denitrifiers progressively transform nitrate into N_2 via the formation of nitrite, NO, and N_2O. All reduction steps are catalyzed by enzymes, which are either membrane-bound or found in the periplasmic space (between the outer and inner membranes of Gram-negative bacteria). The capacity to reduce nitrates under anoxic conditions has been observed in numerous soil bacteria, but soil fungi do not perform this process. Not all nitrate reducers are capable of performing all of the steps of denitrification. In recent years, numerous genes have been identified that are responsible for the synthesis of individual enzymes targeting specific partial steps of the N cycle (Table 4.5). This makes it possible to determine the number of microorganisms that can perform a specific partial step of denitrification, nitrification or N fixation.

Nitrate reduction, as the first step of denitrification, is not the only process inducing the formation of gaseous nitrogen forms. Under facultative anoxic conditions, nitrifiers can initially form nitrite, which can then be reduced to NO, N_2O and finally to N_2. Another reaction performed by special nitrifiers was discovered a few years ago in sewage waters: ammonia can be oxidized under anoxic conditions (**anoxic ammonia oxidation** or **anammox**). In this reaction, ammonia is converted to elemental nitrogen with nitrite as an electron acceptor. Performing this reaction requires the coexistence of two different groups of nitrifiers: one group (e.g. *Nitrosomonas*) produces nitrite through nitrification in oxygen-rich environments, and the second group (e.g. *Brocadia*) uses nitrite and ammonia under anoxic conditions for the anammox reaction. The heterogeneous distribution of oxygen in microaggregates or along biofilms leads to the assumption that the anammox reaction also takes place in soils. Anammox bacteria have been only recently observed in soils (e.g. marsh, rice soils and permafrost soils).

4.3.2 Function of Soil Organisms in Redox Reactions

Soil microorganisms use coupled reduction-oxidation reactions to produce energy for their metabolism. Some soil microorganisms oxidize reduced inorganic compounds under aerobic conditions, and use this reaction to produce adenosine triphosphate (ATP is an energy-rich molecule and universal energy carrier in living organisms). Under anoxic conditions, oxidized compounds are reduced by soil microorganisms (Fig. 4.24, Table 4.6).

Table 4.5 The functional genes of bacteria targeting enzymes involved in N cycling

Process	Enzyme	Functional gene	Reaction
Denitrification	Membrane-bound nitrate reductases	*narG*	$NO_3^- \rightarrow NO_2^-$
	Periplasmic nitrate reductases	*napA*	
	Cd_1 nitrite reductase	*nirS*	$NO_2^- \rightarrow NO$
	Cu nitrite reductase	*nirK*	
	Nitrogen monoxide reductase	*norB*	$NO \rightarrow N_2O$
	Quinol nitrogen monoxide reductase	*qnorB*	
	Dinitrogen oxide reductase	*nosZ*	$N_2O \rightarrow N_2$
Nitrification	Ammonia monooxygenase	*amoA*	$NH_3 \rightarrow NO_2^-$
N fixation	Nitrogenase	*nif*	$N_2 \rightarrow NH_3$

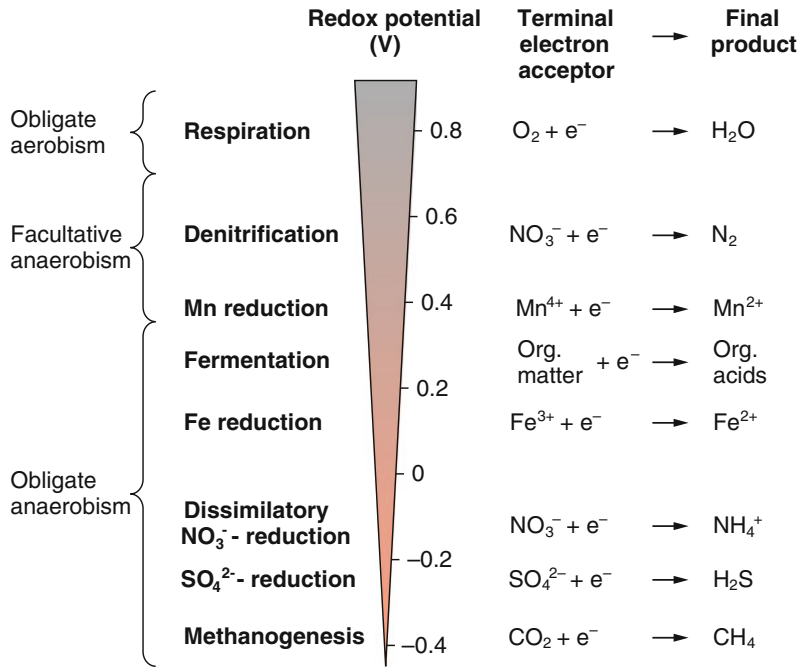

Fig. 4.24 Coupled redox reactions that are performed by soil microorganisms at neutral pH values with a specific redox potential (after van Elsas 2006)

Table 4.6 Soil microorganisms oxidize and reduce metals, and use metals as terminal electron acceptors for anaerobic respiration *AR*, as an energy source *E* or change the metal species for detoxification *D* or non-enzymatic activity *NE* (after Paul 2015)

Element		Reaction	Strategy
Oxidation	Fe	$2Fe^{2+} \rightarrow 2Fe^{3+} + 2e^-$	E
	Mn	$Mn^{2+} \rightarrow Mn^{4+} + 2e^-$	E, D
	Hg	$Hg^0 \rightarrow Hg^{2+} + 2e^-$	NE
	As	$AsO_2^- \rightarrow AsO_4^{3-} + 2e^-$	D
	Se	$Se^{2+} \rightarrow Se^0 + 2e^-$	E
	U	$U^{4+} \rightarrow U^{6+} + 2e^-$	E
Reduction	Fe	$2Fe^{3+} + 2e^- \rightarrow 2Fe^{2+}$	AR
	Mn	$Mn^{4+} + 2e^- \rightarrow Mn^{2+}$	AR
	Hg	$Hg^{2+} + 2e^- \rightarrow Hg^0$	D
	Se	$SeO_4^{2-} + 8e^- \rightarrow Se^{2-}$	AR
	Cr	$Cr^{6+} + 3e^- \rightarrow Cr^{3+}$	AR, D
	U	$U^{6+} + 2e^- \rightarrow U^{4+}$	AR

The microbial oxidation and reduction of iron and manganese play an important role in soil development. The Gram-negative rods *Acidithiobacillus ferrooxidans*, which obtain their energy from the oxidation of Fe^{2+}, reduced forms of sulfur, metal sulfides and hydrogen, are particularly well investigated. Carbon dioxide and ammonium are used by *Acidithiobacillus ferrooxidans* as carbon and nitrogen sources. These microorganisms are found in strongly acidic habitats, such as the tailings piles of coal mines. Various archaea oxidize iron under

extreme thermophilic conditions (65–90 °C). While Mn can be chemically oxidized at higher pH values in the soil, bacteria and fungi are responsible for this reaction at pH values below 8. Different exopolymer structures were discovered in bacteria around their cell walls, in which this enzymatic reaction takes place. Some rhizosphere microorganisms oxidize Mn to MnO_2, which can be observed on the surface of the roots as a black deposit.

Fe and Mn reducers are responsible for the decomposition of organic substances and xenobiotic substances in deeper soil layers. However, the microbial reduction of Fe and Mn takes place only in virtually oxygen-free soil horizons, which are also poor in nitrate and sulfate. The reduction of iron by these microorganisms is coupled with the production of various fermentation products (organic acids, alcohols, hydrogen). Soil microorganisms can also use other inorganic (selenate, arsenic) or organic compounds (fumarate, dimethyl sulfoxide) as electron acceptors.

4.3.3 Function of Soil Organisms in Soil Structure Stabilization

Soil organisms have developed different mechanisms to stabilize soil structure. Soil algae and cyanobacteria produce mucilage in the topmost millimeters of young soils (e.g. volcanic soils, soils in glacier forelands) and in desert soils, to protect themselves from desiccation or to deter competitors. The formation of mucilage stabilizes the surface soil of these sites and protects the soil from erosion. The production of extracellular polysaccharides (EPS) by various soil bacteria primarily serves to attach the microorganisms to surfaces (roots, humus, organo-mineral particles), to recognize host cells, and to provide protection from harmful substances and from desiccation. The adhesive effect of these mucilages leads to the development of microaggregates (<250 μm). Fungi and fine roots promote the stabilization of soil structure through their widely branched hyphal networks.

Soil fauna influence soil structure through intestinal excretions and **bioturbation**. Earthworms and Enchytraeidae combine organic and inorganic constituents in their intestinal tracts to form clay-humus complexes which increase the soil's structural stability. The feces of different earthworm species vary in their stability. For example, *Lumbricus terrestris* forms large, stable feces, while *Lumbricus rubellus* produces comparatively small and unstable excretion products. Earthworm casts are enriched with microorganisms that accelerate decomposition processes. Earthworms can produce up to 40 t ha^{-1} a^{-1} on a meadow site in Central Europe, and in the tropics up to 260 t ha^{-1} a^{-1} of feces. In arid regions, woodlice have a special significance for structure formation, because they transport to the soil surface fecal pellets that are also enriched with clay-humus complexes. Termites contribute to bioturbation through building of their nests. Some termite species use soil particles from specific horizons for the construction of the nests, other species selectively use particles that have a higher clay fraction. Termite hills consist of a mixture of soil particles, saliva and feces, which hardens in the air after passing through the intestine. Ant nests (e.g. subterranean, hill or wood nests) consist of small wood or plant parts, soil crumbs, resin from conifers or other natural materials.

Bioturbation does not only take place through digging, but also through rummaging soil animals (moles, small rodents, wild boars). This form of bioturbation plays a special role in the formation of Chernozems. Small mammals (hamsters, European ground squirrels, prairie dogs) transport humic material to deeper soil layers during both winter cold and summer dryness. Vertebrates (moles, small rodents, boars) can cause bioturbation of the same magnitude as earthworms.

4.4 Soil Organisms as Bioindicators

4.4.1 Effect of Soil Management on Soil Organisms

4.4.1.1 Mineral and Organic Fertilization

Mineral and organic fertilization affect soil organisms directly through the input of nutrients, and indirectly through increased plant growth. The reactions of soil microorganisms depend on the type, quantity and quality of the fertilizer. With the same input of nutrients, manure amendments stimulate the activity of soil microorganisms more strongly than mineral fertilizer treatments (Fig. 4.25). A long-term fertilization trial in Bad Lauchstädt was implemented in 1902 on a humus-rich, carbonate-free soil (Phaeozem), and investigated the long-term effects of different fertilizers. While the quantity of soil organic matter after NPK or farm yard manure fertilization only increased by ca. 10–20 %, microbial biomass and its activity increased by more than 60–100 %. Higher nutrient availability, increased rhizodeposition and litter are responsible for the stimulation of soil microorganism growth. However, the determination of microbial biomass represents only a rough estimate, and does not provide any information on the species distribution of the microbial community under these conditions. Mineral and organic fertilization preferably promote *r*-strategists in the soil, organisms that can react to the input of nutrients with rapid growth; *K*-strategists are specialists in the decomposition of complex substrates and are less competitive under these conditions. Not only does the quantity of an organic fertilizer, but also the quality of the added material play an important role in the reactions of soil organisms (Fig. 4.26). Swedish scientists started a field experiment in Uppsala in 1956 in which they used similar amounts of carbon (2,000 kg ha^{-1} a^{-1}) of different qualities (green manure, farm yard manure, and peat). Soil organic matter increased more strongly in the treatment fertilized with peat than in all of the other treatments. The different dynamics of soil organic matter can be explained by the reactions of soil microorganisms: Peat accumulates in soil organic matter because soil microorganisms can less easily decompose this material than green manure and farm yard manure. Peat also leads to a drop in the soil pH.

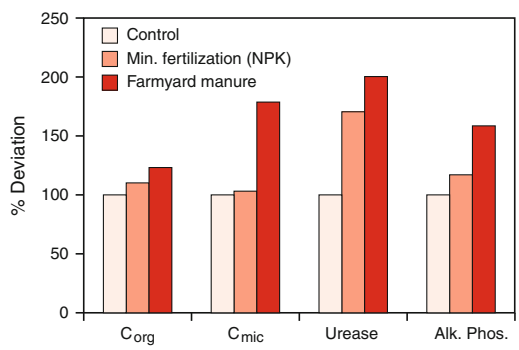

Fig. 4.25 Mineral and organic fertilization increase the abundance and the metabolic capacities of soil microorganisms in the Ap horizon of a Chernozem (Bad Lauchstädt, field experiment established in 1902; annual mineral fertilization, organic fertilizer applied every 2 years). The results of the fertilized treatments are given as a percent deviation from the unfertilized control (100 %). (16 mg C g^{-1}: 100 % of the organic carbon, 4.84 mg C_{mic} g^{-1}: 100 % of the microbial carbon; 13.7 µg N g^{-1} 2 h^{-1}: 100 % of the urease activity, 0.3 mg phenol g^{-1} 3 h^{-1}: 100 % alkaline phosphatase activity) (after Kandeler et al. 1999a)

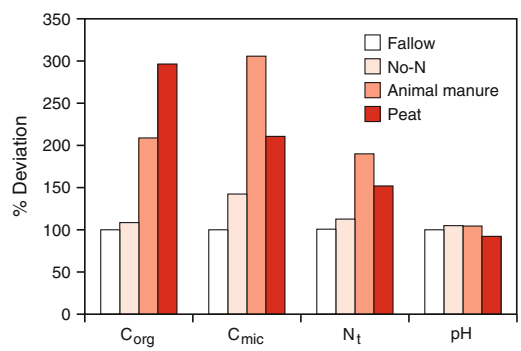

Fig. 4.26 The quality of the organic matter that has been added to a Cambisol in Ultuna (Central Sweden) since 1956 changes the microbial biomass and chemical soil properties: The results of the fertilized treatments are given as a percent deviation from the bare fallow treatment (100 %). (11 mg C g^{-1}: 100 % of the organic carbon, 1.2 mg N_t g^{-1}: 100 % of the total nitrogen, 1.38 mg C_{mic} g^{-1}: 100 % of the microbial carbon; fallow = bare fallow) (after Kirchmann et al. 2004)

At lower pH values in the soil, the species composition of the microbial community shifts towards a higher dominance of soil fungi. Compared to soil bacteria, these microorganisms incorporate more carbon into their own biomass, and thus use carbon more efficiently than bacteria. Carbon accumulates over the long-term in soils with a stronger fungal dominance.

4.4.1.2 Soil Tillage

Soil tillage modifies the habitat of soil organisms. Soil-turning tillage (e.g. plough) leads to a uniform distribution of nutrients and organic substrates in the surface soil. After ploughing, soil microorganisms benefit from the improved aeration and better distribution of organic substrates. Many soil animals (e.g. earthworms), in contrast, are either killed by intensive soil tillage or lose their habitat (e.g. through the destruction of the earthworm burrows). Soil-turning tillage practices have a lasting effect on the functional diversity of earthworms. Anecic and epigeic earthworms, which always or sometimes stay in the surface soil, are more strongly affected by soil tillage than endogeic earthworms. The effect of soil tillage also depends on the season. If soil tillage is performed when the soil is very dry, the soil fauna cannot escape to deeper soil layers quickly enough. Members of the meso- and macrofauna react more sensitively to soil tillage than members of the microfauna (nematodes and protozoa). Soil tillage can also lead to subsoil compaction at greater depths, which has a negative effect on soil flora and fauna.

Minimum and reduced soil tillage practices are considered conservation tillage methods, because the soil is only loosened and not turned over. A reduction in tillage intensity concentrates food resources and soil microorganisms in the topmost soil layers (0–5 or 0–10 cm). A few years after the conversion of soil tillage to non-turning methods (cultivator, direct seeding), phosphatase activity, as a measure of the decomposition of organic phosphorous compounds, had increased in the topmost 10 cm (Fig. 4.27). Soil tillage changes the distribution and function of soil microorganisms in the profile; however, it does not necessarily change the overall turnover by soil microorganisms within the whole soil profile.

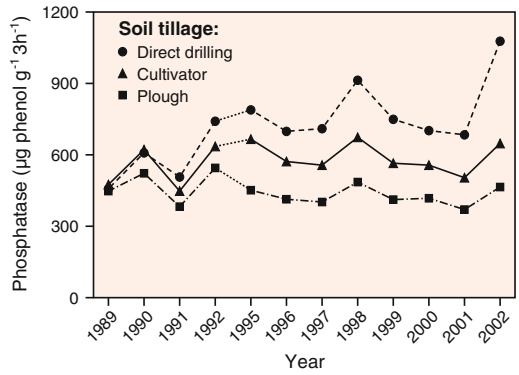

Fig. 4.27 Soil tillage intensity (plow, cultivator or direct drilling) influences the function of soil microorganisms in the surface soil of a Chernozem (0–10 cm) in Fuchsenbigl (Austria) (after Kandeler et al. 1999b)

Conservation tillage promotes the presence of, e.g., deep-burrowing earthworm species (e.g. *Lumbricus terrestris, Aporrectodea longa*), which depend on a food supply at the soil surface. The permanent tunnels of deep-burrowing earthworms increase the infiltration rate of rainwater and contribute to reducing erosion. In general, the abundance and diversity of numerous soil animals (mites, collembolan, diplopods, earthworms) increases after a reduction in soil tillage intensity. For this reason, the activation of soil biota is an important goal of conservation tillage practices.

4.4.1.3 Pesticides

Pesticides can affect soil microorganisms directly or indirectly (Fig. 4.28). Direct damage includes the reversible or irreversible binding of pesticides to the active centre of enzymes. If pesticides change the number of species and species composition of the microbial community, it is considered an indirect effect. In general, the bioavailability of pesticides determines the duration and intensity of the inhibiting effect on non-target organisms (see Chap. 10).

Insecticides have negative effects on the soil animals (nematodes, earthworms, beetles,

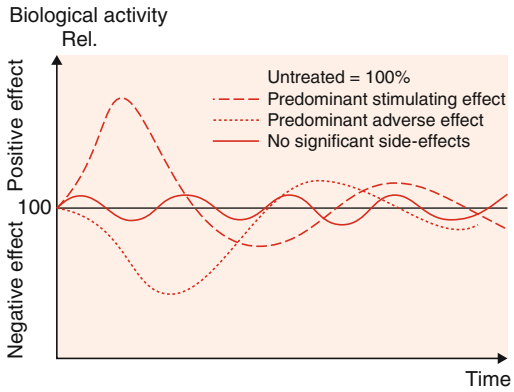

Fig. 4.28 Response of soil microorganisms after application of pesticides

spiders). Chlorinated hydrocarbons have particularly long-lasting effects on soil fauna because of their poor degradability. Phosphoric acid esters, carbamates and pyrethroids have a highly toxic short-term effect.

4.4.2 Environmental Pollution

4.4.2.1 Heavy Metals

Heavy metals can have a toxic effect on both soil microorganisms and soil animals. Because of their ionic character, heavy metals bind to various cellular ligands and replace essential nutrients at their natural binding sites in organisms. For example, phosphate is replaced by arsenate at various binding sites inside the cells. Interactions between heavy metals and DNA and proteins disturb the cell division of soil organisms and the synthesis of proteins. Proteins are partially denatured and lose their functional capacity. As a result, heavy metals reduce organism growth, change the morphological structure or inhibit biochemical processes in the individual cells. Soil fauna absorb heavy metals through their skin and with their food. Earthworms store a large fraction of heavy metals in their cuticle. This leads to bioaccumulation of heavy metals within the food chain. The toxicity of heavy metals varies among different soil organisms. As a result, the abundance and diversity of the soil community change.

Unlike organic pollutants, inorganic contaminants are not biologically decomposable. For this reason, soil organisms have developed different resistance mechanisms to heavy metals (Fig. 4.29). These mechanisms either prevent the cells from ingesting heavy metals, or cause the absorbed heavy metals to be made innocuous inside the cell or be excreted. Cadmium, for example, is bound directly on the outer cell wall or on extracellular polysaccharides (EPS), and thus cannot penetrate into the cells. Some soil microorganisms and plants produce proteins with a high proportion of the amino acid cysteine

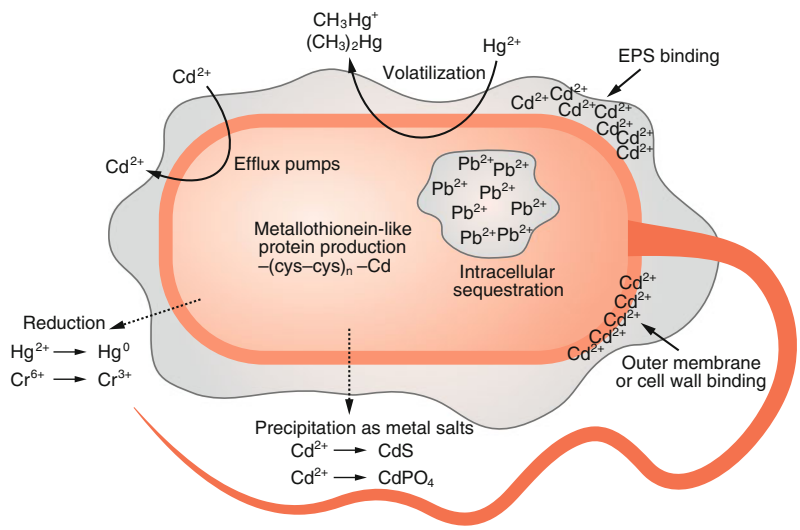

Fig. 4.29 Soil microorganisms have developed resistance mechanisms towards heavy metals. EPS binding: extracellular polysaccharides, efflux pump: heavy metals are transported out of the cell; intracellular sequestration: storage of the heavy metals in the vacuole (after Maier et al. 2000)

(metallothioneins), which bind heavy metals (Cd, Zn, Cu, Ag and Hg) and reduce the availability of heavy metals inside the cell. Efflux pumps transport toxic metals out of the cells. Mercury and silver ions can be transformed into volatile organic compounds and also be discharged. Chapter 10 gives practical examples of the toxic effect of heavy metals on soil organisms and of the use of soil organisms as bioindicators.

4.4.2.2 Organic Pollutants

Soil organisms react to contamination by **organic pollutants** (e.g. mineral oils, pesticides) with either inhibition or promotion of their metabolic activities. If an inhibition of microbial soil respiration is observed, it can be attributed to a death of part of the population or to an impairment of metabolic capacities. Organic pollutants can change the properties of cell membranes and therefore have a negative effect on the transport function of membranes. An increase in soil respiration after pollutant application indicates either a stress reaction from the microorganisms, which require additional energy for cell repair mechanisms, or microbial use of the organic pollutants as a substrate.

Organic pollutants are biodegraded by a series of enzymatic steps. Complete degradation converts the pollutant into CO_2 and water (**biomineralization**). Under sub-optimal environmental conditions (e.g. oxygen limitation), the organic pollutants can only be partially degraded (**biodegradation**). If the compound and the bridges between sub-units of the pollutant (e.g. esther bridges) are similar to natural substances, the organic pollutant is relatively quickly decomposed. The persistence of organic pollutants is generally due to lack of the individual enzymes required for their decomposition. Cometabolism is defined as the simultaneous degradation of two compounds, in which the degradation of the second compound (e.g. an organic pollutant) depends on the presence of the first compound (the primary substrate). Decomposition of the organic pollutant does not yield any energy for the microorganisms (Fig. 4.30). The partial decomposition of chlorophenol by fungi is performed cometabolically: With the simultaneous presence of phenol and the cosubstrate 3,4-dichlorophenol, the nonspecific enzyme phenol hydroxylase can use both compounds at the same time. The fungus does not further decompose the resulting metabolite 4,5-dichlorocatechol. Incomplete decomposition of organic pollutants leads to reactive intermediates that may persist longer in the soil than the initial products. Soil remediation measures make use of the soil microorganisms' capacity to fully mineralize organic pollutants (see Sect. 10.3).

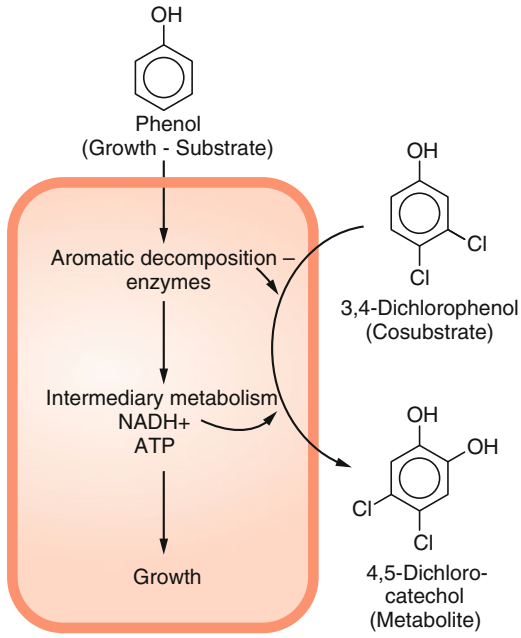

Fig. 4.30 Co-metabolism enables soil microorganisms to decompose toxic substances. Both the substrate (phenol) and 3,4-dichlorophenol (co-substrate) can be decomposed by the same unspecific enzymes (after Fritsche 1998)

4.4.3 Climate Change

The increase in carbon dioxide concentrations in the atmosphere, slow rise in temperatures and changing distribution of rainfall have mainly indirect effects on soil organisms. To date, however, the individual factors have been mostly investigated separately. Elevated atmospheric carbon dioxide concentrations lead to an increase in plant growth as well as to a change in the quantity and quality of organic compounds (litter

substances, rhizodeposits) that are available to soil organisms as substrates. The higher water use efficiency of plants under high CO_2 contents in the atmosphere leads to an increase in soil moisture, which has a positive effect on soil organisms and plants, especially in dry spells during the vegetation period. Many field trials have shown that soil microorganisms rapidly convert the additional substrate, and that additional fixed carbon is quickly mineralized again. Over the long-term, however, changes in litter composition (higher C/N ratio) can cause a shift in the soil microbial community composition towards a higher dominance of soil fungi. Because soil fungi use carbon more effectively than soil bacteria and therefore store more carbon in their biomass, this mechanism may lead to carbon storage in the soil.

An increase in soil temperature has a direct effect on soils by stimulating the growth and activity of soil organisms, and an indirect effect through changes in the chemical-physical soil properties (pressure, volume, viscosity of liquids etc.). Interactions between all climate-relevant factors (climate-relevant gases, temperature, distribution of precipitation) and soil organisms have been insufficiently documented to date.

4.5 Methods in Soil Biology

4.5.1 Microorganisms

4.5.1.1 Field Methods

Various sum parameters for soil biological activities are recorded in the field. To quantify the decomposition of litter by soil organisms, litter bags are exposed at the soil surface or in the topmost soil layers. The weight loss of the litter is then determined, sometimes also the changes in litter quality (C/N ratio, cellulose and lignin content). Because of the significance of these processes for climate change, the microbial and plant production of various gases, which are released from the soil surface into the atmosphere, are of special interest. Different chambers are used to determine the net emissions of CO_2, CH_4 and N_2O from soils. They are placed on the soil and accumulate gases for a certain period of time (e.g. one hour), after which the gas composition is determined. Stable isotopes (e.g. $^{13}CO_2$) are used in the field to record the incorporation of carbon into the plant, the transport of carbon to the roots and into various fractions of the soil organic matter. These results enable an estimation of the carbon balance of a site and an assessment as to whether a specific site shifts toward becoming a source or a sink of climate-relevant gases (CO_2, CH_4 and N_2O) under a specific soil management regime.

4.5.1.2 Physiological, Biochemical and Molecular Methods

Microbiological methods are used in the lab to characterize the abundance, diversity and function of soil microorganisms. To estimate the microbial biomass of a soil, microbial carbon is determined using substrate-induced respiration, the chloroform fumigation extraction method, or the chloroform fumigation incubation method. With the **substrate induced respiration** (SIR) method, glucose is added to the soil and the maximum respiration in a defined time period is determined. Microbial carbon is then calculated either by oxygen consumption or CO_2 production. With the chloroform **fumigation incubation method** (CFI), approximately 90 % of soil microorganisms are killed with chloroform and then mineralized by the remaining microorganisms. The quantity of liberated CO_2 represents the basis for the calculation of microbial carbon (in mg C per kg of soil). The **chloroform fumigation extraction** (CFE) method involves the extraction and quantification of microbial constituents (C, N, P, and S) immediately following chloroform fumigation in soils. Due to a range of shortcomings, culture dependent methods (e.g. most probable counts) are currently used less frequently than in the past. Several methods to quantify signature molecules as biomarkers for specific groups of soil microorganisms have been developed during the last decade. The **ergosterol content**—an important cell wall component in many fungi—serves as a measurement for the fungal biomass. **Phospholipid fatty acids** are constituents of all

membranes in bacteria and fungi; individual phospholipid fatty acids are used as quantitative biomarkers because of their specific synthesis by individual microorganism groups (e.g. Gram-positive bacteria, Gram-negative bacteria, fungi, VA mycorrhiza). It is now also possible to quantify different groups of microorganisms using molecular methods (e.g. **quantitative polymerase chain reaction**: *q*PCR). The results are given as the number of copies of a specific gene sequence of the **ribosomal ribonucleic acid** per gram of soil. Various color reactions in cells are used to determine the spatial distribution of soil microorganisms: DAPI (4′,6 diamidino-2-phenylindol) DNA-binding fluorescent dye and phylogenetic sensors (fluorescent-marked oligonucleotides).

Figure 4.31 shows different methodical approaches in molecular ecology to determine the abundance and diversity of the soil microbial community. First, the DNA/RNA from the soil is extracted and purified through various steps. In quantitative PCR, DNA amplification is monitored at each cycle of PCR. When the DNA is in the log linear phase of amplification, the amount of fluorescence increases above the background level. The point at which the fluorescence becomes measurable is called the threshold cycle (C_T) or crossing point. If the diversity of the soil microbial community is of interest, fingerprint methods (e.g. denaturing gradient gel electrophoresis (DGGE) and restriction fragment length polymorphism (RFLP)) are used; the DNA/RNA of soil organisms are gel electrophoretically separated based on their different DNA sequences. The DGGE method uses a chemical gradient (e.g. urea) to separate fragments of different stabilities. The RFLP methods use restriction endonuclease digestion of the DNA fragments to produce species-specific fragments. The band

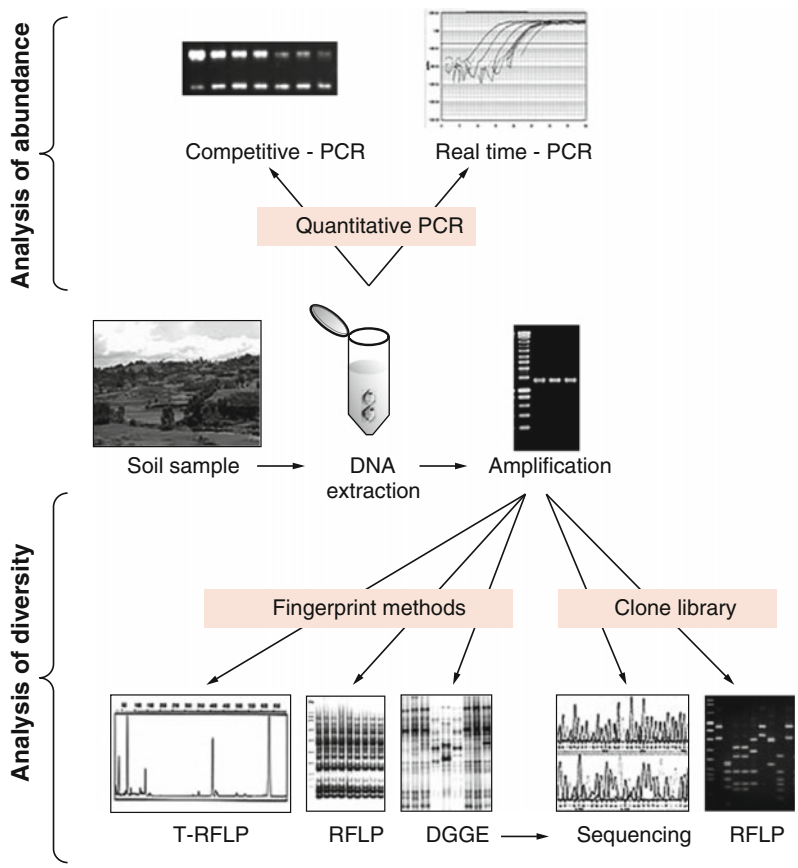

Fig. 4.31 Molecular methods in soil biology. *DGGE* denaturing gradient gel electrophoresis; *RFLP* restriction fragment length polymorphism (after Philippot et al. 2007)

patterns are tested for their similarity using statistical methods (e.g. cluster analysis). Individual DNA fragments that are visible as bands on a gel are inserted into a plasmid, transferred into *Escherichia coli* as a host cell, cloned, and then sequenced (determination of the sequences of individual nucleotides). Information on the individual sequences (clones) are stored in databases (**clone libraries**) and used to identify soil microorganisms and to estimate their phylogenetic alignments. Stable isotope probing techniques (**SIP**) introduce a stable isotope-labelled substrate into a microbial community and monitor the fate of the substrate by extracting signal molecules, such as phospholipid fatty acids and nucleic acids, and determining which specific molecules have incorporated the isotope. SIP approaches allow investigations of substrate assimilation in minimally disturbed communities and provide a tool for linking functional activity to specific members of microbial communities.

The functions of soil microorganisms are determined using physiological, biochemical, isotopic, and molecular methods. The determination of **enzyme activities** allows the characterization of specific reactions within metabolic cycles. Dehydrogenases are **intracellular enzymes** and provide information on the activity of the active microbial biomass. The decomposition of numerous high molecular compounds (e.g. xylan, cellulose, proteins) is catalyzed by enzymes (e.g. xylanase, cellulase, protease) that are excreted by microorganisms. These **extracellular enzymes** are adsorbed onto the humus and clay fractions, and thus protected from rapid decomposition. Functional genes targeting different enzymes involved in N cycling are shown in Table 4.5.

4.5.2 Soil Fauna

Macromorphological observations (earthworm tunnels, feces particles, litter decomposition) in the field are the basis for many soil zoological investigations. Micromorphological investigations using soil thin sections make it possible to describe the degree of litter decomposition, the distribution of feces particles in the soil, as well as bioturbation processes between different soil layers, allowing conclusions to be drawn about animal activities. Evidence for feeding activities can be either obtained directly from the profile by describing the morphology, or through field trials. With the bait-lamina test, a nutritive paste inserted into micro-holes on a test stick is exposed to feeding. After a defined period of exposure, the fillings are checked for losses due to feeding. However, this method does not deliver any information on which animals feed on the bait.

Earthworm sampling is performed with the electric trap method or by hand sorting in the field. To determine the abundance of protozoa, a soil suspension is made and microscopic methods are used to count the individuals. Most of the methods used for microarthropod extraction are either variations of the Tullgren funnel, using heat to desiccate the sample and force the microarthropods into a collection funnel, or flotation in solvent solutions followed by filtration. The activity density of epigeous animals is determined using Barber traps that are dug in at ground level. However, the results cannot be related to a specific unit of area; in addition, less active animals or certain stages of a species (e.g. juveniles) are found more rarely than active adult animals. Insect larvae (Diptera, beetles, Hymenoptera) are caught using emergence traps. These traps are equipped with photo eclectors; they make use of the negative geotropism and positive phototropism of most insects.

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5 Chemical Properties and Processes

Many regulating functions of soils (Sect. 1.2) are based on biogeochemical processes, and are therefore affected by soil chemical properties. Examples are the storage and supply of nutrients, the sorption and degradation of contaminants, as well as the buffering of acid deposition. The chemical processes taking place at biogeochemical interfaces are of outstanding importance. About 40–60 % of the soil volume consists of pores, which can be filled with water (soil solution) or gases (soil air), depending on the actual soil moisture. The soil solids mainly consist of minerals and smaller fractions of organic matter. This porous system of mineral and organic soil particles, gases, aqueous solutions and organisms leads to the formation of very large and chemically reactive interfaces. These interfaces can adsorb, complex, precipitate or chemically transform various ions and molecules. This chapter provides an introduction to the chemical properties and processes regulating the behavior of nutrients and contaminants in soils.

5.1 Soil Solution

The aqueous phase of the soil is called **soil solution**. It consists of free water, dissolved ions and molecules, and dispersed colloidal particles.[1] Structural water bound in the crystal lattice of soil minerals does not belong to the soil solution.

In permeable and well-drained soils, water input primarily takes place through atmospheric precipitation, which also adds some dissolved and suspended substances to the soil.

5.1.1 Composition of Rainwater

Water already reacts with aerosol particles and gases during cloud formation through condensation of water vapor in the atmosphere. Water droplets also take up substances from the atmosphere during precipitation events. Rainwater therefore always contains dissolved ions and suspended solids, which are added to soils with precipitation (Table 5.1). The most important sources of dissolved or suspended substances in rainwater are (depending on the geographical location):

- Marine aerosols (Na, Cl, Mg, SO_4, Ca, K, etc.)
- Terrestrial dusts (Si, Al, Ca, K, Na, Mg, SO_4, CO_3, etc.)
- (Post) volcanic aerosols and gases (Si, Al, Mg, CO_2, CH_4, NH_3, etc.)
- Biological emissions (oxalate, malonate, citrate, acetylene, etc.)
- Natural trace gases (CO_2, N_2O, NO, NO_2, NH_3, HCl, CH_4, etc.)

[1]Colloidal particles are defined as solid particles with a diameter between 1 and 1000 nm in at least one dimension. Colloidal particles do not settle rapidly unless they coagulate, have a very large specific surface area, and

(Footnote 1 continued)
can be transported with seepage water through medium and coarse pores if they are dispersed in the pore water.

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- Anthropogenic emissions (NO_x, SO_2, CO_2, soot particles, mining dusts, industry, and traffic)

Rainwater over marine and coastal areas is enriched in NaCl, because NaCl-rich aerosols are formed through the dispersion of water droplets over the oceans. Marine aerosols are also relatively rich in Mg and SO_4. In contrast, rainwater over the continents contains more $CaSO_4$. Terrestrial dusts are the most important source of Ca, i.e. soil particles that have entered the atmosphere through wind erosion. Another important source of SO_4 is anthropogenic SO_2 emissions from the combustion of fossil fuels. Gaseous SO_2 reacts in the atmosphere with ozone (O_3) and H_2O leading to the formation of sulfuric acid (H_2SO_4), a strong acid. SO_2 emissions are therefore an important factor in the formation of acid rain, with pH values between 3.5 and 5.5. Another important source of acidity is the formation of nitric acid (HNO_3) from mono-nitrogen oxides (NO_x), which are released with the combustion of fossil fuels.

In the atmosphere, NO_x are also formed by N_2 oxidation during lightning discharge, which can significantly contribute to natural nitrogen inputs in terrestrial ecosystems. Atmospheric nitrogen inputs can also be in the form of ammonia (NH_3), which can originate both from natural emissions (e.g. wild ruminants, NH_3 volatilization from calcareous soils) and from anthropogenic sources (e.g. domestic animals, liquid manure and sewage spreading on agricultural fields).

Table 5.1 Typical concentrations of dissolved ions (in mg L^{-1}) and pH-values in rainwater (after Berner and Berner 1996, slightly modified)

Ion	Rainwater, oceans and coastal regions	Rainwater, continents
Cl^-	1–10	0.2–2
Na^+	1–5	0.2–1
Mg^{2+}	0.4–1.5	0.05–0.5
K^+	0.2–0.6	0.1–0.3
Ca^{2+}	0.2–1.5	0.1–3.0
SO_4^{2-}	1–3	1–3
NO_3^-	0.1–0.5	0.4–1.3
NH_4^+	0.01–0.05	0.1–0.5
pH	5–6	4–8.5

5.1.2 Composition of the Soil Solution

5.1.2.1 Dissolved Inorganic Substances

As soon as rainwater comes into contact with soil, the concentrations of dissolved substances change. The chemical weathering of silicates releases $H_4SiO_4^0$, Ca^{2+}, Mg^{2+}, K^+, Na^+ and other ions. Protons are consumed in most silicate weathering reactions, which therefore contribute to the neutralization of acids (Sect. 5.6.4). The dissolved cations are in equilibrium with exchangeable cations on negatively charged surfaces of clay minerals and organic matter. Cation exchange and specific adsorption on surfaces generally determine which ions are stored in the soil, and which are readily leached out with seepage water. There are also microbial conversion processes taking place, such as the microbial oxidation of ammonium (NH_4^+) to nitrate (NO_3^-), a process called **nitrification** (Sect. 9.6.1.3). The metabolism of organisms (e.g. aerobic respiration) leads to the consumption of some gases (e.g. O_2) and the production of others (e.g. CO_2). This also changes the concentrations of dissolved gases in the soil solution. Table 5.2 shows typical ranges for measured concentrations of dissolved substances in soil solutions of soils under forest and arable land in Central Europe.

The composition of the soil solution at a given site is subject to temporal fluctuations, which are caused by seasonal changes in the vegetation, soil moisture, soil temperature and other factors. In periods with high precipitation, the soil solution is diluted by infiltrating rainwater. Vice versa, the concentrations of dissolved substances increase in periods with high evaporation. The composition of the soil solution can also vary

Table 5.2 Typical composition of the soil solution (saturated paste extracts and suction cup solutions) from non-contaminated to weakly contaminated arable soils and acidic forest soils in temperate humid climates

Parameter	Units	Forest soils		Arable soils	
		Range	Frequent values	Range	Frequent values
pH ($CaCl_2$)		2.8–4.0	3.2–3.8	4.1–7.5	5.0–6.8
pH (soil solution)		3.0–4.5	3.2–4.0	4.8–8.2	5.6–7.8
EC	dS m^{-1}	0.2–1.6	0.3–1.2	<0.1–1.8	0.3–0.7
DOC	mg L^{-1}	30–500	50–150	5–500	15–50
$HCO_3^- + H_2CO_3$	mg L^{-1}	(<1–40)	(1–5)	5–210	20–100
Ca	mg L^{-1}	<1–180	1–40	5–600	40–160
Mg	mg L^{-1}	<0.01–30	0.1–10	1–60	5–25
K	mg L^{-1}	0.3–50	1–15	0.1–80	3–30
Na	mg L^{-1}	<1–40	1–20	2–50	2–20
NH_4^+	mg L^{-1}	0.5–20	0.5–10	<0.1–16	0.2–4
NO_3^-	mg L^{-1}	5–450	10–200	1–800	20–200
NO_2^-	mg L^{-1}	(<1)	(<1)	<0.1–30	<0.1–1
Cl^-	mg L^{-1}	3–170	5–70	1–400	6–100
SO_4^{2-}	mg L^{-1}	5–350	15–150	5–300	10–120
$HPO_4^{2-} + H_2PO_4^-$	mg L^{-1}	<0.05–12	<0.05–5	0.4–40	1–10
Si	mg L^{-1}	(2–60)	(5–40)	1–40	4–25
F	mg L^{-1}	200–30,000	0.3–2	0.1–4	0.2–1
Al	µg L^{-1}	200–30,000	500–10,000	<10–10,000	100–5000
Fe	µg L^{-1}	5–10,000	50–5000	<5–8000	20–3000
Mn	µg L^{-1}	20–30,000	50–15,000	<1–3000	<1–700
Cu	µg L^{-1}	<1–800	1–50	1–300	3–60
Zn	µg L^{-1}	30–4000	80–2000	1–800	10–400
Cd	µg L^{-1}	0.5–50	1–25	<0.1–20	<0.1–3
Pb	µg L^{-1}	0.5–250	2–100	<1–120	<1–50
As	µg L^{-1}	<0.1–50	<0.1–10	<0.01–12	1–8

Values in parentheses: few data available (*Sources* Bradford et al. 1971; Campbell and Beckett 1988; Brümmer et al., unpublished)

spatially. Infiltrating water in coarse pores often has a different composition than water that has been stored in fine pores for longer time periods.

Seepage water leaving the soil and moving towards the groundwater through the **vadose zone** contains much higher concentrations of dissolved substances than rainwater. Precipitation, evaporation, and infiltration continuously disturb the chemical equilibria in the soil and thereby drive chemical reactions. This promotes chemical weathering and the formation of new minerals (Sects. 2.2.5 and 2.4.2).

However, precipitation is not the only input of water in all soils. If the groundwater table is high, water can also rise through capillary forces into the unsaturated soil and carry dissolved substances. Mudflats and wet beaches at the coasts are regularly flooded with seawater. Soils affected by lateral subsurface flow or periodic flooding (e.g. floodplains) also receive external inputs of water and dissolved substances. For this reason, riparian floodplain soils are important sinks and/or sources for contaminants in river water. On agricultural fields, the input of irrigation water

can play an important role. Depending on the water quality and quantity, this can lead to considerable inputs of dissolved substances into the soil, and especially in arid regions, to Na accumulation or even soil salinization. External inputs of water and dissolved substances always have a major influence on biogeochemical cycles and chemical properties of soils.

5.1.2.2 Dissolved Organic Matter (DOM)

Microorganisms and plant roots secrete soluble organic compounds (e.g. organic acids, enzymes, siderophores) to mobilize nutrients that are bound in soil solids. Some constituents of humified soil organic matter can also dissolve in water. The dissolved organic substances in the soil solution as a whole is called DOM (dissolved organic matter). The concentration of dissolved organic matter is commonly measured as organic carbon, and is therefore reported as DOC (dissolved organic carbon).[2] Many studies consider substances that pass through a 0.45 μm membrane filter to be "dissolved". However, it must be considered that the transitions between dissolved, macromolecular, and colloidal substances are a continuum, and that this operationally defined "dissolved" fraction may also contain small colloidal particles <0.45 μm.

Depending on soil characteristics and land use, the DOC concentration in the soil solution can range between 5 and 500 mg L^{-1} (Table 5.2). Soil solutions from Ap horizons of arable soils often contain between 15 and 50 mg L^{-1} DOC. The average DOC concentrations are higher in soil solutions from Ah horizons of forest soils, frequently with values between 50 and 150 mg L^{-1}. Both the concentrations and the chemical composition of DOM are subject to seasonal variations caused by changes in soil moisture, soil temperature, input of litter substances, and the biological activity of plants and microorganisms.

Dissolved organic matter consists of a multitude of chemical compounds of various origins. A considerable fraction of the DOM can consist of carbohydrates, especially in densely rooted soil horizons. Polysaccharides often dominate this fraction, but disaccharides (e.g. sucrose) and monosaccharides (e.g. glucose, fructose, galactose, mannose) are also found. However, di- and monosaccharides are rapidly decomposed again by microorganisms. Low-molecular weight organic acids and other complexing ligands are another very important group of organic substances in DOM. It includes simple aliphatic mono- and dicarbonic acids (e.g. acetic acid, oxalic acid, fumaric acid), hydroxycarboxylic acids (e.g. citric acid, tartaric acid, gluconic acid) and ketonic acids (e.g. oxaloacetic acid, ketoglutaric acid) as well as aromatic hydroxycarboxylic acids (e.g. salicylic acid, protocatechuic acid, gallic acid), dihydroxybenzenes (e.g. catechol, hydroquinone) and various aldehydes, polyphenols, amino acids, fatty acids, and siderophores. Siderophores are a group of extremely strong complexing ligands for Fe^{3+} (there are hundreds of different known siderophores). They are excreted by microorganisms (bacteria, fungi) and many grasses (e.g. wheat, barley) under iron-deficient conditions to dissolve Fe from soil particles. The concentrations of these acids and complexing ligands in the soil solution are significantly influenced by the content of decomposable organic matter, the microbial activity, and the amounts of organic substances secreted by plant roots.

In addition to these relatively hydrophilic substances, DOM also contains considerable fractions (30–60 %) of more hydrophobic compounds, which can be present in dissolved or colloidal form. These are mainly degradation products of polysaccharides, lignocellulose, and lignin from plant residues, as well as fulvic and humic acids. These hydrophobic DOM constituents can bind hydrophobic organic chemicals (e.g. PAH, PCB, dioxins, various pesticides) and thus considerably increase their apparent solubility and mobility in the soil. The fulvic and humic acids also act as complexing ligands for

[2]Other abbreviations commonly used in the literature include TOC (=total organic carbon), POM (=particulate organic matter), POC (=particulate organic carbon), DON (=dissolved organic nitrogen), and DOP (=dissolved organic phosphorus).

essential (e.g. Fe^{3+}, Cu^{2+}, Zn^{2+}) and/or potentially toxic (e.g. Hg^{2+}, Al^{3+}, Cd^{2+}, Pb^{2+}, Cu^{2+}) metal cations.

In soils with anthropogenic contamination, synthetic organic compounds can also be found in the soil solution. Some of these compounds are strong complexing ligands for metals (e.g. ethylenediaminetetraacetic acid, EDTA; nitrilotriacetic acid, NTA) or surface-active substances (surfactants). Such substances can enter the soil through spreading of sewage sludge or irrigation with waste water, and then lead to the mobilization of heavy metals.

For microorganisms in deeper soil horizons, DOM represents a very important mobile energy source. About 3–40 % of the DOM in seepage water are readily decomposed by microorganisms, whereas the remaining fraction is more recalcitrant. If the soil is not sufficiently aerated, microbial decomposition of organic matter can lead to anoxic conditions and then promote the reduction of nitrate, manganese and iron oxides, sulfate, and some trace elements (Sect. 5.7.4).

5.2 Gas Equilibria

The larger pores in unsaturated soils are filled with gas, which is called **soil air**. The composition of soil air is described in more detail in Sect. 6.5.1. Due to **soil respiration** by plant roots and aerobic soil organisms, the relative O_2 partial pressure in soil air is decreased, while the CO_2 partial pressure is increased relative to the atmosphere ($P_{O_2} = 0.21; P_{CO_2} = 0.00038$). The less aerated and the more biologically active a soil is, the more these differences will be pronounced. **Soil aeration** can be inhibited by high water content or by soil compaction (Sect. 10.7.2). Under anoxic conditions, other trace gases can be produced in the soil in addition to CO_2, such as nitrous oxide (N_2O), a by-product of the microbial reduction of NO_3^- (denitrification), or **methane** (CH_4), which is formed by certain bacteria under strongly anoxic conditions.

Gases in the soil air can also be partially dissolved in soil water. Inversely, dissolved substances in soil water can outgas into soil air. In addition to the above-mentioned gases, other low molecular weight organic acids and synthetic organic compounds (e.g. pesticides) can outgas, provided that they are sufficiently volatile (Sect. 10.3).

Table 5.3 Henry constants for the solubility of various gases in water (at 25 °C) (after Stumm and Morgan 1996)

Gas	Henry constant (M hPa^{-1})
CH_3COOH	7.56×10^{-1}
NH_3	5.63×10^{-2}
H_2S	1.04×10^{-4}
CO_2	3.35×10^{-5}
N_2O	2.54×10^{-5}
CH_4	1.27×10^{-6}
O_2	1.24×10^{-6}
N_2	6.25×10^{-7}

The equilibrium between the gases in soil air and those dissolved in soil water can be described using Henry's Law. Henry's Law describes a linear relationship between the partial pressure of a gas A in the gas phase (p_A, in hPa) and the concentration of the gas dissolved in water ([$A(aq)$], in M):

$$[A(aq)] = K_H p_A \tag{5.1}$$

where K_H (M hPa^{-1}) is the Henry constant for the corresponding gas at a given temperature. Table 5.3 lists the Henry constants for several important gases at 25 °C. It is obvious from these constants, that the solubility of gases in water is highly variable. For example, acetic acid (CH_3COOH) and ammonia (NH_3) are highly soluble in water, whereas the solubilities of O_2 and N_2 are several orders of magnitude lower.

5.3 Speciation and Complex Formation

Dissolved ions and molecules in the soil solution can form complexes with each other. Thereby, their chemical form, the **speciation**, changes.

The chemical forms (i.e. oxidation state, coordination chemistry, and bonding partners), in which the chemical elements or molecules exist, are called **species**.

Aqueous solution speciation is particularly important for trace elements. It influences their chemical behavior in the soil, including their mobility, availability to organisms, and toxicity. Because the soil solution contains many different metal cations, inorganic anions, and dissolved organic molecules, every element may be found in a large number of different species (Table 5.4).

The analytical determination of the dissolved species of an element can be difficult, costly, and time-consuming, and in many cases, it is not yet feasible at all. Alternatively, the concentrations of dissolved species can be calculated based on their thermodynamic stabilities (if known). This section briefly explains some basic principles required for aqueous speciation calculations.

Table 5.4 Examples of important species of dissolved metal cations in soil solutions

Cation	Species (examples)
Na^+	Na^+, $NaHCO_3^0$
K^+	K^+, KSO_4^-
Mg^{2+}	Mg^{2+}, $MgSO_4^0$, $MgCO_3^0$, Mg-DOM
Ca^{2+}	Ca^{2+}, $CaSO_4^0$, Ca-DOM, $CaHCO_3^+$, Ca-DOM
Al^{3+}	Al^{3+}, AlF^{2+}, AlF_2^+, $AlSO_4^+$, $AlOH^{2+}$, $Al(OH)_2^+$, Al-DOM
Fe^{2+}	Fe^{2+}, $FeSO_4^0$, $FeH_2PO_4^+$, $FeCO_3^0$, $FeHCO_3^+$, Fe-DOM
Fe^{3+}	$FeOH^{2+}$, $Fe(OH)_3^0$, Fe-DOM
Cu^{2+}	Cu^{2+}, $CuCO_3^0$, Cu-DOM
Zn^{2+}	Zn^{2+}, $ZnSO_4^0$, $ZnHCO_3^+$, $ZnCO_3^0$, Zn-DOM
Cd^{2+}	Cd^{2+}, $CdSO_4^0$, $CdCl^+$, $CdHCO_3^+$, Cd-DOM
Pb^{2+}	Pb^{2+}, $PbSO_4^0$, $PbHCO_3^+$, $PbCO_3^0$, $PbOH^+$, Pb-DOM

The importance of individual species strongly depends on the pH and composition of the soil solution. Carbonate species are most important in neutral to alkaline soils (*DOM* dissolved organic matter)

5.3.1 Ionic Strength, Concentration, and Activity

The chemical **activity** of a dissolved species not only depends on its **concentration**, but is also influenced by the **ionic strength** of the solution. The ionic strength I is a sum parameter reflecting the total concentration of dissolved ionic charges in an aqueous solution. It is defined as:

$$I = \frac{1}{2}\sum_{i} m_i Z_i^2 \tag{5.2}$$

where m_i is the molality[3] and Z_i is the charge of each ion i in solution. The activity a_i of an ion i can be expressed as:

$$a_i = \gamma_i \left(\frac{m_i}{m_i^0}\right) \tag{5.3}$$

where γ_i is the **activity coefficient** (dimensionless) for the ion i, m_i is the molality of the ion i, and m_i^0 is the standard molality $(m_i^0 = 1\,\text{mol}\,\text{kg}^{-1})$. Note that the activity a_i, contrary to the concentration, is also dimensionless.

Various (semi-)empirical equations, only two of which are introduced here, have been developed to estimate the activity coefficients for dissolved ions. The extended Debye-Hückel equation is frequently used for the calculation of the activity coefficients up to ionic strengths of $I = 0.1$ M:

$$\log \gamma_i = \frac{-AZ_i^2\sqrt{I'}}{1 + B\alpha_i\sqrt{I'}} \tag{5.4}$$

where A and B are temperature-dependent constants (A = 0.5116 and B = 0.33 at 25 °C), and the ion-specific parameter α_i depends on the effective diameter of the ion i in solution (Langmuir 1997). The ionic strength I' is expressed here as the ionic strength (I, molal) relative to the ionic strength under standard conditions ($I^0 = 1$ molal) ($I' = I/I^0$), whereby the units cancel out.

[3]The molality m_i is the concentration of an ion i in mol kg^{-1}. In dilute aqueous solutions, the molality can be approximated with the molarity M_i, the concentration of the ion i in mol L^{-1} (or M).

Another frequently used empirical equation is the DAVIES equation:

$$\log \gamma_i = -AZ_i^2 \left(\frac{\sqrt{I'}}{1+\sqrt{I'}} - 0.3I' \right) \quad (5.5)$$

This equation offers the advantage that it does not contain any ion-specific parameters, and provides a good estimation of activity coefficients up to an ionic strength of $I = 0.5$ M. The same activity coefficient γ_i is obtained for all ions with the same absolute charge $|Z|$. Figure 5.1 shows the activity coefficients calculated using the DAVIES equation for mono-, di-, and trivalent ions ($|Z| = 1$, 2, and 3) as a function of the ionic strength. In extremely dilute aqueous solutions, $\gamma_i \approx 1$ and the activity of each ion approximately corresponds to the value of its molality (or molarity). The greater the ionic strength, the smaller the activity coefficient ($0 < \gamma_i < 1$), and the activity of an ion is much lower than the value of its molality. This effect is also stronger the higher the ionic charge $|Z|$.

The calculation of activity coefficients for solutions with very high ionic strengths (>0.5 M) requires more complex equations, such as the PITZER model (Langmuir 1997; Suarez 1999). However, such high ionic strengths are only encountered in saline soils.

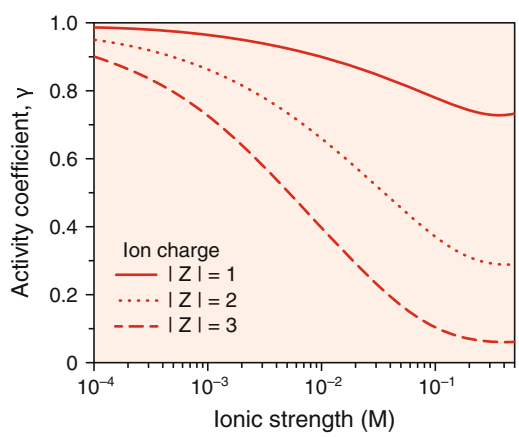

Fig. 5.1 Activity coefficients γ_i according to the Davies equation [Eq. (5.5)] for mono-, di- and trivalent anions and cations ($|Z| = 1, 2, 3$) as a function of the ionic strength of the solution

5.3.2 Solution Speciation

5.3.2.1 Dissolved Complexes and Ion Pairs

Let us consider the trace element copper (Cu), which is mainly present in its +2 oxidation state in well-aerated soils. Under acidic conditions and in the absence of ligands, dissolved Cu(II) is mainly found as a hexaquo complex ($Cu(H_2O)_6^{2+}$), i.e. Cu^{2+} is surrounded by six water molecules in the first hydration shell. This species is also called **free** Cu^{2+} species. With rising pH values, a continuously increasing fraction of the dissolved Cu^{2+} is subject to hydrolysis, i.e. water molecules in the first hydration shell deprotonate according to:

$$Cu(H_2O)_6^{2+} \rightleftharpoons Cu(H_2O)_5OH^+ + H^+$$

$$\log K_1 = -7.497 \quad (5.6)$$

$$Cu(H_2O)_5OH^+ \rightleftharpoons Cu(H_2O)_4OH_2^0 + H^+$$

$$\log K_2 = -8.733 \quad (5.7)$$

This leads to the formation of the two first hydroxo species, written as $CuOH^+$ and $Cu(OH)_2^0$ without the water molecules. Other hydroxo species include $Cu(OH)_3^-$, $Cu(OH)_4^{2-}$, and the polynuclear species $Cu_2(OH)_2^{2+}$ and $Cu_3(OH)_4^{2+}$. However, the fractions of these species contributing to total dissolved Cu(II) are generally low. Nonetheless, species that are only present in small fractions can still be of great ecological significance, e.g. if they are highly toxic for organisms. A well-known example is the polyvalent Al^{13} cation, $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$, which is considered to be extremely toxic to plant roots.

Similarly, many other metal cations also form hydroxo species in water, whereby the log K_1 values decrease in the sequence $Hg^{2+} > Cr^{3+} > Al^{3+} > Cu^{2+} > Pb^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+} > Cd^{2+} > Mn^{2+}$ (a smaller log K_1 value means that the first hydroxo species will become significant at higher pH values).

Metal cations can also form complexes or ions pairs with other ligands, which results in a multitude of possible metal species (e.g. $CuCl^+$, $CuSO_4^0$, $CuHPO_4^0$, Cu-citrate$^-$ and Cu-oxalate^0).

Important inorganic ligands in soil solutions include F^-, Cl^-, SO_4^{2-}, NO_3^-, PO_4^{3-}, and HCO_3^-. Organic ligands include low-molecular weight carboxylic acids (e.g. citric, oxalic, malonic acid) that are excreted by plant roots and microorganisms, but also higher-molecular weight fulvic and humic acids and other polymeric organic molecules. Many ligands are Brønsted acids (or their anions), and can thus donate (or accept) protons. Their speciation and reactivity in terms of metal complexation therefore change with pH. For example, orthophosphate (PO_4^{3-}, fully deprotonated anion of phosphoric acid H_3PO_4) is mainly found as $H_2PO_3^-$ in acidic soils, while HPO_4^{2-} dominates in weakly acidic to neutral soils.

Depending on the metal cation and the ligand, different types of complexes can be formed. In **outer-sphere complexes** (also called **ion pairs**), the metal cation retains its complete first hydration shell (Fig. 5.2, left). The ligand remains outside of the metal's hydration shell and the ions in the complex are held together by electrostatic attractive forces. Several examples of ion pairs in soil solutions are $CuCl^+$, $NaHCO_3^0$, $CaCO_3^0$, $CaHCO_3^+$, $MgSO_4^0$, and $CaSO_4^0$.

In contrast, if the ligand penetrates the first coordination shell surrounding the metal, it forms an **inner-sphere complex** (Fig. 5.2, right). The bond can have ionic or covalent character. Inner-sphere complexes are generally more stable than outer-sphere complexes. Several examples for inorganic inner-sphere complexes in soil solutions are AlF^{2+}, AlF_2^+ and $AlSO_4^+$. Table 5.4 provides several other examples for important species of dissolved metals in soil solutions.

Another factor influencing the stability of dissolved complexes is the number of bonds between a metal cation and a ligand. This is called the **denticity** of a complex. **Monodentate** complexes only have one bond from the ligand to the metal cation. In contrast, if the ligand is doubly-coordinated with the metal cation, it is called a **bidentate** complex (Fig. 5.3). Several ligands are capable of multiple coordination with a metal cation (**polydentate** complexes). Organic

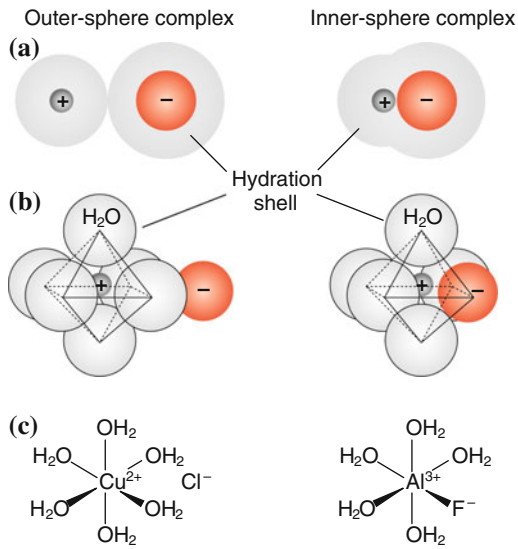

Fig. 5.2 Outer-sphere and inner-sphere complexes: **a** schematically, **b** as a polyhedral model, **c** example of $CuCl^+$ as an outer-sphere and AlF^{2+} as an inner-sphere complex. In *the outer-sphere* $CuCl^+$ complex, the Cu^{2+} cation is coordinated with six water molecules. The Cl^- anion is electrostatically attracted, but does not penetrate the first coordination shell. In *the inner-sphere* AlF^{2+} complex, the ligand F^- is in the first coordination shell surrounding the Al^{3+} cation

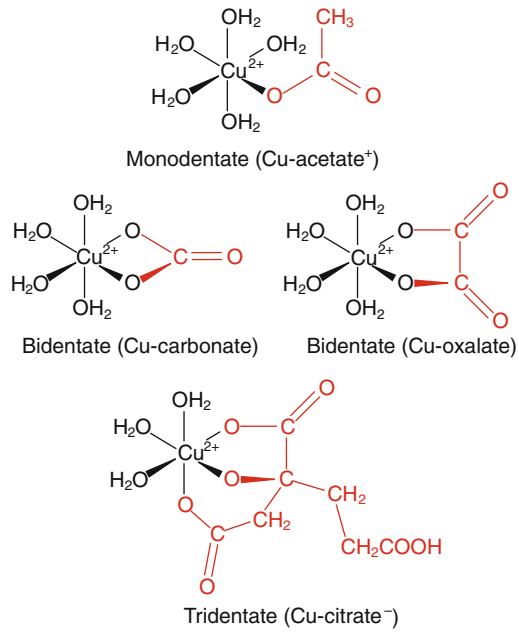

Fig. 5.3 Examples for monodentate complexes, bidentate complexes, and chelate complexes in solution (after Essington 2004)

ligands, which are capable of bidentate or polydentate coordination with a metal, are also called **chelating agents**, and accordingly, their complexes are called **chelate complexes** (Greek *chele* = claw). Bidentate or polydentate complexes are generally more stable than corresponding monodentate complexes. CO_3^{2-} und SO_4^{2-} are two inorganic ligands capable of forming both monodentate and bidentate complexes. Examples of chelating agents found in soil solutions are oxalate (bidentate), salicylate (bidentate), and citrate (tridentate).

5.3.2.2 Mass Action Law and Stability Constants

The formation of a dissolved complex can be described using the following general reaction equation:

$$aM^{m+} + bL^{n-} \rightleftharpoons M_aL_b^q \tag{5.8}$$

where M^{m+} is the metal cation with a positive charge m, L^{n-} is the ligand with a negative charge n, a and b are the stoichiometric coefficients and q is the charge of the complex ($q = am - bn$). At chemical equilibrium, the following equation applies[4]:

$$K^0 = \frac{\{M_aL_b^q\}}{\{M^{m+}\}^a\{L^{n-}\}^b} \tag{5.9}$$

where K^0 is the **thermodynamic stability constant** of the complex $M_aL_b^q$. Using the activity coefficient, the thermodynamic stability constant can be converted into a **conditional stability constant** K^c, which is expressed in terms of concentrations and thus only applies at a given ionic strength I.

$$K^c = K^0\frac{\gamma_M^a\gamma_L^b}{\gamma_{M_aL_b}} = \frac{[M_aL_b^q]}{[M^m]^a[L^n]^b} \tag{5.10}$$

The activity coefficients γ_i can be calculated using the extended Debye-Hückel or the Davies Equation [Eqs. (5.4) and (5.5)].

[4]Activities are represented here with curly brackets {…} and concentrations with square brackets […].

5.3.2.3 Mass Balance Equations

In addition to the reaction equations and the corresponding stability constants, a speciation calculation must also take account of the mass balances for all involved components. For the metal M and the ligand L, the mass balance equations are:

$$M_T = [M^{m+}] + a[M_aL_b^q] + \cdots \tag{5.11}$$

$$L_T = [L^{n-}] + b[M_aL_b^q] + \cdots \tag{5.12}$$

where M_T and L_T are the total concentrations of the metal and ligand, respectively, and all relevant complexes must be accounted for in the sum as shown for the species $M_aL_b^q$.

5.3.2.4 Computer Programs for Chemical Speciation Calculations

Numerous computer programs are available for chemical **speciation calculations** in aqueous geochemical systems. Several of these programs are available as freeware (e.g. Visual-MINTEQ, MINTEQA2, PHREEQC), while others require a license (e.g. ECOSAT, MINEQL+, The Geochemists Workbench). Most speciation programs can couple solution speciation calculations with mineral dissolution/precipitation, partitioning of gases, adsorption/desorption, as well as redox reactions, and are thus suited for the calculation of thermodynamic equilibria in complex geochemical systems such as soils. However, only some programs can take reaction kinetics and reaction pathways into account (e.g. PHREEQC, The Geochemists Workbench).

5.4 Solubility and Dissolution Kinetics

The soil solution is in direct contact with the surfaces of soil minerals and the solid organic matter. Dissolution and precipitation reactions, in addition to many other reactions, take place at these water-solid interfaces. Such reactions lead to e.g. the precipitation or dissolution of salts,

gypsum, or carbonates. They also play an important role in the bioavailability of nutrients and potentially toxic trace elements in the soil. Surface reactions also have a significant effect on the weathering of primary silicates and the formation of secondary minerals (oxides, clay minerals).

The formation and dissolution (or chemical weathering) of various minerals in the soil depend on the activities of the dissolved ions in the soil solution, as well as on the thermodynamic stability of all the minerals involved (**mineral solubility**). The **kinetics** of the individual reactions determines the temporal course of these processes. Even minerals that are commonly considered to be "insoluble" are soluble to a certain degree in water, and can weather over long time periods in the soil (the term "sparingly soluble" is therefore preferred).

5.4.1 Solubility Constant, Ion Activity Product, and Saturation Index

The solubility or thermodynamic stability of minerals can be expressed using a solubility constant. Consider the following general dissolution reaction for a mineral with the sum formula $M_aL_b(OH)_c$:

$$\mathrm{M_aL_b(OH)_c}(s) + c\mathrm{H^+}(aq) \rightarrow a\mathrm{M^{m+}}(aq) + b\mathrm{L^{n-}}(aq) + c\mathrm{H_2O}(l) \tag{5.13}$$

where (s) designates a solid phase, (aq) an aqueous species, and (l) the solvent, and the electroneutrality must be fulfilled by the condition $am - bn - c = 0$. As already introduced in Sect. 5.3.2, M^{m+} is a metal cation with positive charge m and L^{n-} is a ligand with negative charge n. At chemical equilibrium, the following equation applies:

$$K_{\mathrm{diss}} = \frac{\{\mathrm{M^{m+}}\}^{\mathrm{a}}\{\mathrm{L^{n-}}\}^{\mathrm{b}}\{\mathrm{H_2O}\}^{\mathrm{c}}}{\{\mathrm{M_aL_b(OH)_c}\}^{\mathrm{a}}\{\mathrm{H^+}\}^{\mathrm{c}}} \tag{5.14}$$

where K_{diss} is the solubility constant of the mineral. The solubility constants of minerals can be calculated from the free enthalpies (Gibbs energy) of the individual components. Such thermodynamic constants represent the basis for long-term stability predictions of minerals in soils and the calculation of ion concentrations in equilibrium with mineral phases.

For pure phases (mineral, water, gas), the activities under standard conditions (T = 25 °C or 298 K and p = 1013 hPa) are equal to unity. This value can also be used as an approximation for the activity of H_2O in dilute aqueous soil solutions and for most mineral phases in the soil. Under this assumption, the solubility constant reduces to the **solubility product constant** K_{SP}:

$$K_{\mathrm{SP}} = \frac{\{\mathrm{M^{m+}}\}^{\mathrm{a}}\{\mathrm{L^{n-}}\}^{\mathrm{b}}}{\{\mathrm{H^+}\}^{\mathrm{c}}} \text{(at chemical equilibrium)} \tag{5.15}$$

Table 5.5 lists the solubility product constants for selected minerals that are commonly found in soils.

The term on the right hand side of Eq. (5.15) also corresponds to the **ion activity product** (*IAP*) of a solution with respect to the specific mineral. The ratio between the actual *IAP* of an aqueous solution and the constant K_{SP} of the mineral is used to calculate the saturation index *SI* of the solution with respect to the mineral:

$$SI = \log\left(\frac{IAP}{K_{\mathrm{SP}}}\right) \tag{5.16}$$

The saturation index indicates whether a solution is over-saturated ($SI > 0$), under-saturated ($SI < 0$), or at chemical equilibrium ($SI = 0$) with the mineral phase.

5.4.2 Stability Diagrams

The solubility of different minerals can be represented graphically in **stability diagrams** (Sect. 2.4.4). Such diagrams show which minerals can dissolve or form under specified conditions. Let

Table 5.5 Solubility product constants (log K_{SP}) for selected minerals with the corresponding ion activity products (IAP) (based on Robarge 1999 and Visual-MINTEQ database)

Mineral	Molecular formula	IAP	log K_{SP}
Carbonates			
Calcite	$CaCO_3$	$\{Ca^{2+}\}\{CO_3^{2-}\}$	−8.48
Dolomite	$CaMg(CO_3)_2$	$\{Ca^{2+}\}\{Mg^{2+}\}\{CO_3^{2-}\}^2$	−17.09
Siderite	$FeCO_3$	$\{Fe^{2+}\}\{CO_3^{2-}\}$	−10.24
Sulfates			
Gypsum	$CaSO_4{\cdot}2H_2O$	$\{Ca^{2+}\}\{SO_4^{2-}\}$	−4.61
Jarosite	$KFe_3(SO_4)_2(OH)_6$	$\{K^+\}\{Fe^{3+}\}^3\{SO_4^{2-}\}^2\{H^+\}^{-6}$	−14.80
Phosphates			
Variscite	$AlPO_4{\cdot}2H_2O$	$\{Al^{3+}\}\{PO_4^{3-}\}$	−21.8
Strengite	$FePO_4{\cdot}2H_2O$	$\{Fe^{3+}\}\{PO_4^{3-}\}$	−26.4
Octacalcium phosphate	$Ca_4H(PO_4)_3{\cdot}3H_2O$	$\{Ca^{2+}\}^4\{H^+\}\{PO_4^{3-}\}^3$	−47.08
Hydroxyapatite	$Ca_5(PO_4)_3(OH)$	$\{Ca^{2+}\}^5\{PO_4^{3-}\}^3\{H^+\}^{-1}$	−44.33
Oxides			
Quartz	α-SiO_2	$\{H_4SiO_4^0\}$	−4.00
$SiO_2(am)$	SiO_2	$\{H_4SiO_4^0\}$	−2.74
Gibbsite	γ-$Al(OH)_3$	$\{Al^{3+}\}\{H^+\}^{-3}$	8.29
$Al(OH)_3(am)$	$Al(OH)_3$	$\{Al^{3+}\}\{H^+\}^{-3}$	10.80
$Fe(OH)_3(am)$	$Fe(OH)_3$	$\{Fe^{3+}\}\{H^+\}^{-3}$	3.19
Hematite	α-Fe_2O_3	$\{Fe^{3+}\}\{H^+\}^{-3}$	−0.71
Goethite	α-FeOOH	$\{Fe^{3+}\}\{H^+\}^{-3}$	0.49
Silicates			
Forsterite	Mg_2SiO_4	$\{Mg^{2+}\}^2\{H_4SiO_4^0\}\{H^+\}^{-4}$	28.29
Anorthite	$CaAl_2Si_2O_8$	$\{Ca^{2+}\}\{Al^{3+}\}^2\{H_4SiO_4^0\}^2\{H^+\}^{-8}$	26.10
Albite	$NaAlSi_3O_8$	$\{Na^+\}\{Al^{3+}\}\{H_4SiO_4^0\}^3\{H^+\}^{-4}$	3.67
Microcline	$KAlSi_3O_8$	$\{K^+\}\{Al^{3+}\}\{H_4SiO_4^0\}^3\{H^+\}^{-4}$	0.61
Muscovite	$K(Al_2)(AlSi_3)O_{10}(OH)_2$	$\{K^+\}\{Al^{3+}\}^3\{H_4SiO_4^0\}^3\{H^+\}^{-10}$	13.44
Kaolinite	$Al_2Si_2O_5(OH)_4$	$\{Al^{3+}\}^2\{H_4SiO_4^0\}^2\{H^+\}^{-6}$	5.45

The activity of H_2O was assumed to equal unity (dilute aqueous solutions). Amorphous to weakly-crystalline phases are identified as (*am*); here, $Fe(OH)_3(am)$ represents ferrihydrite, which is also often written as $5Fe_2O_3{\cdot}9H_2O$

us consider a lead-contaminated soil as an example and ask the following questions: Which of the possible Pb solid phases could control the activity of Pb^{2+} in the soil solution? Would the addition of phosphate lead to a reduction in the solubility of Pb^{2+}? Relevant minerals in this system are e.g. alamosite [$PbSiO_3$], lead hydroxide [$Pb(OH)_2$], cerussite [$PbCO_3$], hydroxypyromorphite [$Pb_5(PO_4)_3(OH)$], hydroxyapatite [$Ca_5(PO_4)_3(OH)$], and brushite [$CaHPO_4{\cdot}2H_2O$]. Assuming that the soil is calcareous (calcite) and the relative partial pressure of CO_2 in the soil air, P_{CO_2}, is 0.0038 (i.e. 10-fold higher than in the atmosphere), the solution equilibrium of calcite (at 25 °C) controls the activities of dissolved Ca^{2+}, CO_3^{2-} and H^+ ions ($\{Ca^{2+}\} = 8.8 \times 10^{-4}$; $\{CO_3^{2-}\} = 3.76 \times 10^{-6}$; pH 7.57). Assuming further that the activity of dissolved silicic acid is controlled by the solubility of amorphous silica [$SiO_2(am)$]

($\{H_4SiO_4^0(aq)\} = 1.82 \times 10^{-3}$), the dissolution reactions with the corresponding solubility product constants for the considered minerals can be written as (after Essington 2004):

$$PbSiO_3(s) + 2H^+ + H_2O \rightarrow Pb^{2+} + H_4SiO_4^0$$

$$\log K_{SP} = 5.94 \tag{5.17}$$

$$Pb(OH)_3(s) + 2H^+ \rightarrow Pb^{2+} + 2H_2O$$

$$\log K_{SP} = -8.15 \tag{5.18}$$

$$PbCO_3(s) \rightarrow Pb^{2+} + CO_3^{2-}$$

$$\log K_{SP} = -13.13 \tag{5.19}$$

$$Pb_5(PO_4)_3(OH)(s) + 4H^+ \rightarrow 5Pb^{2+} + 3HPO_4^{2-} + H_2O$$

$$\log K_{SP} = -25.67 \tag{5.20}$$

$$Ca_5(PO_4)_3(OH)(s) + 4H^+ \rightarrow 5Ca^{2+} + 3HPO_4^{2-} + H_2O$$

$$\log K_{SP} = -7.21 \tag{5.21}$$

$$CaHPO_4 \cdot 2H_2O(s) \rightarrow Ca^{2+} + HPO_4^{2-} + 2H_2O$$

$$\log K_{SP} = -6.62 \tag{5.22}$$

The following relationships can be derived from the respective equations for the solubility product constants:

For alamosite:

$$\log\{Pb^{2+}\} = \log K_{SP} - \log\{H_4SiO_4^0\} - 2pH \tag{5.23}$$

For lead hydroxide:

$$\log\{Pb^{2+}\} = \log K_{SP} - 2pH \tag{5.24}$$

For cerussite:

$$\log\{Pb^{2+}\} = \log K_{SP} - \log\{CO_3^{2-}\} \tag{5.25}$$

For hydroxypyromorphite:

$$\log\{Pb^{2+}\} = \frac{1}{5}\log K_{SP} - \frac{3}{5}\log\{HPO_4^{2-}\} - \frac{4}{5}pH \tag{5.26}$$

For hydroxyapatite:

$$\log\{HPO_4^{2-}\} = \frac{1}{3}\log K_{SP} - \frac{5}{3}\log\{Ca^{2+}\} - \frac{4}{3}pH \tag{5.27}$$

For brushite:

$$\log\{HPO_4^{2-}\} = \log K_{SP} - \log\{Ca^{2+}\} \tag{5.28}$$

By inserting the values for K_{SP} and the given activities of Ca^{2+}, CO_3^{2-}, $H_4SiO_4^0$, and H^+ (pH value), the stability diagram shown in Fig. 5.4 is obtained. A soil solution can be represented as a point in the diagram according to its activities of HPO_4^{2-} and Pb^{2+}. If the point is located to the

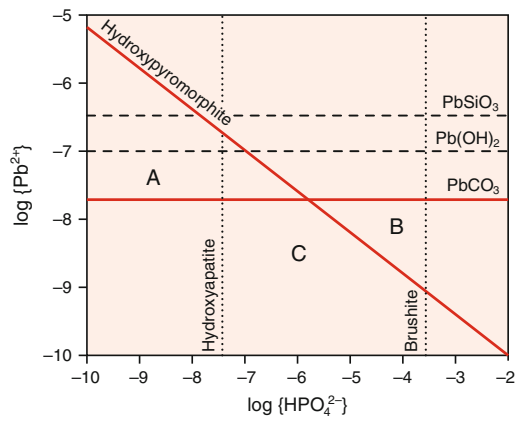

Fig. 5.4 Stability diagram for phosphate and lead solid phases at equilibrium with calcite, SiO_2(am) and $P_{CO_2} = 0.0038$. Examples: (*A*) The solution is over-saturated with respect to cerussite ($CaCO_3$), but under-saturated with respect to all other solid phases. (*B*) The solution is over-saturated with respect to hydroxyapatite and hydroxypyromorphite, but under-saturated with respect to brushite, cerussite, lead hydroxide ($Pb(OH)_2$) and alamosite ($PbSiO_3$). (*C*) The solution is over-saturated with respect to hydroxyapatite ($CaCO_3$), but under-saturated with respect to all other solid phases

left or below the stability line of a particular mineral, the solution is under-saturated with respect to this solid phase (SI < 0). If the point is located to the right or above the line, the solution is over-saturated (SI > 0). Points located on the line itself indicate that the solution is in equilibrium with respect to the solubility of the respective mineral (SI = 0).

The following information can be concluded from Fig. 5.4: When the activity of HPO_4^{2-} in the soil solution is low ($\{HPO_4^{2-}\} < 10^{-6}$), the activity of Pb^{2+} in solution may be controlled by the solubility of cerussite (if present). The maximum possible activity of Pb^{2+} is 1.97×10^{-8}; above this value, cerussite would precipitate until equilibrium with cerussite is reached. Alamosite and lead hydroxide are not the most stable phases. If they are present, they would dissolve and the released Pb^{2+} would precipitate as cerussite. Soil fertilization with brushite could increase the activity of HPO_4^{2-} in the soil solution up to a maximum of 2.73×10^{-4}. This reduces the solubility of lead, because hydroxypyromorphite is now the most stable lead solid phase. Cerussite would dissolve under formation of hydroxypyromorphite, and the activity of Pb^{2+} in the soil solution would drop to a minimum of 9.88×10^{-10}.

The above-mentioned effects can be used in practice to immobilize lead in contaminated soils. However, the mineral transformation kinetics under soil conditions is slow, so that a significant reduction in the solubility of lead is often observed only years after the application of phosphate fertilizer.

5.4.3 Dissolution and Precipitation Kinetics

The **kinetics**, i.e. the rates at which minerals dissolve and precipitate, vary greatly with mineral type and strongly depend on environmental conditions in the soil (e.g. temperature, pH value, complexing ligands, dissolved ions). Because soils are open systems, chemical equilibria, provided that they are even ever reached, are frequently disturbed by fluxes of matter and energy. For example, chemical weathering and soil formation under humid climate conditions are driven by frequent rainfall and leaching of dissolution products, because thereby the soil solution remains under-saturated with respect to the primary silicates.

Many silicates dissolve fastest under strongly acidic or strongly alkaline conditions (Fig. 2.26). Weathering under the influence of protons is due to **proton-promoted** dissolution. The weathering rates of silicates in soils increase after complete leaching of carbonates and the onset of soil acidification, because the rate of proton-promoted dissolution generally increases with decreasing pH.

In addition to protons, organic ligands can also accelerate the weathering of minerals, which is due to **ligand-promoted** dissolution (Fig. 5.5, Sect. 2.4.3). Many organisms (higher plants, bacteria, fungi) make use of this effect to mobilize nutrients by excreting complexing ligands that attack the mineral structures. An example is the excretion of siderophores and/or organic acids by fungi, bacteria, and plant roots. These organic ligands form surface complexes at mineral surfaces and accelerate the dissolution of

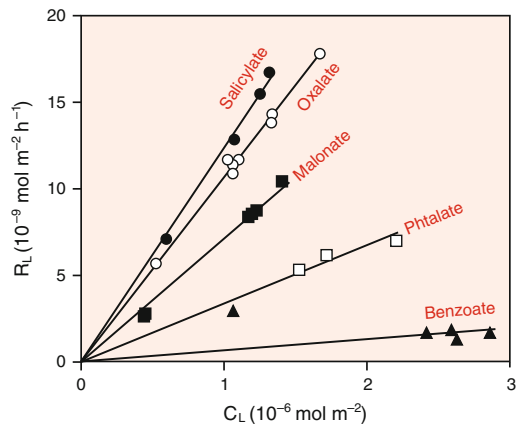

Fig. 5.5 Dissolution rate R_L of δ-Al_2O_3 depending on the *adsorbed* concentration C_L of different organic ligands on the surface. The dissolution rate increases proportional to the adsorbed concentration of a ligand. The effect of the ligands on the dissolution rate increases in the sequence benzoate, phthalate, malonate, oxalate, salicylate (after Furrer and Stumm 1986)

minerals by extracting metal ions from the crystal lattice. Siderophores are extremely strong complexing ligands for Fe(III). The formation of complexes with dissolved Fe(III) leads to a strong reduction in the activity of dissolved Fe^{3+} ions, and thus also increases the dissolution rates of iron minerals.

The chemical weathering of primary silicates can be irreversible in soils, because most primary minerals are only formed at elevated pressure and/or temperature. Even if the soil solution were strongly oversaturated with respect to these minerals, other secondary minerals would precipitate first. Thermodynamic calculations alone are therefore not sufficient to determine which minerals are formed. Besides their thermodynamic stability, it also depends on how fast the different possible minerals are formed, i.e., on the kinetics of crystal growth processes. Amorphous or poorly-crystalline phases often form rapidly and are therefore the first weathering products. However, they can then slowly dissolve or recrystallize under formation of other, more stable phases. The precipitation of iron hydroxides is an important example. If the weathering of silicates liberates Fe(II) and it is oxidized to Fe (III) by O_2, it initially forms a poorly-crystalline iron hydroxide (ferrihydrite, 5 $Fe_2O_3 \cdot 9\ H_2O$). However, ferrihydrite is not the most stable phase thermodynamically, and it can therefore slowly dissolve again under formation of goethite (α-FeOOH) or hematite (α-Fe_2O_3), depending on the soil conditions (Fig. 2.20). For this reason, kinetics plays a very important role in many chemical processes in soils involving dissolution or precipitation processes.

5.5 Sorption

Adsorption and desorption of substances are among the most important processes taking place at interfaces between solid, gas, and solution phases in soils. **Adsorption** and **desorption** are defined as the enrichment and release of dissolved or gaseous ions or molecules at the surfaces of solids. The solid phase involved is called **sorbent** and the adsorbing substance is the **sorbate**. Not only dissolved ions, but also uncharged inorganic species and molecules (e.g. organic compounds, water) can be adsorbed on surfaces.

The nature of the interaction forces between the sorbate and the surface of the sorbent can vary (Fig. 5.6). Charged ions can be attracted to oppositely charged surfaces by electrostatic forces. This type of interaction is relatively weak, and the kinetics of such adsorption and desorption processes are fast. For this reason, ions adsorbed solely by electrostatic forces can be easily replaced by other dissolved ions; they are called **exchangeable ions** and the process is called **ion exchange**. Stronger bonds with the surface arise when a sorbate forms coordinative bonds with reactive surface functional groups. This process is also called **specific adsorption** or **chemisorption**. The adsorption and desorption kinetics are then often much slower, especially desorption. Organic molecules can also be adsorbed onto mineral surfaces and organic matter through the formation of hydrogen bonds or through hydrophobic interactions (Sect. 10.3.3).

The adsorption of some metal ions onto mineral surfaces can lead to the formation of polymeric sorbate species and even promote the precipitation of a new solid phase on the surface (**surface precipitation**). Inversely, desorption can be considered an important partial step of the dissolution of solid phases. The boundaries between ion exchange, specific adsorption, and surface precipitation in soils are gradual, and the processes can often only be differentiated using spectroscopic methods.[5] For this reason, the term **sorption** is often used as an umbrella term for adsorption and surface precipitation.

[5]One of the most important spectroscopic methods in this context is extended X-ray absorption fine structure spectroscopy (EXAFS), which requires the use of synchrotron X-ray radiation (extremely brilliant, monochromatic radiation).

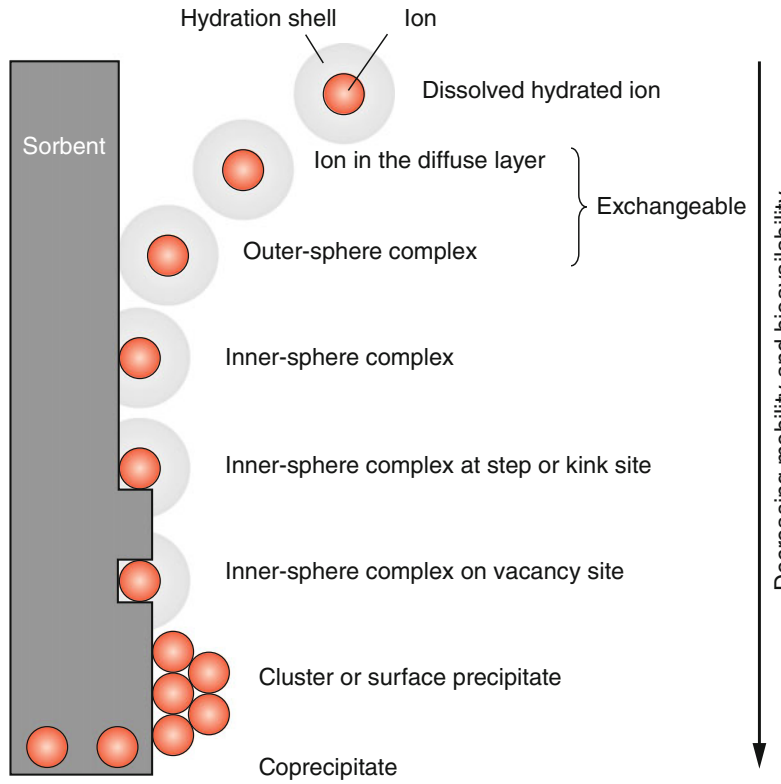

Fig. 5.6 Sorption of ions (sorbate) on a mineral surface (sorbent) (schematic). The mobility and bioavailability decrease with increasing bonding strength (*from top to bottom*)

5.5.1 Reactive Surfaces and Surface Charge

The capacity of a soil to adsorb dissolved or gaseous substances significantly depends on the type (charge density, reactivity, hydrophobicity) and size (area, roughness) of its surfaces (solid-water and solid-gas interfaces). In moist to wet soils, interfaces between solid and gaseous phases play a secondary role, because the hydrophilic surfaces of soil minerals are covered at least by a film of water. Processes at the mineral-water interface play the larger role, except under very dry soil conditions.

5.5.1.1 Specific Surface Area

The size of the surface area per unit mass of a solid substance is referred to as **specific surface area** (in $m^2\ g^{-1}$).[6] It depends on the size, shape, and surface roughness of the particles. Small platy particles have a much greater specific surface area than large spherical particles of the same density. For this reason, the particle size distribution (especially the clay content) of a soil has a significant effect on its specific surface area. The specific surface area of the sand fraction is less than 0.1 $m^2\ g^{-1}$, while the silt fraction typically has 0.1–1 $m^2\ g^{-1}$, and the clay fraction has 5–500 $m^2\ g^{-1}$ specific surface area. Thus, in a clay loam soil with equal weight fractions of clay, silt, and sand, the clay fraction accounts for approximately 99 % of the soil's total specific surface area. The clay fraction, consisting mainly of secondary layer silicates and smaller fractions of secondary oxides and oxyhydroxides of Fe,

[6]The specific surface area is usually determined using the N_2-BET method. This is accomplished by measuring an adsorption isotherm for N_2-gas at -196 °C, and using the

(Footnote 6 continued)
data to calculate the specific surface area. However, the N_2-BET method does not detect internal surface area of swelling clays and humic substances. These can be estimated from the adsorption of polar molecules (e.g. EGME, ethylene glycol methyl ether).

Al, and Mn, is therefore the most important size fraction as a sorbent for dissolved and gaseous substances.

The specific surface areas of soils vary greatly (between 1 and 500 $m^2\ g^{-1}$), and in addition to soil **texture**, also depend on the clay mineralogy and the organic matter content. Among the clay minerals, smectite and vermiculite have the largest specific surface area with 600–800 $m^2\ g^{-1}$. Most of this surface area (up to 80–90 %), however, is located in the interlayers of these swelling 2:1-type phyllosilicates (Sect. 2.2.4.5) and is called **internal surface area**. In contrast to the external surface area, it is largely independent of the particle size. However, only ions and molecules that are capable of penetrating the interlayers of clay minerals (e.g. water, hydrated ions, polar organic molecules in smectites) can be adsorbed onto these surfaces. In contrast, the interlayers of illites are mostly non-swelling, and are therefore not accessible to water and dissolved substances. For this reason, illites mainly have external surface area and have a much lower specific surface area (50–200 $m^2\ g^{-1}$) than swelling clays. More than 70 % of the external surface area of phyllosilicates is found on the basal surfaces, and only up to 30 % at the edges of the platy clay particles. The same is also true for kaolinites, which typically have specific surface areas between 10 and 150 $m^2\ g^{-1}$, depending on the particle size.

Allophanes and imogolites, which are mainly found in young soils with volcanic ashes, have exceptionally high specific surface areas (700–1100 $m^2\ g^{-1}$). These nano-crystalline minerals are responsible for the strong fixation of phosphate in soils developed from volcanic ashes. Poorly crystalline iron hydroxides (e.g. ferrihydrite) also have a very high specific surface area (200–600 $m^2\ g^{-1}$), because the primary particles are only a few nm in size. These primary nanoparticles form microporous aggregates, so that a large fraction of the total surface area is only accessible by diffusion through micropores. More crystalline iron oxides, such as goethite and hematite, have much lower specific surface areas (50–150 $m^2\ g^{-1}$) and a greater fraction of the total surface is freely accessible for solutes. The specific surface area of humic substances is estimated at 800–1200 $m^2\ g^{-1}$, whereby the measured values also depend on the method used.

5.5.1.2 Significance of Surface Charge

The surfaces of minerals and organic substances in contact with aqueous solutions almost always carry negative or positive electrical charges. The sum of these charges is called **(net) surface charge**. It is always balanced by the charges of ions that are adsorbed directly to the surface or reside in a **diffuse layer** surrounding the surface (Fig. 5.6). This solid-liquid interface, including the adsorbed ions and the diffuse layer, is called the **electrical double layer**.

The surface charge of colloidal particles in the clay fraction is of great significance for chemical and physical processes in soils. Especially the adsorption of water, ions, and organic molecules is strongly affected by the surface charge. The adsorption of water and ions, in turn, determines the swelling behavior of the clay minerals (particularly in smectites), and thus the physical properties of clayey soils. The stability of soil aggregates, transport of clay particles, and colloidal transport of contaminants also strongly depend on the surface charge of the soil colloids (Sect. 6.2.1).

Surface charge can arise through two principal mechanisms: (a) Isomorphic substitution in the crystal lattice of minerals, resulting in structural, pH-independent surface charge (**permanent charge**, mostly negative), and (b) Protonation or deprotonation of reactive surface hydroxyl groups, resulting in pH-dependent surface charge (**variable charge**, negative or positive). These two types of surface charge will be explained in the following sections.

5.5.1.3 Permanent Surface Charge

Permanent negative surface charge is mainly found in primary and secondary 2:1 layer silicates (e.g. micas, illites, vermiculites, smectites). The 1:1 layer silicates (e.g. kaolinites, halloysites, serpentines) have no or only very low permanent charge. Negative permanent surface charge arises

through **isomorphic substitution** of higher valence by lower valence metal cations in tetrahedral or octahedral positions (Sect. 2.2.2). For example, tetrahedral positions can be partly filled with trivalent cations such as Al^{3+} (or Fe^{3+}) instead of Si^{4+}, or octahedral positions in di-octahedral sheets can be filled with divalent cations like Mg^{2+} or Fe^{2+} instead of Al^{3+}. Because the number and arrangement of oxygen atoms in the crystal lattice remains unchanged, a negative excess charge arises. This **structural charge** is compensated by cations in the **interlayers** and at the external basal surfaces of layer silicates. In micas and illites, the structural charge in the interlayers is compensated solely by non-hydrated K^+ ions, which are non-exchangeable. In vermiculites and smectites, in contrast, the interlayer cations can be exchanged by other (hydrated) cations. Thus, the total structural charge contributes to the cation exchange capacity of these minerals. In primary and secondary chlorites, the negative structural charge of the 2:1 layers is compensated by the positive charge of additional octahedral sheets in the interlayers (Fig. 2.7).

5.5.1.4 Variable Surface Charge and Point of Zero Charge

Many minerals have hydroxyl (−OH) groups at their surfaces, which can accept or donate protons (and thus positive charges). These include especially the oxides and hydroxides of Fe, Al, Ti, Si, and Mn, but also the edges of clay minerals, which also possess reactive surface hydroxyl groups. At low pH values (i.e. high H^+ activity in solution), the surfaces are more strongly positively charged due to protonation of surface functional groups. In contrast, the surface becomes more negatively charged at high pH values (i.e. low H^+ activity in the solution), when more surface functional groups are deprotonated. In addition to pH, protonation and thus the surface charge are also influenced by the ionic strength of the solution. This type of charge is therefore called **variable charge**. Variable charges are compensated for by specifically or nonspecifically adsorbed cations or anions (see ion exchange and surface complexation).

The protonation of surface hydroxyl groups that are only coordinated with one metal cation (Me) in the crystal structure can be schematically written as:

$$\equiv \mathrm{MeOH}^{0.5-} + \mathrm{H}^+ \rightarrow \equiv \mathrm{MeOH}_2^{0.5+} \qquad (5.29)$$

where ≡Me represents a trivalent metal center (e.g. Al^{3+}, Fe^{3+}) in octahedral coordination with six oxygen atoms (including the surface OH group). The OH group at the surface can be assigned a nominal partial charge of −0.5. Through protonation, the partial charge increases to +0.5 and the OH group turns into a water molecule (Lewis acid). This water molecule can be substituted by other specifically adsorbing ligands, such as phosphate (see surface complexation).

Analogously, the protonation of surface groups that are coordinated with three metal atoms of the crystal lattice can be written as:

$$(\equiv \mathrm{Me})_3\mathrm{O}^{0.5-} + \mathrm{H}^+ \rightarrow (\equiv \mathrm{Me})_3\mathrm{OH}^{0.5+} \qquad (5.30)$$

This also results in a nominal charge of −0.5 or +0.5, depending on the protonation of the group. Doubly-coordinated OH groups $[(\mathrm{Me})_2\mathrm{OH}^0]$ are thought to be less reactive in the pH range found in soils, and hardly contribute to the variable charge of oxide surfaces.

Although the surface hydroxyl groups of oxides may exhibit different protonation constants (pK_a), the two above-mentioned protonation reactions (Eqs. 5.29 and 5.30) are often represented by a single equation:

$$\equiv \mathrm{SOH}^{0.5-} + \mathrm{H}^+ \rightarrow \equiv \mathrm{SOH}_2^{0.5+} \qquad (5.31)$$

where ≡SOH is a general term representing a reactive surface hydroxyl group. The pH value at which the surfaces of a mineral carry an equal amount of positive and negative charges, i.e. have a net-charge of zero, is called **point of zero charge** (pH_{PZC}).

5.5.1.5 Surface Charge of Individual Soil Components

Layer silicates in the clay fraction (clay minerals) carry permanent negative charge on their basal surfaces, caused by isomorphic substitution in the crystal lattice. The **charge density** (C m^{-2} or mol_c m^{-2}) of different clay minerals varies strongly: It decreases in the sequence illites ≈ vermiculites > smectites ≫ kaolinites, halloysites. Kaolinites and halloysites have no (or very little) permanent negative charge.

In addition to the permanent negative charge on basal surfaces, clay minerals also exhibit some variable charge at the edge surfaces, which possess reactive surface hydroxyl groups. In 2:1 layer silicates, silanol groups (Si-OH) dominate at the edges with a low point of zero charge (pH_{PZC}) (Table 5.6). For this reason, in the pH range found in soils, these surfaces are predominantly negatively charged. In kaolinites, aluminol groups (Al–OH) play a more prominent role and the point of zero charge of the edge surfaces is therefore higher (pH_{PZC} ≈ 4.8). Thus, in strongly acidic soils, the edge surfaces of kaolinite are positively charged and act as an anion exchanger.

Iron and aluminum oxides occurring in soils exhibit only variable charge with a high point of zero charge, typically between pH 8.5 and 9.5 (Table 5.6; Fig. 5.7). These oxide surfaces are therefore positively charged in acidic soils, while their surface charge is very low in neutral to weakly alkaline soils. Especially in acidic soils, oxides act as anion exchangers. Allophanes and imogolites also carry only variable charge, with a point of zero charge in the alkaline pH range (pH_{PZC} ≈ 8.5). Under acidic conditions, allophanes and imogolites are therefore predominantly positively charged and act as anion exchangers.

Humic substances have variable charges, mainly originating from the deprotonation of

Table 5.6 Points of zero charge (pH_{PZC}) of several soil minerals in the absence of CO_2 and specifically adsorbing cations and anions

Mineral	Point of zero charge (pH_{PZC})
Oxides	
Ferrihydrite	8.5–9.5
Goethite	8.5–9.5
Hematite	8.5–9.5
Gibbsite	8.5–9.5
Rutile and anatase	5.0–6.0
Birnessite	3.0–4.0
Silicates	
Allophane	8.0–9.0
Kaolinite	4.0–5.0
Illite, smectite	2.0–3.0
Feldspar	2.0–3.0
Quartz	2.0–3.0

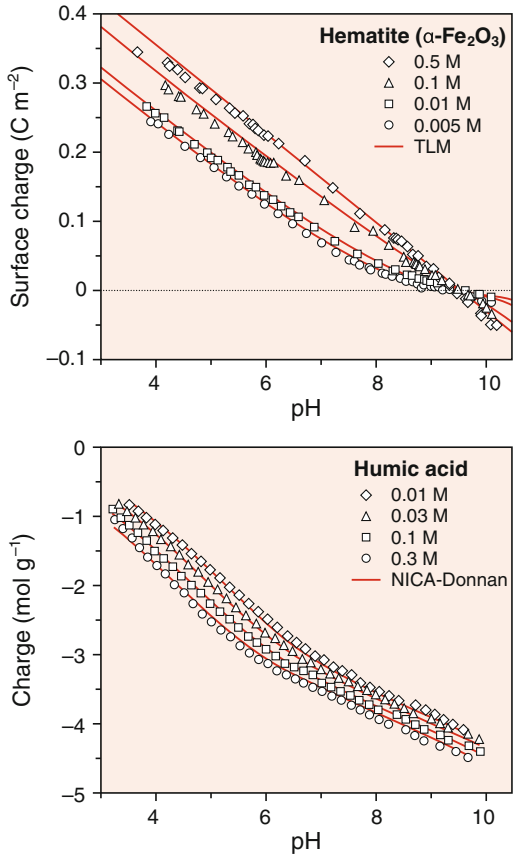

Fig. 5.7 Acid-base titrations of pure hematite (α-Fe_2O_3) (Christl and Kretzschmar 1999) and of humic acid isolated from an organic surface horizon (Christl et al. 2000) at different ionic strengths. For hematite, the titration curves intersect at the point of zero charge at pH 9.3. Below this, the surface charge is positive. For humic acid, there is no common intersection point and the charge is negative over the entire pH range

carboxyl (–COOH) and phenolic OH groups. These groups are Brønsted acids of varying strength, i.e. they can each donate one proton and then carry a negative charge (e.g. R-COOH → R-COO^- + H^+). The pK_a values of carboxylic acids are in the strongly to weakly acidic pH range, while phenols only donate a proton in the neutral to alkaline range. Carboxyl groups therefore contribute most to the negative charge of humic substances. In addition to these acid groups, humic substances also have base groups that can accept protons and are then positively charged (e.g. amino groups, $-NH_3$). However, the concentrations of such groups are much lower than those of acid groups, so that the net charge of humic substances is always negative (Fig. 5.7).

The points of zero charge given in Table 5.6 apply for pure mineral phases in contact with aqueous solutions in the absence of specifically adsorbing anions or cations. In comparison, the points of zero charge of iron and aluminum oxides in soils can be considerably lowered by the specific adsorption of anions, e.g. HCO_3^-, HPO_4^{2-}, and organic acids (including fulvic and humic acids).

5.5.1.6 Surface Charge in Soils

Based on the charging properties of different soil components, the surface charge of soils depends on its solid phase composition (e.g. clay minerals, oxides, organic matter), the pH value, and the concentrations of specifically adsorbing anions, cations, and organic matter. Figure 5.8 shows several examples for the positive and negative surface charge in soils, determined from cation and anion adsorption as a function of pH.

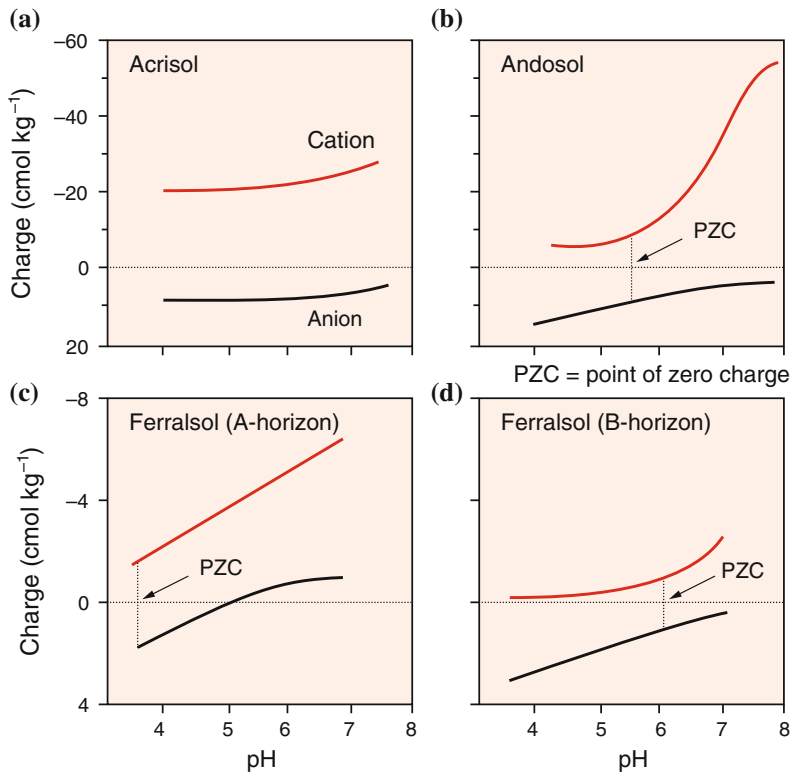

Fig. 5.8 Positive and negative surface charge in soils differing in clay mineralogy and organic matter content, determined from non-specific anion and cation adsorption. **a** Acrisol developed from graywacke, New Zealand, subsoil with similar proportions of 2:1 and 1:1 clay minerals and **b** Andosol developed from rhyolite, New Zealand, subsoil with 100 % allophane (after Fieldes and Schofield 1960). **c** Ferralsol developed from basalt, Brazil, with ~90 % gibbsite, goethite and hematite and ~10 % kaolinite, A horizon with 2.5 % C_{org} and **d** corresponding B horizon with 0.7 % C_{org} (after van Raij and Peech 1972)

The net charge of weakly to moderately weathered soils (Fig. 5.8, e.g. Acrisol) is negative across the entire pH range, because these soils still contain considerable amounts of 2:1 layer silicates with negative permanent surface charge. Additionally, organic matter carrying negative variable charge can significantly contribute to the cation exchange capacity (CEC, Sect. 5.5.2.1), especially in topsoils. Even under acidic conditions, the positive surface charge on oxide surfaces is comparably low, so that the anion exchange capacity (AEC) of these soils is always much lower than the CEC. In topsoils, the positive charge on oxide surfaces is further diminished or even reversed by specifically adsorbed organic substances or phosphate.

In contrast, mainly Fe and Al oxides and the clay mineral kaolinite dominate the clay fraction of highly weathered tropical soils (Fig. 5.8, e.g. Ferralsol). The organic matter content is particularly low in the subsoil (B horizon). Especially under acidic conditions, these soils have more positive than negative surface charge and can store more anions than cations through ion exchange. The CEC of these soils is very low (<10 $cmol_c\ kg^{-1}$), because kaolinite does not have much negative permanent charge and the pH is close to the point of zero charge of edge surfaces of kaolinite ($pH_{PZC} \approx 4.8$), resulting in low variable charge as well. Only the organic matter in the topsoil is capable of storing considerable amounts of cations. If the topsoil is eroded, these soils loose a large portion of their storage capacity for exchangeable Ca^{2+}, Mg^{2+} and K^+.

The CEC is higher (up to 50 $cmol_c\ kg^{-1}$) in volcanic soils rich in allophane (Fig. 5.8, e.g. Andosol), although allophanes also only carry variable charge. This is due to the high concentration of reactive hydroxyl groups at the surfaces of allophanes, and the often strong accumulation of organic matter in such soils.

5.5.2 Ion Exchange

Ion exchange plays a vital role in the storage of plant-available nutrients in soils, especially Ca^{2+}, Mg^{2+}, K^+ and NH_4^+, but also in the behavior of trace metals (e.g. Cd^{2+}, Zn^{2+}) and anions (e.g. Cl^-, NO_3^-). The term **ion exchange** is defined as the nonspecific adsorption of ions on oppositely charged surfaces, whereby the ions are mainly held at the surface by electrostatic (Coulomb) forces and can be easily exchanged by other ions in the soil solution. The following will mainly focus on cation exchange, because the negative surface charge strongly dominates in most soils. However, the important principles of cation exchange also apply to the nonspecific adsorption of anions onto positively charged surfaces. Anion exchange mainly plays a role in acidic, highly weathered soils (e.g., Ferralsols) and volcanic soils (Andosols).

5.5.2.1 Cation Exchange Capacity (CEC)

The sum of all permanent and variable negative surface charges in a soil, which is balanced by exchangeable cations, corresponds to the **effective cation exchange capacity** (CEC_{eff}, in $cmol_c\ kg^{-1}$). It is usually determined from the sum of exchangeable major cations (Ca^{2+}, Mg^{2+}, K^+, Na^+, Al^{3+}, H^+) at the soil's native pH. Inversely, the sum of all positive surface charges of a soil corresponds to its anion exchange capacity (AEC), which is also pH-dependent.

The fraction of the CEC_{eff} occupied with the **base cations**[7] Ca^{2+}, Mg^{2+}, K^+, and Na^+, is called effective **base saturation** (*BS*). It is defined as

$$BS_{\mathrm{eff}}(\%) = \frac{2q_{\mathrm{Ca}} + 2q_{\mathrm{Mg}} + q_{\mathrm{K}} + q_{\mathrm{Na}}}{\mathrm{CEC_{eff}}} \times 100 \tag{5.32}$$

where q_i represents the concentration of exchangeable cation i (in mmol kg^{-1}).

If the CEC of a soil is determined in a buffered solution at pH 7 to 8, it is called **potential**

[7]The cations Ca^{2+}, Mg^{2+}, K^+ and Na^+ are called **base cations** in soil science, although they are not bases in a chemical sense. The term refers to the fact that the hydroxides of these cations (e.g. NaOH, KOH) are strong bases. The cations H^+ (or H_3O^+) and Al^{3+} are called **acid cations**. Al^{3+} ions in an aqueous solution act as acid, because they can release protons through hydrolysis reactions.

cation exchange capacity (CEC_{pot}). In acidic soils the CEC_{eff} is usually smaller than the CEC_{pot}, because raising the pH results in increased negative variable surface charge. The difference between CEC_{eff} and CEC_{pot} is particularly pronounced in acidic organic-rich sandy soils, highly weathered kaolinitic soils, and allophane-rich soils, where the relative contribution of variable charge to total surface charge is high. The CEC_{pot} may be interpreted as the maximum CEC that can be achieved by liming an acidic soil to increase the soil's pH. However, the CEC_{pot} is primarily used as a quantitative parameter in soil classification. According to Eq. (5.32), the base saturation can also be calculated relative to the potential CEC (BS_{pot}). This value is used in soil classification as indicator for the soil nutrient status.

The effective CEC of soils varies widely, with extreme values of <1 $cmol_c\ kg^{-1}$ (e.g. pure sands) and >200 $cmol_c\ kg^{-1}$ (e.g. strongly humified peats). The clay and humified organic matter contents, clay mineralogy, and soil pH are the most important factors influencing the CEC_{eff}. The contribution of humic substances to the CEC_{eff} increases with increasing soil organic matter content and with increasing soil pH. It often accounts for 25–35 % of the CEC_{eff} in Ap horizons of loamy, silty, and clayey soils used for agriculture, 40–50 % in Chernozems due to the high soil organic matter content, more than 50 % in sandy soils, O and A horizons of grassland and forest soils and in the Bh horizons of Podzols, and finally often close to 100 % in peats.

The potential CEC of a soil depends primarily on its clay content and clay mineralogy, as well as on its organic matter content. The organic matter contributes between 60 and 300 cmol kg^{-1} of humus to the CEC_{pot}, depending on the degree of humification (Sect. 3.4.2).

In soils containing predominantly 2:1 layer silicates in the clay fraction (illite, vermiculite, smectite), the potential CEC of the clay fraction[8] is often 40–60 $cmol_c\ kg^{-1}$, while the fine and medium silt fractions have much lower values. For soils with 2–3 % humus, this results in mean CEC_{pot} ranges of 5–10 $cmol_c\ kg^{-1}$ for sands, 10–25 for sandy loams, loams and silt loams, and 20–50 for clay loams and clays, respectively. In contrast, kaolinitic-oxidic Acrisols and Ferralsols only have a CEC_{pot} < 5–16 $cmol_c\ kg^{-1}$ of clay. For this reason, the CEC in deeper horizons of these soils is usually below 3 $cmol_c\ kg^{-1}$, however, it can increase to up to 10 $cmol_c\ kg^{-1}$ in the mineral topsoil due to the contribution of humus. Allophane-rich soils (Andosols) have CEC_{pot} values ranging from 10 to 50 $cmol_c\ kg^{-1}$, with a variable charge fraction of 80–90 %.

5.5.2.2 Cation Exchange

Cation exchange reactions on mineral surfaces in contact with aqueous solutions can be described as kinetically fast, fully reversible, and charge balanced. The overall kinetics of cation exchange in soils, however, is often limited by slow **diffusion** of cations between the bulk solution and exchanger surfaces. While chemical equilibrium with external surfaces is reached rapidly, slow diffusion through micropores of soil aggregates, the interlayers of clay minerals (e.g. vermiculites, smectites), or thin water films in dry soils limits the overall rates of cation exchange.

The most important surfaces in soils acting as cation exchangers are the basal surfaces and interlayers of clay minerals with permanent negative charge, and the deprotonated acid groups of soil organic matter (e.g. carboxyl, $R\text{-}COO^-$). The surfaces of oxides and edges of clay minerals play a minor role for cation exchange, if at all. The affinity of different cations to negatively charged surfaces depends strongly on their charge (valence) and size (hydrated radius). The higher the valence, the stronger the cations are attracted to negatively charged surfaces by electrostatic forces, i.e. their affinity to the surface increases (e.g. $Na^+ < Mg^{2+} < Al^{3+} < Th^{4+}$). For

[8]Despite their low charge density, vermiculites and smectites always have a higher cation exchange capacity (CEC) than illites, because in addition to the external surfaces, the interlayers are also accessible to cation exchange. With illites, the majority of the structural

(Footnote 8 continued)
negative charge is compensated by non-exchangeable K^+ ions in the interlayers, so that the CEC is lower. Kaolinite and halloysite have no (or very little) permanent negative charge.

cations with the same valence, the affinity increases with increasing ionic radius (e.g. $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$). This correlation can be explained by the fact that smaller cations have a higher hydration energy, and thus a thicker hydration shell in aqueous solutions, than larger cations of the same valence (Table 5.7). For this reason, the **hydrated radius** of the cations (i.e. radius including the hydration shell) increases in the opposite sequence than the actual ionic radius (e.g. $Cs^+ < Rb^+ < K^+ < Na^+ < Li^+$). The lower hydration energy allows cations with a larger ionic radius to approach the surface more closely than smaller, but more strongly hydrated cations. Because electrostatic attraction decreases with the square of the distance to the surface, larger cations have a higher affinity to the exchanger surface than smaller cations. This **hydration effect** is particularly pronounced in monovalent cations.

The affinity of Cs^+, Rb^+, K^+ and NH_4^+ to basal surfaces and interlayers of 2:1 clay minerals is additionally increased by the fact that by losing their hydration shell, these cations can be pulled into the ditrigonal cavities formed by the basal oxygen atoms of Si-tetrahedral sheets (Sect. 2.2.5), where they are held even more strongly by electrostatic forces. In the same way, the adsorption of dehydrated K^+ ions in the interlayers of vermiculites and expanded edges of illites causes the interlayers to collapse to d(001) = 1 nm, and K^+ is then fixed within these interlayers (**K^+ fixation**, Sect. 9.6.4). Even if the relative fraction of such highly specific sorption sites is low, they are still significant because the K^+ saturation of many soils is only a few percent of the CEC (Table 5.8).

The specificity for NH_4^+ and Cs^+ is similarly strong or even stronger than for K^+. Because they collapse the interlayers, both cations can retard (NH_4^+) or completely block (Cs^+) the liberation of K^+ from interlayers. However, blocking by NH_4^+ is of limited significance if nitrification, like in most aerated soils, maintains the NH_4^+ concentration of the soil solution so low that NH_4^+ is desorbed. Radioactive ^{137}Cs from nuclear bomb tests and nuclear accidents (e.g. in Chernobyl 1986), which entered the soils through precipitation, has remained almost completely immobile in soils over decades, due to the strong fixation by clay minerals (Sect. 10.2.6).

In saline soils, the salt concentration in the soil solution also influences the cation saturation of the exchanger surfaces. The ratio of monovalent to divalent cations (e.g. Na^+/Ca^{2+}) on the exchanger surfaces tends to increase with increasing salt concentration. Inversely, dilution of the soil solution, e.g. through rainwater, leads to an exchange of Na^+ for Ca^{2+} and thus a reduction in the Na^+ saturation of the cation exchanger surfaces. The relationships between the cation concentrations in solution and on exchanger surfaces can be described quantitatively using cation exchange equations (Sect. 5.5.6.2).

Table 5.7 Ionic radius (r_i), hydration energy (ΔH_h) and hydrated radius (r_h) of mono-, di-, and trivalent cations (after Essington 2004)

Cation	r_i (pm)	Z^2/r_i (pm^{-1})	ΔH_h (kJ mol^{-1})	r_h (pm)
Li^+	90	0.0111	−515	382
Na^+	116	0.0086	−405	358
K^+	152	0.0066	−321	331
Rb^+	166	0.0060	−296	329
Cs^+	181	0.0055	−263	329
Mg^{2+}	86	0.0465	−1922	428
Ca^{2+}	114	0.0351	−1592	412
Sr^{2+}	132	0.0303	−1445	412
Ba^{2+}	149	0.0268	−1304	404
Al^{3+}	67	0.1343	−4660	480

The ratio between the squared ion valency and the ionic radius (Z^2/r_i) is closely correlated with the hydration energy

5.5.3 Surface Complexation of Cations and Anions

The adsorption of ions or molecules in a defined spatial arrangement at the surface (i.e. interatomic distances, orientation, coordination with surface groups) is called **surface complexation**. **Outer-sphere** surface complexes are formed when the sorbate ion or molecule keeps its first hydration shell and is adsorbed to oppositely charged surfaces by electrostatic forces and/or

Table 5.8 Soil pH (in 0.01 M $CaCl_2$), organic carbon (C_{org}) content, potential and effective cation exchange capacity (CEC_{pot} and CEC_{eff}) and cation saturation in selected mineral topsoils under field and forest (Central Europe) as well as topsoils from other climates

	Soil pH	C_{org}	CEC_{pot}	CEC_{eff}	Cation Saturation (% of CEC_{eff})				
		(%)	($cmol_c$ kg^{-1})		Al	Ca	Mg	K	Na
Arable soils (Germany)									
Luvisol (loess, Straubing)	6.3	1.4	17	14	0	80	15	5	<1
Chernozem (loess, Hildesheim)	7.2	1.6	18	18	0	90	9	<1	<1
Podzol (sand, Celle)	5.2	2.5	12	3	0	86	6	7	1
Vertisol (Lias clay, Franconia)	6.7	2.4	22	17	0	83	8	9	0
Gleysol (deltaic clayey sediment, Wesermarsch)	5.1	2.7	37	25	0	50	42	3	5
Forest soils (Germany)									
Podzol (granite, Bavarian Forest)	2.6	11.7	–	7	65	22	6	5	2
Stagnosol (loess, Bonn)	3.6	4.9	15	7	79	16	3	2	0
Cambisol (loess/pumice, Mount Vogelsberg)	2.9	19.8	60	12	85	6	4	5	0
Soils from other climates									
Vertisol (Sudan)	6.8	0.9	47	47	0	71	25	<1	4
Andosol (Hawaii)	4.5	11.7	53	13	4	71	20	4	2
Ferralsol (Brazil)	3.5	2.8	13	3	89	3	4	3	1
Acrisol (Puerto Rico)	3.5	3.3	26	7	72	15	8	3	2
Solonchak (Arizona, USA)	9.9	0.4	36	–	0	45	6	3	47

hydrogen bonding (see Sect. 5.3.2.1). This type of adsorption is relatively weak and the adsorption typically exhibits an ionic strength dependence. **Inner-sphere** complexes, in contrast, are formed when the sorbate ion or molecule loses part of its hydration shell and instead coordinates directly with one or several surface atoms in the first shell, e.g. with oxygen atoms from surface hydroxyl groups of oxides or edges of clay minerals. This type of adsorption is stronger and typically exhibits much less ionic strength dependence. It is called **specific adsorption** or **chemisorption**. The specific adsorption not only depends on the charge of surfaces and sorbate ions or molecules, but also on the type, arrangement, and reactivity of functional groups at the mineral surface.

Figure 5.9 shows a diagram depicting different types of surface complexes. Strongly hydrated monovalent ions, such as Cl^-, NO_3^-, and Na^+, form weak outer-sphere surface complexes or reside in a diffuse ion swarm surrounding an oppositely charged surface. In contrast, many oxyanions (e.g. $H_2PO_4^-/HPO_4^{2-}$; $H_2AsO_4^-/HAsO_4^{2-}$), transition metals (e.g. Cu^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}), and low-molecular weight organic acids (e.g. oxalate, malate) form much more stable inner-sphere surface complexes with reactive hydroxyl groups of oxide surfaces and edges of clay minerals. Depending on whether the sorbate ion is coordinated with only one or two surface groups, the complexes are called **monodentate** or **bidentate**, respectively. Furthermore, the complexes are called **mononuclear** or **binuclear** if the involved surface groups are coordinated with one or two metal nuclei of the sorbent.

The formation of a monodentate, mononuclear surface complex of Cu^{2+} on an oxide surface can be represented by the following equation:

$$\equiv SOH^{0.5-} + Cu^{2+} \rightleftharpoons \equiv SOCu^{0.5+} + H^+ \quad (5.33)$$

where $\equiv SOH^{0.5-}$ represents a surface hydroxyl group. The equation reflects that the formation of

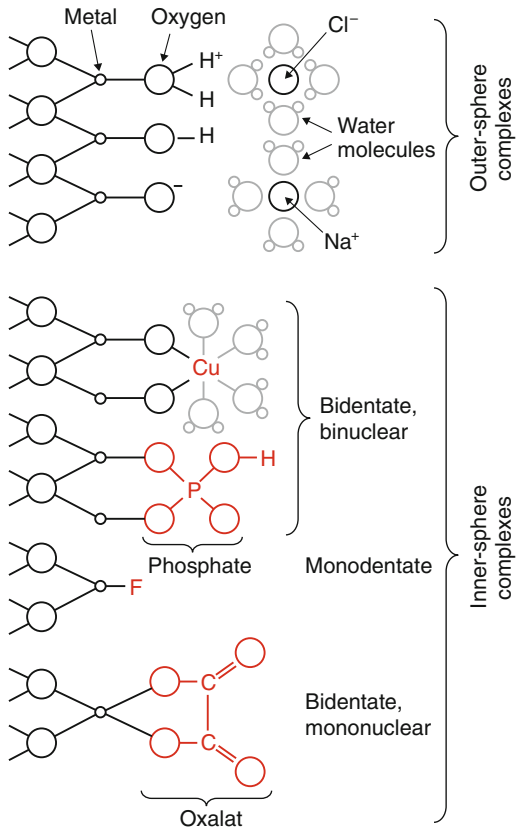

Fig. 5.9 Examples for various types of surface complexes on an oxide surface (schematic): Cl^- and Na^+ ions form outer-sphere complexes through electrostatic attraction to positively or negatively charged surface groups, respectively. Cu^{2+} and HPO_4^{2-} form bidentate, binuclear inner-sphere complexes. F^- forms a monodentate inner-sphere complex, and oxalate forms a bidentate, mononuclear inner-sphere complex (after Stumm 1992)

inner-sphere complexes with metal cations on oxide surfaces leads to the liberation of protons, although the stoichiometry can take different values. Decreasing solution pH would shift the equilibrium to the left, i.e. adsorption of Cu^{2+} is expected to decrease with decreasing pH. The equation also illustrates that the specific adsorption of metal cations can lead to addition of positive charge to the mineral surface.

The pH-dependency of the adsorption of Cu^{2+}, Pb^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, and Mn^{2+} on goethite is shown in Fig. 5.10. All metal cations demonstrate strong adsorption at pH values that are considerably below the point of zero charge of the oxide

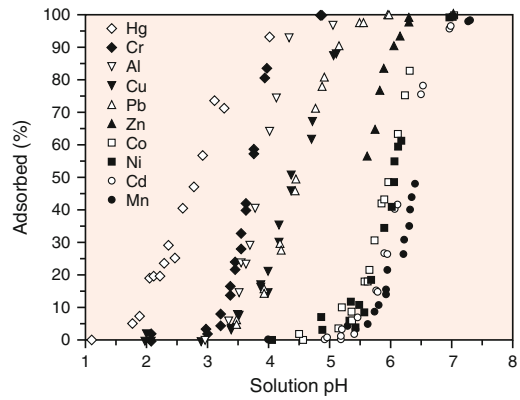

Fig. 5.10 Adsorption of Hg^{2+}, Cr^{3+}, Al^{3+}, Cu^{2+}, Pb^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+} and Mn^{2+} on goethite as a function of solution pH (after Fischer et al. 2007)

surface. Thus, they adsorb onto a positively charged mineral surface, which can be explained by the formation of inner-sphere surface complexes overcoming the electrostatic repulsion. The steep increase of adsorption within 2–3 pH units is typical for metal cations adsorbing to oxide surfaces, and is called **adsorption edge.** The pH at which the adsorption edge occurs depends somewhat on experimental conditions (e.g. sorbent and sorbate concentrations), but it also varies systematically among different metals: Cu^{2+} and Pb^{2+} are more strongly adsorbed at lower pH than e.g. Ni^{2+} and Mn^{2+}. The adsorption sequence ($Hg^{2+} > Cr^{3+} > Al^{3+} > Cu^{2+} \sim Pb^{2+} > Zn^{2+} > Co^{2+} \sim Ni^{2+} > Cd^{2+} > Mn^{2+}$) correlates with the respective first hydrolysis constants of the metals, indicating that hydroxo-species ($MeOH^+$) may play an important role in the formation of the surface complexes.

Anions can also be specifically adsorbed to oxide surfaces and edges of clay minerals. The adsorption of phosphate (HPO_4^{2-}) on an oxide surface can be represented e.g. by the following equation:

$$\equiv SOH^{0.5-} + H^+ + HPO_4^{2-} \rightleftharpoons \equiv SHPO_4^{1.5-} + H_2O \qquad (5.34)$$

Here, the surface hydroxyl groups $\equiv SOH^{0.5-}$ are protonated and then substituted by the ligand HPO_4^{2-} under liberation of H_2O. The specific

adsorption of anions on oxide surfaces is therefore also called **ligand exchange reaction**. In the surface complex $\equiv SHPO_4^{1.5-}$, one oxygen atom is coordinated both with P and a structural metal center at the surface of the oxide; it is thus a monodentate mononuclear complex. Phosphate can potentially also adsorb as a bidentate, binuclear or bidentate mononuclear complex. The equation accounts for the fact that protons are consumed during the specific adsorption of anions on an oxide surface, and the surface becomes more strongly negatively charged, although the exact stoichiometry may again exhibit different values. The reaction equilibrium is shifted to the left when the pH of the solution is increased. The adsorption of phosphate and other oxyanions on oxide surfaces therefore typically decreases with increasing pH. The pH-dependency of anion sorption also depends on the speciation of the sorbate anions in the solution, whereby the slope of the curve changes near pH values corresponding to the pK_a values of the respective acid (e.g. for phosphate: H_3PO_4 with $pK_1 = 2.15$; $pK_2 = 7.20$ and $pK_3 = 12.38$). Maximum adsorption is typically observed at a pH close to or below the acid's pK_1 value, because the undissociated (and thus uncharged) acid dominates when $pH < pK_1$ (Fig. 5.11).

The oxyanions arsenate, molybdate, and selenite are also adsorbed in a similar way as phosphate. In comparison, the anions sulfate, chromate, arsenite, and selenate are more weakly adsorbed, possibly also through the formation of outer-sphere complexes. The varying bonding strength causes the anions to compete with one another (anion competition). Thus, for example, the adsorption of arsenate and particularly arsenite on Fe oxides is reduced in the presence of phosphate, silicate, and organic anions.

Because of their high specific surface area, ferrihydrite and allophone have a particularly high sorption capacity for phosphate and other anions, while goethite and hematite sorb less. Gibbsite, calcite, and quartz are sorbents with a lower sorption capacity for phosphate. Humic substances are also capable of sorbing some anions such as arsenite or arsenate, e.g. if complexed Fe^{3+} is bound to the functional groups or if arsenite is complexed by reduced thiol groups of humic substances.

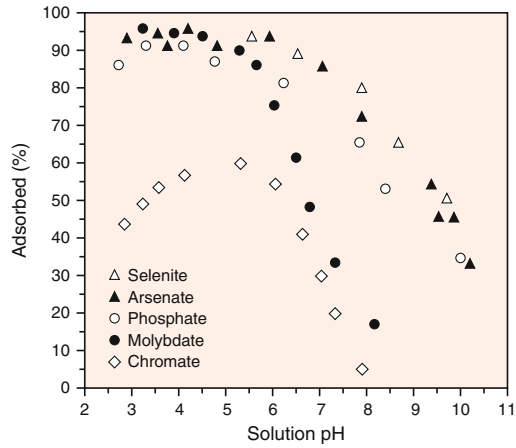

Fig. 5.11 Adsorption of anions on goethite as a function of solution pH (6 g/l goethite with 0.3 mM PO_4, AsO_4, SeO_3, MoO_4 and CrO_4 (after Okazaki et al. 1989)

5.5.4 Sorption of Organic Substances on Mineral Surfaces

Natural organic substances in soils, including humic substances, are mostly negatively charged and have reactive functional groups (e.g. carboxylic, phenolic). Therefore, they can be adsorbed by electrostatic forces and specific interactions with surface functional groups on oxide and clay mineral surfaces. The sorption of humic substances to mineral surfaces generally increases with decreasing pH and increasing ionic strength of the soil solution. To a more limited extent, humic substances are also adsorbed to the basal surfaces of layer silicates, presumably by hydrophobic interactions. Aromatic and high-molecular weight humic matter fractions are preferentially adsorbed compared to aliphatic and low-molecular weight humic substances.

The adsorption of organic matter on mineral surfaces in soils with high contents of poorly-crystalline mineral phases leads to an

inhibition of microbial decomposition, and thus, to a stabilization of the soil organic matter. This results in the formation of stable mineral-humus complexes, which contributes to the sequestration of organic carbon in these soils. Inversely, organic substances inhibit the transformation of poorly-crystalline phases into more crystalline minerals (e.g. iron oxides).

Adsorption of natural organic substances typically also adds negative charge to the mineral surface, so that the net particle charge becomes more negative. For this reason, iron and aluminum oxide particles coated with adsorbed organic substances are often negatively charged, even under acidic conditions. These interactions between mineral surfaces and organic substances have a great influence on the adsorption of metal cations and anions in soils. Adsorbed organic substances increase the adsorption of metal cations. Experiments with iron oxides, kaolinite, humic acids, and fulvic acids have shown that these effects can not only be explained by the addition of sorption sites, but that electrostatic interactions between the sorbents also play a role. Adsorbed organic substances typically cause a decrease in the adsorption of anions, which is explained by the competition for sorption sites and increased repulsive electrostatic forces. Organic substances can therefore lead to a mobilization of phosphate, arsenate, and other anions in soils.

5.5.5 Sorption Kinetics

Adsorption and desorption reactions rarely reach true chemical equilibrium in soils, which can complicate the prediction of the behavior of substances in soils (e.g. reactive transport). While cation exchange processes take place rapidly, the kinetics of the formation of inner-sphere complexes is slower. Also, desorption is generally much slower than adsorption, especially in the case of inner-sphere surface complexation. This can lead to cases where the experimentally determined adsorption isotherm does not concur with the corresponding desorption isotherm, which is often interpreted as **sorption hysteresis** (Fig. 5.12). In many cases, however, the sorption reactions are still reversible and the observed hysteresis is caused by slow desorption kinetics.

Sorption kinetics is always limited by the slowest of all reaction steps. The most important steps of adsorption are: (1) **diffusion** of the sorbate through the bulk solution toward the surface of the sorbent phase, (2) diffusion through the stationary water film at the surface (film diffusion), (3) adsorption at the surface, e.g. by formation of a surface complex, (4) other changes in the surface speciation, e.g. conversion from a monodentate to a bidentate surface complex, (5) surface diffusion, e.g. from sorption sites with lower to sites with higher affinity for the sorbate,

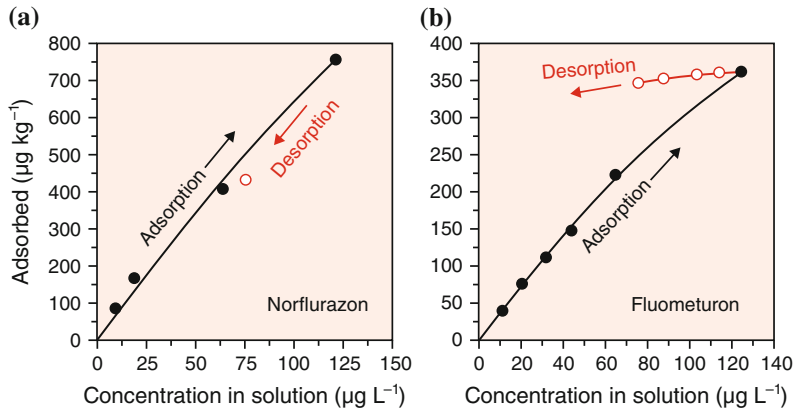

Fig. 5.12 Hysteresis of adsorption and desorption processes. **a** Sorption of norflurazon and **b** of fluometuron on a silt-loam surface soil (after Essington 2004)

and (6) micropore diffusion (in porous sorbents). Micropore diffusion not only plays a very important role in porous aggregates of poorly-crystalline minerals, such as ferrihydrite, but also in more crystalline oxides, such as goethite. Diffusion in the interlayers of clay minerals can also be considered as micropore diffusion. In some cases, slow sorption kinetics can also be caused by the slow formation of surface precipitates. For example, the sorption of Ni^{2+} or Zn^{2+} on clay minerals under neutral pH conditions leads to the slow formation of new Zn or Ni solid phases on the surfaces of clay minerals. These solid phases were identified using spectroscopic methods (e.g. EXAFS) to be layered double hydroxides (LDH) or layer silicate structures containing Ni or Zn in octahedral positions.

5.5.6 Sorption Modeling

The modeling of adsorption and desorption processes in soils is an important prerequisite for the prediction of reactive transport (e.g. leaching of herbicides or heavy metals) and buffering of the soil solution when substances are added or removed (e.g. fertilization, contamination, plant uptake, leaching). This chapter introduces different approaches of modeling sorption equilibria.

5.5.6.1 Sorption Isotherms

Adsorption equilibria in soils can be assessed experimentally by determining **sorption isotherms**. Sorption isotherms represent the relationship between the sorbed concentration of the sorbate (in mol kg^{-1}) as a function of its equilibrium concentration (or activity) in the solution (in mol L^{-1}) under otherwise constant conditions (e.g. temperature, pH, concentrations of other ions). Sorption isotherms represent an attempt to characterize sorption equilibria, but do not provide any information on the kinetics of the adsorption or desorption processes. Sorption isotherms can be modelled using various empirical equations, such as the Freundlich or the Langmuir isotherm equations (Fig. 5.13).

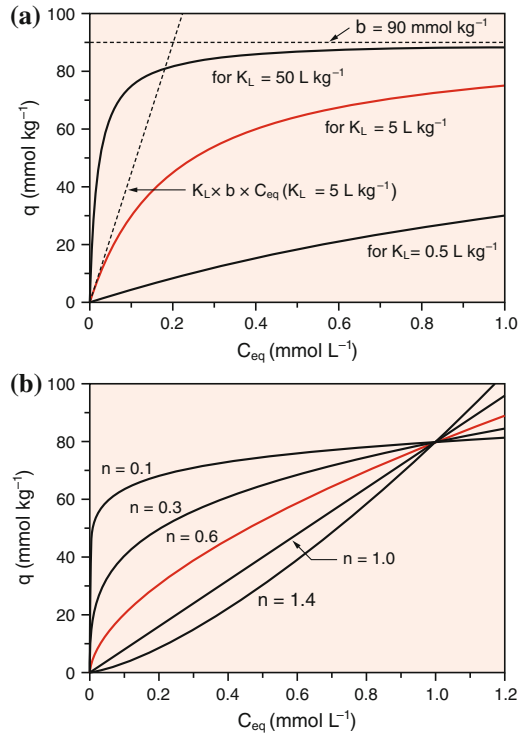

Fig. 5.13 Examples for sorption isotherms calculated according to the **a** Langmuir and **b** Freundlich equation. **a** Three Langmuir isotherms with the same sorption maximum (b = 90 mmol kg^{-1}), but with different bonding strengths between the sorbate and sorbent (K_L = 0.5; 5 and 50 L kg^{-1}). **b** Five Freundlich isotherms with K_F = 80 and n = 0.1; 0.3; 0.6; 1:0 and 1.4. One example each is highlighted in *color*

The strictly empirical Freundlich isotherm is given by:

$$q = K_f c^n \tag{5.35}$$

where q is the adsorbed concentration of the sorbate (in mol kg^{-1}) and c is the dissolved concentration (in mol L^{-1}). The Freundlich coefficient K_f relates to the affinity of the substance to the surface of the sorbent, while the parameter n determines the curvature of the sorption isotherm. If $n = 1$, the sorption isotherm is linear and K_f is equal to a constant distribution coefficient K_d. If $n < 1$, the shape of the sorption isotherm is concave and describes a decreasing sorption affinity with increasing concentration of the sorbate. The Freundlich isotherm does not

describe a sorption maximum, and it is therefore only applicable in concentration ranges considerably below full surface coverage (and should never be extrapolated!). If $n > 1$, the shape of the sorption isotherm is convex and it describes an increasing affinity of the sorbent with increasing concentration at the sorbent surface (this is less common, but can occur for some organic sorbates). The logarithmic form of the Freundlich isotherm is also commonly used:

$$\log q = \log K_f + n \log c \tag{5.36}$$

This equation represents a straight line with slope n in a plot of log q versus log c. The Freundlich isotherm is commonly applied to describe the adsorption of trace metals and pesticides in soils.

The Langmuir isotherm is given by:

$$q = \frac{bK_L c}{1 + K_L c} \tag{5.37}$$

where b is the adsorption maximum (in mol kg^{-1}) and K_L is the Langmuir coefficient (in L kg^{-1}). K_L reflects the affinity of the sorbate to the sorbent surface, and bK_L is the initial slope of the isotherm at very low sorbate concentrations (i.e. at $c \rightarrow 0$). The Langmuir isotherm was originally developed for the adsorption of gas molecules onto solid surfaces. At the time, Irving Langmuir made the following assumptions: (1) the surface is homogenous, i.e. all bonding sites are equal, (2) adsorbed molecules do not interact with each other, (3) there is only one sorption mechanism, and (4) only a single layer of adsorbed molecules is formed (monolayer). The adsorption maximum is reached when all of the sorption sites are occupied. Under similar assumptions, the Langmuir equation can also be applied to the adsorption of dissolved substances on solid surfaces. However, all of these conditions are far from reality in soils, so that the Langmuir parameters b and K_L should only be interpreted as empirical parameters with little or no physical meaning.

The Freundlich and Langmuir equations only describe the adsorption as a function of sorbate concentration under otherwise constant conditions (e.g. pH, concentration of competing species). The parameters in the isotherm equations, therefore, must be determined for each set of given conditions of interest, and cannot be extrapolated to vastly different conditions or other soils. These equations also do not describe competitive adsorption involving several sorbate ions or molecules, nor can they account for the pH-dependency of many adsorption processes.

5.5.6.2 Cation Exchange Modeling

Cation exchange is generally modeled as a competitive adsorption process, in which the negative charge of sorption sites X^- is always balanced by equivalent amounts of positive charge of exchangeable cations. The exchange of cations with the same valence (e.g. Ca^{2+}–Mg^{2+}) is called **homovalent** ion exchange, and the exchange of cations with different valence (e.g. Ca^{2+}–Na^+) is called **heterovalent** ion exchange. Cation exchange processes can be described using reaction equations with defined stoichiometries. For example, the following equations can be used to describe Ca^{2+}–Mg^{2+} and Ca^{2+}–Na^+ exchange on a surface with exchange sites X^-:

$$X_2Mg + Ca^{2+} \rightleftharpoons X_2Ca + Mg^{2+} \tag{5.38}$$

$$2XNa + Ca^{2+} \rightleftharpoons X_2Ca + 2Na^+ \tag{5.39}$$

According to this equation, one Ca^{2+} replaces one Mg^{2+} or two Na^+ ions on the surface, whereby the substituted Mg^{2+} and Na^+ ions are released to the solution. The equilibrium of each of these two binary exchange reactions can be described using an **equilibrium constant** K_{ex}, according to the law of mass action (Sect. 5.3.2.2):

$$K_{ex} = \frac{\{X_2Ca\}\{Mg^{2+}\}}{\{X_2Mg\}\{Ca^{2+}\}} \tag{5.40}$$

and

$$K_{ex} = \frac{\{X_2Ca\}\{Na^+\}^2}{\{X_2Na\}^2\{Ca^{2+}\}} \tag{5.41}$$

where the curly brackets represent activities. The activities of dissolved ions can be calculated from measured concentrations and the

corresponding activity coefficients (Sect. 5.3.1). In contrast, the determination of the activities of adsorbed cations is problematic, which led to the formulation of different **selectivity coefficients**. For example, the VANSELOW selectivity coefficient K_V is based on the assumption that the activity of adsorbed cations under ideal conditions can be set to be equal to their molar fraction N_i on the exchanger surface. As a result, K_V for binary Ca–Na exchange [Eq. (5.39)] is:

$$K_v = \frac{N_{Ca}\{Na^+\}^2}{N_{Na}^2\{Ca^{2+}\}} \tag{5.42}$$

with

$$N_{Ca} = \frac{q_{Ca}}{q_{Ca} + q_{Na}} \tag{5.43}$$

and

$$N_{Na} = \frac{q_{Na}}{q_{Ca} + q_{Na}} \tag{5.44}$$

In contrast, the GAINES-THOMAS selectivity coefficient K_{GT} is based on the assumption that the activity of adsorbed cations corresponds to the charge equivalent fractions E_i on the exchanger surface. As a result, K_{GT} for binary Ca–Na exchange is:

$$K_{GT} = \frac{E_{Ca}\{Na^+\}^2}{E_{Na}^2\{Ca^{2+}\}} \tag{5.45}$$

with

$$E_{Ca} = \frac{2q_{Ca}}{2q_{Ca} + q_{Na}} \tag{5.46}$$

and

$$E_{Na} = \frac{q_{Na}}{2q_{Ca} + q_{Na}} \tag{5.47}$$

Inserting the two equivalent fractions into Eq. (5.45) and rearranging yields:

$$\begin{aligned} K_{GT} &= 2(2q_{Ca} + q_{Na})\frac{q_{Ca}\{Na^+\}^2}{q_{Na}^2\{Ca^{2+}\}} \\ &= 2CEC\frac{q_{Ca}\{Na^+\}^2}{q_{Na}^2\{Ca^{2+}\}} \end{aligned} \tag{5.48}$$

In a binary Ca–Na system, a modified GAINES-THOMAS selectivity coefficient $K_{GT}^* = K_{GT}/(2CEC)$ can be used instead of K_{GT}. This results in a simple relationship between the dissolved activities and the concentrations of Ca^{2+} and Na^+ adsorbed on the cation exchanger:

$$K_{GT}^* = \frac{q_{Ca}\{Na^+\}^2}{q_{Na}^2\{Ca^{2+}\}} \tag{5.49}$$

The GAPON selectivity coefficient K_G is based on adsorbed and dissolved concentrations and on a different formulation of the exchange reaction [see Eq. (5.39)], e.g. for heterovalent Ca–Na exchange according to:

$$X\mathrm{Na} + 1/2\mathrm{Ca}^{2+} \rightleftharpoons X\mathrm{Ca}_{1/2} + \mathrm{Na}^+ \tag{5.50}$$

For this reaction, K_G is given as

$$K_G = \frac{[X\mathrm{Ca}_{1/2}][\mathrm{Na}^+]}{[X\mathrm{Na}][\mathrm{Ca}^{2+}]^{1/2}} \tag{5.51}$$

The square brackets represent the concentrations of dissolved (in $mmol^{-1}$) and adsorbed cations (in $mmol_c\ kg^{-1}$), respectively. The GAPON equation is widely used in irrigation agriculture for predicting the Na^+ saturation of soils as a function of the concentrations of Na^+, Ca^{2+}, and Mg^{2+} in the irrigation water. Because Ca^{2+} and Mg^{2+} exhibit a similar exchange selectivity, the reaction

$$\begin{aligned} &X(\mathrm{Ca}+\mathrm{Mg})_{1/2} + \mathrm{Na}^+ \rightleftharpoons \\ &X\mathrm{Na} + 1/2(\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+}) \end{aligned} \tag{5.52}$$

enables the derivation of the Gapon selectivity coefficient for the substitution between Na^+ and the divalent cations Ca^{2+} and Mg^{2+}

$$K_G = \frac{[X\mathrm{Na}][\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+}]^{1/2}}{\left[X(\mathrm{Ca}+\mathrm{Mg})_{1/2}\right][\mathrm{Na}^+]} = \frac{ESR}{SAR} \tag{5.53}$$

with

$$ESR = \frac{[X\mathrm{Na}]}{\left[X(\mathrm{Ca}+\mathrm{Mg})_{1/2}\right]} \approx \frac{[X\mathrm{Na}]}{CEC - [X\mathrm{Na}]} \tag{5.54}$$

and

$$SAR = \frac{[Na^+]}{[Ca^{2+} + Mg^{2+}]^{1/2}} \quad (5.55)$$

The **exchangeable sodium ratio** (ESR) expresses the ratio between Na^+ and the divalent cations Ca^{2+} and Mg^{2+} on the exchanger surfaces, while the **sodium adsorption ratio** (SAR) expresses the Na^+ content of the water relative to the dissolved Ca^{2+} and Mg^{2+}. In irrigation agriculture, *SAR* is interpreted as an indicator for water quality, which enables an estimation of the risk of soil degradation due to excessive Na^+ saturation (ESP, exchangeable sodium percentage). Here, an ESP of 15 % is considered as the critical upper limit. The ESR can be converted to ESP using the following equation:

$$ESP = \frac{ESR}{1 + ESR} \times 100 \quad (5.56)$$

5.5.6.3 The Diffuse Double Layer

The charge of a solid surface in contact with an aqueous solution is always compensated by an excess of opposite ion charge close to the liquid-solid interface, i.e. a cation charge excess for a negatively charged surface and an anion charge excess for a positively charged surface, respectively. As a result, the ion composition in the solution close to the surface differs from that in the bulk solution (Fig. 5.14). The solid-liquid interface can be viewed as an electrical double layer, in which the charge of the solid surface is spatially separated from the excess charge in solution, creating an electrical field with an electrical potential that decreases with increasing distance from the charged surface. The magnitude and drop of this potential with increasing distance from the surface depend on the surface charge, and the concentrations and valence of adsorbed and dissolved ions. The potential at some distance from the surface influences the colloidal properties of the soil particles, especially their interactions with other particles (e.g. repulsion and attraction), and thus also affects colloid aggregation and dispersion processes (Sects. 6.2.1 and 6.2.2).

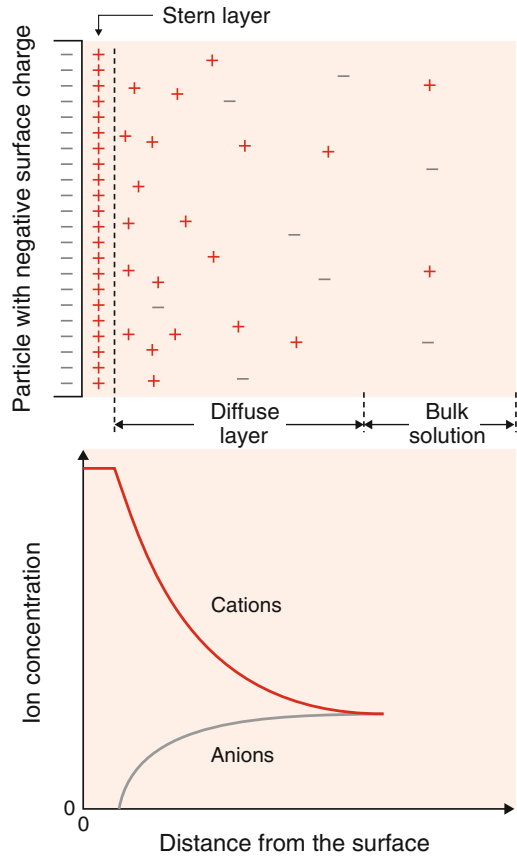

Fig. 5.14 Ion distribution (*top*) and concentration gradient (*bottom*) in the electrical double layer around a cation exchanger surface according to the Gouy and Stern model

Different models exist describing the structure of this electrical double layer, which can be used to model the distribution of sorbed ions on the sorbent surface and the relationship between surface charge and potential. Based on the considered forces between the sorbate and sorbent, these models can be assigned to two groups. The models in the first group only take account of electrostatic interactions and are based on the diffuse double layer model according to Gouy-Chapman. The models in the second group,

in contrast, also take account of the formation of surface complexes in addition to the diffuse layer. These are called **surface complexation models**.

The diffuse double layer model is suitable for sorption on the basal surfaces of layer silicates. Exchangeable cations accumulate as a diffuse cation swarm on these permanently negatively charged surfaces. In the ion swarm, the concentration of cations decreases with the distance from the surface in form of a BOLTZMANN distribution; in contrast, the anion concentration increases with increasing distance until it equals the bulk solution. The equilibrium bulk solution begins at the point where the sum of anion and cation charges in solution is zero.

This double layer model was refined by subdividing the ion swarm into an inner layer, lying close to the surface and densely occupied (STERN layer), and a diffuse outer layer, which most strongly affects the physical behavior of the colloidal particles (e.g. aggregation and dispersion). While the ions in the diffuse layer are completely hydrated, the ions in the STERN layer are presumably partly dehydrated and more strongly attracted by the surface charge of the sorbent. Higher valency ions such as Ca^{2+} and Al^{3+} are preferentially bound in the STERN layer, in contrast, Na^{+} preferentially resides in the diffuse layer. The cation fraction in the diffuse layer thus increases with increasing Na^{+} saturation of the cation exchanger surfaces.

5.5.6.4 Modeling of Surface Complexation on Mineral Surfaces

Various surface complexation models have been developed for the description of anion and cation adsorption on oxide surfaces and edges of clay minerals, including its pH and ionic strength dependence. Several examples for surface complexation models are: constant capacitance model (CCM), basic Stern model (BSM), triple layer model (TLM), Stern variable surface charge-variable surface potential (Stern VSC-VSP) model, one-pK model, and charge-distribution multi-site surface complexation (CD-MUSIC) model. All surface complexation models have the following features in common: (1) There is a specific number of sorption sites (≡*S*OH) per unit surface area (site density in m^{-2}), (2) The adsorption of protons and other ions and molecules on these sorption sites takes place according to a defined stoichiometry, which is expressed in the models using reaction equations, (3) The change in the surface charge and thus in the electrical potential at the surface through the adsorption of protons, metal cations and anions is taken into account, and (4) The effects of the surface charge on the adsorption of ions (electrostatic effects) are taken into account. The various models differ mainly in their formulation of the protonation reactions (1-p*K* vs. 2-p*K* approach) and in the conceptual description of the electrical double layer. For example, the BSM only accounts for one Stern layer and one diffuse layer, while the TLM allows the assignment of charges in three layers and thus a differentiation between inner-sphere and outer-sphere surface complexes, in addition to a diffuse layer. The CD-MUSIC model is the most differentiated, where in addition to the charge distribution, the model can account for the different reactivity of surface functional groups and thus the chemical heterogeneity of mineral surfaces.

5.5.6.5 Modeling Cation Binding to Organic Matter

Modeling cation binding to soil organic matter is a particular challenge, because the organic matter is chemically very heterogeneous and has a large number of functional groups with different affinities for protons and metal cations. In addition, the composition of organic matter varies depending on the vegetation, degree of humification, and other factors. Various modeling approaches have been developed and further improved in recent years for the comprehensive description of proton and metal binding to humic substances, including sorption competition and the pH and ionic strength dependence of sorption. The two most important models are the NICA-Donnan Model (NICA = non-ideal

competitive adsorption) and the Humic Ion-Binding Model VII.

In the NICA-Donnan model, the binding of protons and metal cations is described using the NICA equation, which can be derived from competitive Langmuir equations and continuous affinity distributions. Two types of functional groups with low and high pK_a values are taken into account, which are conceptually interpreted by some researchers as carboxyl and phenolic-OH groups. The DONNAN model takes account of electrostatic effects as a function of the ionic strength, describing humic substances as a DONNAN gel with negative charge and ionic strength-dependent volume.

Humic Ion-Binding Model VII, in contrast, assumes a discrete affinity distribution. Proton and metal cation binding is described by two groups of four log K values each, which are evenly distributed around a mean value. This helps in reducing the number of model parameters to be optimized. A BOLTZMANN factor is used to account for electrostatic effects, which depends on the charge of the cations and the ionic strength.

Both models are capable of describing the binding of protons and metal cations on humic and fulvic acids as well as other natural organic substances over a very wide range of concentrations. Extensive sets of parameters exist for both models, if more specific binding parameters are lacking.

5.6 Soil Reaction and pH Buffering

The pH value[9] of a soil (=soil reaction) reflects its development and the resulting soil chemical properties. It allows conclusions on the behavior of nutrients and contaminants, and on the soil's suitability for plant growth, habitat for soil organisms, and filter for pollutants. For this reason, soil pH (in addition to color, texture, and organic matter content) is considered to be the most important and meaningful **soil parameter** that can be easily measured in the field or laboratory.

The acidification of soils over the course of pedogenesis under humid climate conditions is a natural process, because (1) more protons are added or liberated per unit of time through precipitation or soil-internal processes than the soils are capable of neutralizing, and (2) the soluble products of all chemical reactions in which protons are consumed are leached with seepage water and are thereby lost from the soil. This leads to an increasing (and often irreversible) depletion of the soil's **buffer systems**, i.e. the acid neutralization capacity (ANC) of the soil decreases. The soil develops increasing **soil acidity**, which would require addition of bases (e.g. lime) to be neutralized, i.e. its base-neutralizing capacity (BNC) simultaneously increases. In arid climates, however, the alkaline weathering products are not leached out, so that these soils may exhibit **alkalinization** (e.g. with Na_2CO_3 accumulation). The following sections explain the causes and characteristics of soil acidity and alkalinity.

5.6.1 Soil Reaction

Most natural soils have pH values between 3 and 10. Table 5.9 shows a grouping scheme of soils according to their pH.

5.6.1.1 Alkaline Soils

Soils containing Ca carbonates (e.g. calcite) but no Na carbonates have a neutral to weakly alkaline pH (7.0–8.2). These include e.g. Calcaric Leptosols that developed on carbonate rocks. Soils only become more strongly alkaline if the bases are not leached out, but rather accumulate.

[9]The pH value of an aqueous solution is defined as the negative logarithm of the H^+ activity, $pH = -\log\{H^+\}$. The **soil pH** is the pH value that is established in an aqueous solution in equilibrium with the soil. In practice, 10 g of dry soil are mixed with 25 ml of 0.01 M $CaCl_2$ solution (or water), the suspension is agitated for at least 30 min, and then the pH of the solution is measured using an electrode.

Table 5.9 Classification of soil pH ranges (measured in 0.01 M $CaCl_2$) and examples for their occurrence

pH range	Classification	Occurrence
<3.0	Extremely acidic	Acid sulfate soils
3.0–3.9	Very strongly acidic	Podzols, Histosols (peat bogs)
4.0–4.9	Strongly acidic	Dystric Cambisols/Luvisols
5.0–5.9	Moderately acidic	Eutric Cambisols/Luvisols
6.0–6.9	Weakly acidic	Gypsic Solonchaks, Gypsisols
7.0	Neutral	
7.1–8.0	Weakly alkaline	Rendsic Leptosols
8.1–9.0	Moderately alkaline	Solonchaks, Solonetz
9.1–10.0	Strongly alkaline	Solonchaks, Solonetz
10.1–11.0	Very strongly alkaline	Solonchaks with soda
>11.0	Extremely alkaline	Solonchaks with soda

Strongly alkaline soils are therefore mainly found in arid climate regions, often together with high salinity. The high pH values are caused by an accumulation of $NaHCO_3$ and Na_2CO_3 in combination with high Na^+ saturation of the cation exchanger surfaces. If Na carbonates and clay minerals with high Na saturation (*X*Na) come into contact with water, OH^- ions are released according to:

$$Na_2CO_3 + H_2O \rightleftharpoons HCO_3^- + 2Na^+ + OH^- \tag{5.57}$$

$$NaHCO_3 \rightleftharpoons Na^+ + CO_2(g) + OH^- \tag{5.58}$$

$$XNa + H_2O \rightleftharpoons XH + Na^+ + OH^- \tag{5.59}$$

The pH values of soils with Na carbonates range from strongly to very strongly alkaline. Soils with high Na^+ saturation but without Na carbonate formation are typically in the weakly to moderately alkaline range. High contents of neutral salts (e.g. NaCl, $MgCl_2$) lead to somewhat lower pH values, because the hydrolysis reaction on Na-saturated clay mineral surfaces is inhibited [Eq. (5.59)]. Likewise, high CO_2 partial pressures in the soil air lead to lower pH values due to the formation of carbonic acid in the soil solution [Eq. (5.58)].

5.6.1.2 Acidic Soils

Acidic soils are very widespread in humid climate regions. As soon as the lithogenic carbonates are dissolved and leached, the soils start to become acidified. The pH values of intensively cultivated agricultural soils (e.g. Cambisols, Luvisols) lie in the weakly acidic range, provided that they are limed regularly. Carbonate-free Gleysols and riparian Fluvisols that are in regular contact with water containing bicarbonate ions (HCO_3^-) also have weakly acidic or neutral pH values. The pH value of such soils is controlled by the base saturation of weakly acidic groups on variably charged surfaces. For this reason, it is generally higher (pH 6.4–6.9) than the pH of pure water in equilibrium with CO_2 in the soil air (pH 5.6). Carbonate-free Gypsisols in deserts also exhibit a weakly acidic reaction.

The mineral soil horizons of many forest soils of Central Europe (e.g. Cambisols, Luvisols, Stagnosols, Podzols) are strongly acidic. The same is true for most highly weathered tropical and subtropical soils (e.g. Ferralsols, Acrisols). The organic horizons (O) of many soils under coniferous forests (e.g. Podzols) are very strongly acidic, as are the peat horizons of ombrotrophic peat bogs. Extremely strongly acidic pH values are observed in organic layers of forest soils and in acid sulfate soils, where the oxidative weathering of iron sulfides leads to the formation of H_2SO_4.

5.6.1.3 Soil Acidification and Exchangeable Cations

The saturation of the cation exchanger surfaces in soils changes dramatically during the course of soil acidification. In weakly acidic to weakly alkaline soils of humid climate regions, Ca^{2+} is almost always the most abundant exchangeable cation (>80 % of CEC_{eff}). The saturation of the CEC_{eff} with Mg^{2+} is much lower (5–15 %),

followed by K^+ (2–5 %) and Na^+ (<2 %). Higher Mg-saturation is observed in young soils developing from ultramafic or mafic rocks, because high amounts of Mg^{2+} are released by weathering of Mg-rich silicates. Significantly higher Na^+ saturation is found in coastal marshes, in soils affected by road salt, and in soils of arid regions. Table 5.8 shows several examples.

The saturation of a soil's CEC_{eff} with Al^{3+} increases with increasing soil acidification; especially below pH 4.5. Accordingly, the base saturation decreases. The Al-saturation can rise to above 90 % of the CEC_{eff} in strongly acidic mineral soil horizons, so that only small amounts of exchangeable base cations remain. Because the elements Ca, Mg and K are essential plant nutrients, the supply of these nutrients to the plants decreases with increasing soil acidification. At the same time, a high Al concentration in the soil solution, which is in equilibrium with the exchangeable Al^{3+}, can lead to aluminum toxicity in sensitive plants, and thus to a strong inhibition of root growth. Secondary effects of inhibited root growth can include phosphate deficiency and increased susceptibility to drought stress.

The relationships between soil pH, cation exchange capacity, and base saturation are depicted schematically in Fig. 5.15. In neutral to weakly alkaline soils (pH 7–8), the total CEC_{eff} is saturated with the base cations Ca^{2+}, Mg^{2+}, K^+, and Na^+. Here, per definition, the CEC_{pot} equals the CEC_{eff}. If the soil pH drops, first the base cations on variable charge sites are substituted by H^+, and the CEC_{eff} decreases accordingly. However, the base saturation (BS_{eff}) is still close to 100 %. Below pH ~ 4.5, Al^{3+} increasingly occupies cation exchanger sites, at the expense of base cations. In the acidic to strongly acidic range (depending on the acid strength of the functional groups), the CEC_{eff} reaches its minimum and is then increasingly dominated by surfaces with permanent negative charge. Exchangeable H^+ ions, probably originating from humic substances, dominate in very acidic organic layers. In contrast, exchangeable H^+ occupies only a minor fraction of the CEC_{eff} in mineral soils, because it reacts with clay minerals and liberates Al^{3+} ions.

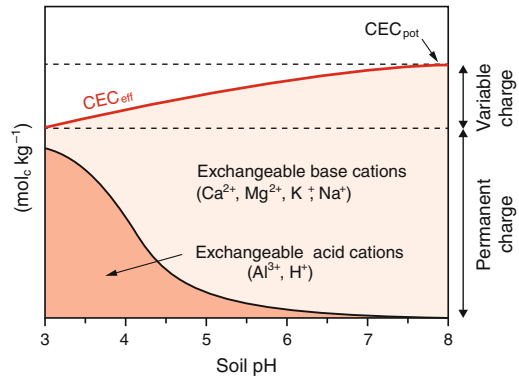

Fig. 5.15 Potential and effective cation exchange capacity (CEC_{pot} and CEC_{eff}), exchangeable base cations (Ca^{2+}, Mg^{2+}, K^+, Na^+), and exchangeable acidic cations (H^+, Al^{3+}) depending on the soil pH (schematic). The CEC_{eff} decreases with decreasing soil pH, because the negative variable charge on mineral surfaces and humic substances decreases. The proportion of exchangeable acidic cations relative to the CEC_{eff} increases, and the base saturation drops with decreasing soil pH

5.6.2 Soil Acidity and Base Neutralization Capacity (BNC)

Although the soil pH value indicates whether a soil is acidic or alkaline, it does not provide quantitative information on the **soil acidity**. Soil acidity corresponds to the quantity of bases that must be added to an acidic soil to raise its pH to the neutral range. Thus, it is a measure for a soil's pH **buffering** upon addition of bases. It is equal to the **base neutralization capacity** (BNC) of the soil, which can be used to calculate the lime requirement for agricultural soils (see Sect. 5.6.5).

The **total soil acidity** includes the sum of all solid and dissolved acids in a soil, which can release protons within a short time and thus neutralize bases. By far the greatest portion of the total soil acidity is attributed to the acidic exchangeable cations H^+ and Al^{3+}, and it is therefore called **exchangeable acidity**. The exchangeable acidity can be determined by titrating a 1 M KCl soil extract. The **actual acidity** (all dissolved acids in the soil solution, especially carbonic acid, organic acids, HNO_3, and H_2SO_4) and the **reserve acidity**

(all solid acids that are non-exchangeable with 1 M KCl) only account for a small portion of the total acidity. In mineral soils, the greatest portion of the exchangeable acidity is attributed to exchangeable Al^{3+} ions, which are always coordinated with six water molecules in aqueous solutions (hexaquo complex, $Al(H_2O)_6^{3+}$) and can release protons through several hydrolysis reactions:

$$Al(H_2O)_6^{3+} \rightleftharpoons Al(OH)(H_2O)_5^{2+} + H^+$$

$$\log K = -4.97 \tag{5.60}$$

$$Al(OH)(H_2O)_5^{2+} \rightleftharpoons Al(OH)_2(H_2O)_4^{+} + H^+$$

$$\log K = -4.93 \tag{5.61}$$

$$Al(OH)_2(H_2O)_4^{+} \rightleftharpoons Al(OH)_3(H_2O)_3^{0} + H^+$$

$$\log K = -5.70 \tag{5.62}$$

An acidic solution containing Al^{3+} is buffered by these reactions. When titrating such a solution up to pH 7, three protons are liberated by each Al^{3+} cation, under precipitation of amorphous to weakly crystalline $Al(OH)_3$(*am*) at higher Al concentrations. Accordingly, the total exchangeable Al^{3+} must be neutralized when liming acidic soils.

The remaining exchangeable acidity is mainly attributed to exchangeable H^+, in some cases also to smaller quantities of exchangeable Mn^{2+} and Fe^{2+}/Fe^{3+}, which (after oxidation of Mn^{2+} and Fe^{2+}) can also release protons through metal hydrolysis. However, exchangeable Fe^{2+}/Fe^{3+} and Mn^{2+} ions only play a role in strongly acidic and/or anoxic soils. Exchangeable protons are mainly bound to organic matter, especially humic substances. In organic layers and peats, H^+ ions dominate the exchangeable acidity, because only little exchangeable Al^{3+} is available.

The actual acidity includes all of the acids dissolved in the soil solution at a given point in time. Dissolved carbonic acid (H_2CO_3) dominates in many soils, the concentration of which strongly depends on the CO_2 partial pressure in the soil air and thus on the biological activity and aeration of the soil. In addition, soil solutions also contain organic acids, which are mainly weak acids and have pK_a values between 2 and 6 (e.g. oxalic acid: $pK_1 = 1.25$, $pK_2 = 4.27$; malic acid: $pK_1 = 3.46$, $pK_2 = 5.10$; citric acid: $pK_1 = 3.11$, $pK_2 = 4.78$, $pK_3 = 6.40$). HNO_3 and H_2SO_4 are the most common strong acids found in soil solutions, which are fully dissociated in the pH range of soils and therefore do not act as a buffer.

The reserve acidity includes all "solid acids", i.e. all solid materials that can donate protons in response to an increase in pH, and thus contribute to the BNC. These include, for example, the surfaces of oxides and edges of clay minerals with hydroxyl groups on their surfaces that can bind or release protons. Also included are solid organic substances in the soil that have a large number of different acidic functional groups. Carboxyl groups play the most important role in the pH buffering of soils, because they strongly dominate in terms of quantities and their pK_a values lie in the acidic pH range (pK_a = 2–6). Moreover, in very strongly acidic soils, surfaces of Fe and Al oxides may be covered with adsorbed oxyanions such as $H_2PO_4^-$ or SO_4^{2-}. When such soils are limed, the release of these sorbates also consumes OH^- ions, which are therefore important for the BNC and pH buffering of soils (Sect. 9.7.7). When acidic soils are limed, the oxide surfaces, edges of clay minerals, and soil organic matter release protons that must be neutralized. This causes an increase in negative surface charge of soil components, and thus, the CEC_{eff} increases until the CEC_{pot} is reached at pH $\sim$ 7.5.

5.6.3 H^+ Sources

5.6.3.1 Input Through Precipitation

Water in equilibrium with CO_2 in the atmosphere ($P_{CO_2} = 0.00038$) has a pH value of about 5.6. The pH values of precipitation in Central Europe, however, are often considerably below this value (pH < 5), which can be mainly attributed to strong acids such as H_2SO_4 and HNO_3. These inorganic acids mainly originate from anthropogenic emissions, which are produced e.g. with

the combustion of fossil fuels. The emission of nitrogen oxide (NO_x) and sulfur dioxide (SO_2, from industry, traffic, energy production) leads (through reactions with O_3 or $^{\cdot}OH$ radicals in the atmosphere) to the formation of HNO_3 and H_2SO_4. In several regions of the world, this causes pH values in rainwater to be at pH 4 or lower ("acid rain"). Installation of filters and the use of low-sulfur coal have led to a significant drop in sulfuric acid emissions in Central Europe in the past decades; in other parts of the world, however, it is still high (e.g. China). Nitric acid concentrations in the precipitation are also still elevated in Central Europe.

In addition, ammonia emissions from livestock farming (e.g. from liquid manure) can result in elevated inputs of NH_4^+ to the surrounding soils. Because protons are released during the nitrification of NH_4^+ to NO_3^- (Sect. 5.6.3.5), this process also contributes significantly to soil acidification in regions with high livestock densities.

In Germany, depending on the location and vegetation, H^+ input with precipitation varies from <1 to >5 kmol ha^{-1} a^{-1}, about 75 % of which can be attributed to N inputs (NH_4^+ and NO_3^-). Inputs are particularly high under coniferous forests, because evergreen coniferous trees are very effective at filtering acids from the atmosphere (interception). The protons from H_2SO_4 and HNO_3 react with the solid phases of the soil and cause the release of metal cations, which are leached together with SO_4^{2-} and NO_3^-.

5.6.3.2 Formation of Carbonic Acid Through Soil Respiration

The aerobic respiration of soil organisms (microorganisms, soil fauna, roots) leads to the formation of large quantities of CO_2 (ca. 10 kmol ha^{-1} a^{-1}). Because gas exchange between the soil air and the atmosphere is not very rapid, the relative CO_2 partial pressure in the soil air can be several orders of magnitude higher than in the atmosphere (up to ($P_{CO_2} = 0.1$)). According to HENRY's Law (Sect. 5.2), the concentration of H_2CO_3* in the soil solution is also strongly elevated.[10]

5.6.3.3 Exudation of Organic Acids

Plant roots and microorganisms exude organic acids, which in many cases is a specific adaptation to nutrient deficiency. Exudation of organic acids enables them to mobilize nutrients in the soil. For example, white lupines (*Lupinus albus* L.) and several other plant species exude large amounts of citric acid into the rhizosphere under phosphate-deficient conditions. Similarly, a deficiency in iron or other trace nutrients can induce increased exudation of organic acids in many plant species. Examples for organic acids that are found in the soil solution, and notably in the rhizosphere of plants, include citric acid, malic acid, fumaric acid, succinic acid, and oxalic acid.

5.6.3.4 Exudation of H^+ by Plant Roots

Plants take up all essential nutrient elements from the soil. In most plants, the requirements for macronutrients increase in the sequence $S < P < Mg < Ca \ll K \ll N$. The sum of cation ($K^+$, Mg^{2+}, Ca^{2+}) uptake is therefore often much greater than the sum of anion ($HPO_4^{2-}/H_2PO_4^-$, SO_4^{2-}) uptake. Nitrogen can be taken up as NH_4^+ and NO_3^-, i.e. both in cationic and anionic forms. If mineral nitrogen in the soil is mainly present as NH_4^+, a plant inevitably must absorb much more cations than anions. To maintain their electroneutrality, they must exude a corresponding quantity of H^+ to balance the charge. This causes the rhizosphere to become acidified relative to the bulk soil, i.e. the pH value of the rhizosphere is lowered. If the plant N-supply is in the form of NO_3^-, the difference between cation and anion uptake is smaller, and the plants do not need to exude as many protons. If a large quantity of NO_3^- is taken up by the plant, the rhizosphere pH can even increase, because the plants release OH^-, HCO_3^-, or organic anions to balance the charge.

Internally, the plant compensates for the excess cation uptake by formation of salts of weak organic acids, which are stored in the

[10]Because the dissolved carbonic acid (H_2CO_3) cannot be analytically differentiated from dissolved CO_2 ($CO_2 \cdot H_2O$), H_2CO_3* is defined as the sum of H_2CO_3 and $CO_2 \cdot H_2O$.

vacuoles ($R\text{-}COO^-M^+$). When the plant dies, these salts re-enter the soil as litter and neutralize acidity according to:

$$R{-}COO^-M^+ + H^+ \rightleftharpoons R{-}COOH + M^+ \quad (5.63)$$

Thus, the soil H^+ balance is restored. However, cation uptake occurs in the entire root zone, but the neutralization of protons by the litter mainly takes place in the topsoil. Therefore, the two processes are spatially separated, which explains why many natural, more strongly weathered soils (e.g. Acrisols, Ferralsols) have higher pH values and base saturation in the topsoil than in the subsoil. The vegetation acts here as a "base pump". This natural cycle is interrupted in soils used for agriculture and forestry, because a large portion of the formed biomass is removed as harvested biomass. The exudation of protons by plant roots then leads to a net acid input and contributes to soil acidification.

5.6.3.5 Oxidation of NH_4^+ to NO_3^-

The microbial decomposition of organic matter in the soil liberates organically bound nitrogen as NH_4^+, a process called **N mineralization**. N fertilization (e.g. liquid manure, mineral fertilizer containing NH_4^+) and atmospheric inputs also add NH_4^+ to the soil. Under aerobic conditions, the aerobic bacteria *Nitrosomonas* and *Nitrobacter* oxidize NH_4^+ in two steps to form NO_3^-, a process that is called **nitrification** (Sect. 9.6.1). Thereby, two H^+ are released for each NH_4^+, which is illustrated in the following reaction equation:

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O \quad (5.64)$$

The acidifying effect of nitrification is weakened if the plants take up more NO_3^- and less NH_4^+, and therefore also exude less H^+ into the rhizosphere. Still, the nitrification of NH_4^+ leads to excess H^+, and thus many fertilizers containing ammonium have an acidifying effect on the soil. The H^+ quantities attributed to N input in Central and Western Europe range between 1 and 3 kmol ha^{-1} a^{-1}; in areas with high liquid manure production, however, the values can rise to 7 kmol ha^{-1} a^{-1}.

5.6.3.6 Oxidation of Soluble Fe^{2+} and Mn^{2+} Ions and of Fe Sulfides

Under oxic conditions, redox reactions can take place in the soil that release protons, while under anoxic conditions, protons tend to be consumed by reductive processes (Sect. 5.7.1.1). An important example is the oxidation of Fe^{2+} to Fe^{3+} in the presence of oxygen, and the resulting precipitation of Fe(III) oxyhydroxides:

$$Fe^{2+} + H^+ + 1/4O_2 \rightleftharpoons Fe^{3+} + 1/2H_2O \quad (5.65)$$

$$Fe^{3+} + 2H_2O \rightleftharpoons FeOOH(s) + 3H^+ \quad (5.66)$$

$$Fe^{2+} + 3/2H_2O + 1/4O_2 \rightleftharpoons FeOOH(s) + 2H^+ \quad (5.67)$$

Although one proton is consumed in the oxidation of Fe^{2+} to Fe^{3+} [Eq. (5.65)], Fe^{3+} is immediately hydrolyzed and precipitated as sparingly soluble Fe(III) oxyhydroxide (e.g. FeOOH) at the pH ranges found in soils (pH > 3). In the hydrolysis process, every Fe^{3+} releases three protons [Eq. (5.66)]. Analogously, the oxidation and hydrolysis of Mn^{2+} to MnO_2 also liberates two H^+. However, because the reverse reactions, i.e. the reduction and dissolution of FeOOH and MnO_2, respectively, consume two H^+, the pH increases again up to the neutral range under Mn- and Fe-reducing conditions. Reductive dissolution of Fe oxyhydroxides can lead to the release of high concentrations of dissolved Fe^{2+} ions, which displace base cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) from cation exchanger surfaces, allowing them to be leached with seepage water. When the soil is aerated again, Fe^{2+} is oxidized and protons are liberated by hydrolysis of Fe^{3+}. This process (ferrolysis) contributes to the acidification of periodically anoxic soils (e.g. Stagnosols). The oxidation of Fe^{2+} released during the chemical weathering of Fe(II)-bearing silicates, in contrast, does not lead to soil acidification, because the silicate acts as a base and binds the protons (Sect. 5.6.4.4).

Marine or coastal sediments often contain iron sulfides, which can become an important source

of protons when they are subject to oxidative weathering in soils. Iron sulfides occur as FeS_2 (pyrite) and FeS (mackinawite). Under aerobic conditions, both Fe^{2+} and S^{2-} can be oxidized under formation of Fe(III) oxyhydroxides and sulfuric acid:

$$FeS_2(s) + 15/4O_2 + 5/2H_2O \rightleftharpoons FeOOH(s) + 2SO_4{}^{2-} + 4H^+ \tag{5.68}$$

$$FeS(s) + 9/4O_2 + 3/2H_2O \rightleftharpoons FeOOH(s) + SO_4{}^{2-} + 2H^+ \tag{5.69}$$

If iron sulfide-rich and carbonate-poor soils are drained and therefore well-aerated, they can become very strongly acidic through sulfide oxidation. In tropical regions, such soils (termed **acid sulfate soils**) are often used for paddy rice cultivation, because strong acidification and resulting aluminum toxicity to plants can only be prevented by keeping the soils permanently flooded. The formation of sulfuric acid through oxidative pyrite weathering also plays a very important role in carbonate-poor mine tailings containing metal sulfides, which leads to strongly acidic seepage water (pH < 2, **acid mine drainage**) with high concentrations of dissolved Fe^{2+}, Mn^{2+}, $SO_4{}^{2-}$, and toxic trace metals that pollute the environment (Sect. 2.4.2.3).

5.6.4 pH Buffering, Soil Acidification and Acid Neutralization Capacity (ANC)

The acidification rate in soils under humid climate conditions depends, in addition to the proton input per unit time, on its capacity to buffer acid inputs. The soil's buffering capacity results from its **acid neutralization capacity** (ANC), a capacitive parameter, and the reaction rates of all relevant buffer systems as kinetic parameters. Buffer systems include all chemical reactions involving the conversion of free protons into an undissociated form. A proton input always leads to a reduction in the soil's ANC, however, not necessarily to a corresponding drop in the pH value. During the course of soil development in humid climate regions, the ANC gradually decreases through the constant input of H^+. For Central Europe, the analyses of numerous soil profiles indicate that the ANC has decreased in the post-glacial period on average by ca. 8000 kmol ha^{-1}. Because more H^+ has been added to soils through the atmosphere in industrial countries in the past century, their remaining ANC is of great importance for their critical loads of acid deposition. Buffering is mainly accomplished by solid soil components (carbonates, clay minerals, oxides, organic matter) and only to a limited extent by dissolved substances.

Weakly alkaline to weakly acidic soils are capable of buffering acid inputs rapidly and completely, because they either contain carbonates or at least have high base saturation of the cation exchanger surfaces. A more rapid drop in soil pH occurs if the carbonate buffer system and the cation exchange buffer system are largely depleted, because the neutralization of acid inputs by silicate weathering is slow in moderately acidic soils. Soils developed from mafic and ultramafic igneous or metamorphic rocks, due to their high contents of readily weatherable silicate minerals, can remain buffered near pH 5.5–6.0 over longer time periods (Sect. 5.6.4.4). In contrast, soils developed from felsic igneous or metamorphic rocks acidify within short time periods to about pH ~ 4. This pH value is caused by the high Al-saturation on the exchanger surfaces. Elevated acid input from the atmosphere has caused the pH of many forest soils in Northern and Central Europe to decrease by 1.5 units in the second half of the 20th century, in some cases within a decade. The above-mentioned course of soil acidification explains why the pH values of forest soils in

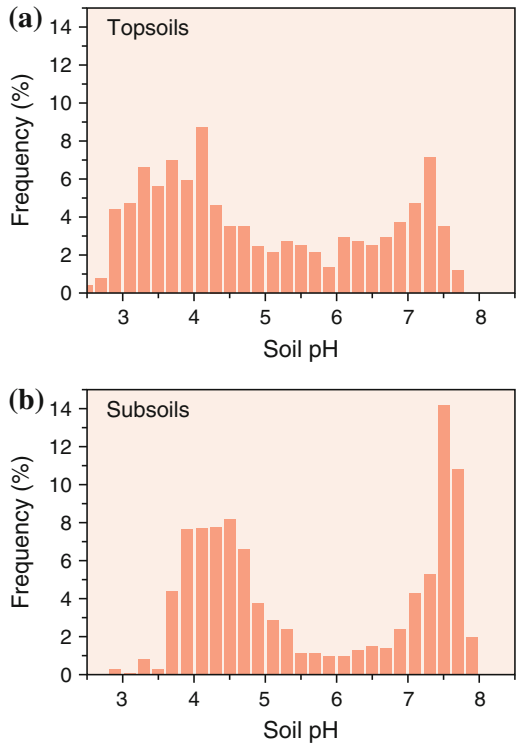

Fig. 5.16 Distribution of soil pH values (in 0.01 M $CaCl_2$) of 262 forest soils in Switzerland: **a** 818 mineral topsoil samples, **b** 796 subsoil samples (>20 cm depth) (after Walthert et al. 2004)

Central Europe follow a bimodal distribution, with frequency maxima at pH 3.8–4.5 and at pH 7.9–7.5 (Fig. 5.16).

5.6.4.1 Buffering by Carbonates

In soils containing carbonates, the dominant buffer system is the dissolution of carbonates under consumption of protons. The following reaction shows that one mol H^+ is buffered per mol $CaCO_3$ (calcite):

$$CaCO_3(s) + H^+ \rightleftharpoons Ca^{2+} + HCO_3^- \quad (5.70)$$

The HCO_3^- dissolved in the pore water is leached together with Ca^{2+} (or other cations). The removal of dissolution products leads to an irreversible loss in ANC of the soil. Because the kinetics of this buffer reaction is relatively fast, the pH value established in the soil can be

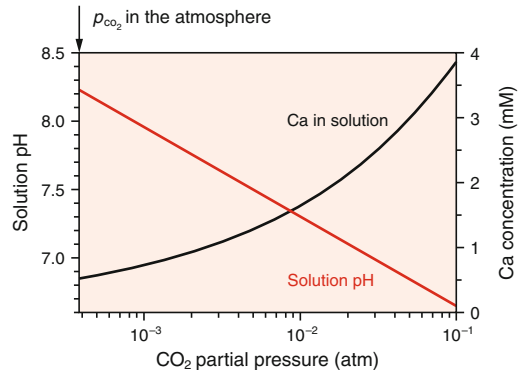

Fig. 5.17 pH-value and Ca^{2+} concentration in the solution at equilibrium with calcite ($CaCO_3$) depending on the relative CO_2 partial pressure at 25 °C (calculation with Visual-MINTEQ)

estimated from the chemical equilibrium of calcite in water at a given CO_2 partial pressure in the soil air. As can be seen in Fig. 5.17, the calculated pH value varies between 8.2 and 6.9 ($pH = 5.9925 - 0.653 \log P_{CO_2}$) if the relative CO_2 partial pressure is varied from atmospheric to 100-fold elevated ($P_{CO_2} = 0.00035$ to 0.035). The calculation also demonstrates that elevated CO_2 partial pressure in the soil air leads to increased dissolution of calcite, and that HCO_3^- and Ca^{2+} are the most important dissolved species involved in the buffer reaction.

The relatively fast reaction of calcite with protons often results in a sharp decarbonatization boundary in the soil profile. Only if carbonate is present exclusively in coarse limestone gravel can the soil pH drop to values below pH 7 before the soil horizon is completely carbonate-free. This is because the dissolution of carbonates in gravel pieces with a small reactive surface area is not fast enough to neutralize acid inputs. Dolomite ($CaMg(CO_3)_2$) reacts similar to calcite, although much more slowly due to its lower solubility.

The stoichiometry of the reaction is somewhat different when strongly acidic soils (pH < 5) are limed with $CaCO_3$. Under strongly acidic conditions, HCO_3^- is no longer the dominant dissolved carbonate species, but rather H_2CO_3*:

$$CaCO_3(s) + 2H^+ \rightleftharpoons Ca^{2+} + H_2CO_3^* \quad (5.71)$$

and H_2CO_3* is in equilibrium with the soil air according to:

$$H_2CO_3{}^* \rightleftharpoons CO_2(g) + H_2O \qquad (5.72)$$

Thus, two mol H^+ are neutralized per mol $CaCO_3$. The main products of this buffer reaction are Ca^{2+}, CO_2(g) and H_2O. The formed CO_2(g) leaves the soil through gas exchange with the atmosphere.

5.6.4.2 Buffering by Surfaces with Permanent Charge

Through cation exchange, clay minerals with permanent negative charge (X^-) and high base saturation can act as a rapid pH buffer, e.g.:

$$X_2Ca + 2H^+ \rightleftharpoons 2XH + Ca^{2+} \qquad (5.73)$$

Such exchange reactions result in the adsorption of free protons onto the exchanger surfaces, thus buffering the pH value of the soil solution. Because H^+-saturated clay minerals are not stable, only a small fraction of the cation exchanger sites X^- in mineral soils are typically occupied by H^+. Protons attack the silicate structures and are neutralized by slow silicate weathering reactions. Thus, cation exchange on clay minerals with permanent negative charge can only be considered as a temporary, but nevertheless rapid and effective buffer system. Such rapid buffer systems play an important role in the rhizosphere of plants, because they have an influence on the short-term pH decrease by root exudates.

5.6.4.3 Buffering by Surfaces with Variable Charge

Solids with variable (i.e. pH-dependent) surface charge can bind and release protons and thereby act as a pH buffer. In the neutral pH range, humic substances are mainly negatively charged, because a large fraction of the acidic functional groups, especially carboxyl groups, are present in a dissociated form. The negative charge is compensated by exchangeable adsorbed cations, e.g. Ca^{2+}. These dissociated acid groups act as Brønsted bases and can be protonated:

$$R-(COO^-)_2Ca^{2+} + 2H^+ \rightleftharpoons R-(COOH)_2 + Ca^{2+} \qquad (5.74)$$

This leads to a decrease in both the soil's ANC and CEC_{eff}. The exchanged Ca^{2+} ions can be leached with the seepage water. Humic substances act as a buffer substance across the entire soil pH range (pH 3–10), because they have a large number of different functional groups covering a wide range of pK_a values. The ANC of humic substances often accounts for the largest fraction of the total ANC of topsoils in the pH range 5–7, in which the ANC of topsoils closely correlates with the humus content.

The edges of clay minerals and surfaces of oxides and hydroxides also carry variable surface charge and act as a pH buffer. Above their point of zero charge (pH_{PZC}), the surfaces are negatively charged (e.g. edges of clay minerals in the neutral pH range). Like with humic substances, the binding of protons results in a decrease in the negative surface charge, and thus in the CEC_{eff}, and a release of exchangeable cations. Below the point of zero charge (e.g. Fe and Al oxides in the acidic pH range), proton absorption increases the positive surface charge and therefore the anion exchange capacity of the soil. Acidic soils that are rich in Fe and Al oxides and hydroxides owe a significant fraction of their buffering capacity to the functional groups of these constituents (e.g. Ferralsols). Similarly, the variable charge of allophanes contributes to pH buffering in allophane-rich soils (e.g. Andosols).

5.6.4.4 Buffering Through Silicate Weathering

The chemical weathering of many silicates (Sect. 2.4.2) leads to a consumption of protons and to a buffering of the soil pH. For this reason, high contents of readily weatherable silicates counteract rapid acidification, and therefore contribute significantly to ANC of the soil. However, silicate weathering reactions, and thus also pH buffering, take place much more slowly than adsorption reactions or the dissolution of carbonates. As a result, silicate weathering represents a slow-acting

buffer system. In addition to the mineral stability, the weathering rate also depends on the grain size and specific surface area, pH value, as well as other environmental conditions (e.g. temperature, leaching of weathering products). At neutral pH, silicate weathering is very slow. Because silicate weathering is promoted by protons, the weathering rates increase logarithmically with decreasing pH.

Consider for example the weathering of anorthite, a Ca feldspar:

$$CaAl_2Si_2O_8(s) + 8H^+ \rightarrow Ca^{2+} + 2Al^{3+} + 2H_4SiO_4^0 \quad (5.75)$$

This reaction initially consumes 8 protons. Further reactions of Al^{3+}, however, release protons again so that the net consumption of protons is lower. In weakly acidic soils, a large portion of the released Al^{3+} is precipitated again in the form of secondary minerals, for example with silicic acid resulting in the formation of kaolinite:

$$2H_4SiO_4{}^0 + 2Al^{3+} + H_2O \rightarrow Al_2Si_2O_5(OH)_4(s) + 6H^+ \quad (5.76)$$

If the concentration of silicic acid in the soil solution is very low (e.g. in highly weathered soils), gibbsite is also formed:

$$2Al^{3+} + 6H_2O \rightarrow 2Al(OH)_3(s) + 6H^+ \quad (5.77)$$

In both cases, the formation of secondary minerals results in the liberation of 3 protons per Al^{3+}. Another important reaction of Al^{3+} is the adsorption on negatively charged surfaces of clay minerals and humic substances. Cation exchange or the complex formation of Al^{3+} on organic substances liberates other base cations, e.g. through cation exchange according to:

$$3X_2Ca + 2Al^{3+} \rightleftharpoons 2X_3Al + 3Ca^{2+} \quad (5.78)$$

Under humid climate conditions, the dissolved Ca^{2+} ions and the silicic acid ($H_4SiO_4^0$) remaining in solution are leached from the soil with seepage water. The Al-saturation on the cation exchanger surfaces increases, and thus also the soil's exchangeable acidity. The neutralization of 2 exchangeable Al^{3+} ions would require 6 OH^-, i.e. in this case the resulting exchangeable acidity also corresponds to 3 protons per Al^{3+} ion. Altogether, only 2 H^+ are buffered per $CaAl_2Si_2O_8$ during the chemical weathering of anorthite.

Silicates containing no or only little Al and Fe (II) have a greater net buffering effect. Consider for example the weathering of augite, a pyroxene:

$$Ca_2Si_2O_6(s) + 2H_2O + 4H^+ \rightarrow 2Ca^{2+} + 2H_4SiO_4{}^0 \quad (5.79)$$

This reaction consumes 4 protons, but no acid cations are released. In addition to Ca and Si, most augites also contain smaller amounts of Al, Fe and Mg (Sect. 2.2.3.3, Table 2.3). The higher the Al and Fe(II) content, the more the buffering effect of augite weathering is reduced. Through oxidation and hydrolysis, every liberated Fe^{2+} ion leads to the formation of 2 protons [Eq. (5.67)].

Silicate buffering is of great ecological importance. On the one hand, it results in the release of plant nutrients (Ca, Mg, K, Fe, Mn), but on the other hand, it can also lead to the release of phytotoxic Al^{3+} below pH 4.5, and promote the depletion of exchangeable nutrient cations in the soil. The latter plays a particularly important role for the Mg supply of forest trees.

5.6.5 Liming of Acidic Soils

5.6.5.1 Optimum pH Value for Agricultural Soils

Soil pH has numerous direct and indirect effects on plant growth and crop yields, and it is therefore considered to be one of the most important soil chemical parameters. In addition to the plant species, the optimum pH of agricultural soils depends on a number of ecologically relevant soil properties, which are influenced in different ways by pH. These include the potentially toxic effects of Al^{3+} and Mn^{2+}, the availability of macro- and micronutrients, the mobility of toxic trace metals, humus decomposition, soil

structure, and growth and diversity of the accompanying flora. In any case, the soil pH should be kept sufficiently high (pH > 5) to exclude Al and Mn toxicity. However, significant further increases in soil pH can result in decreased availability of micronutrients such as Mn, Cu, Zn, and B (Sect. 9.7). The same is true for phosphate, which becomes less plant available above pH 6 (Sect. 9.6.2). Because a rise in pH stimulates microbial activity, organic matter can be more strongly decomposed leading to enhanced N-mineralization. Finally, aggregation in clayey soils is promoted by a higher percentage of exchangeable Ca^{2+}, and especially by a higher Ca^{2+} concentration in the soil solution.

These considerations are reflected in recommended pH values for agricultural soils depending on their clay and humus contents. In soils with <4 % organic matter and <5 % clay the recommended pH lies between 5.0 and 5.5, with 5 to 12 % clay between pH 5.4 and 6.0, and with >13 % clay between pH 6.0 and 6.5, respectively. The rising pH optimum with increasing clay content primarily reflects the belief that more clayey soils require a more stable soil aggregate structure, and that this can be promoted through liming. However, this could not be confirmed beyond a reasonable doubt in field trials. If the organic matter content is above 4 %, a lower pH value is typically recommended regardless of the clay content, e.g. a soil pH of 5.0–6.0 at 9–15 % organic matter, and a pH of 4.0 in drained peat bogs used for arable farming. In any case, Al and Mn toxicity is not a problem in these organic soils. For grasslands, pH values of 5.0–5.5 in the topsoil of mineral soils are sufficient for the production of good quality fodder (in terms of species composition and micronutrient contents), while soil pH values around 4.5 are sufficient for peat bogs used as grassland.

In highly weathered tropical and subtropical soils (e.g. Ferralsols, Acrisols), the primary aim is to raise and keep the soil pH at a value where the plant-available Al is reduced to a harmless level, especially since lime is not always easily available.

5.6.5.2 Liming and Lime Requirement

If the pH of an arable soil drops below its desired value, it can be raised by adding neutralizing alkaline materials. Such alkaline materials include limestone, marl, and dolomite, which are naturally available in large quantities in many regions of the world, as well as burnt lime (CaO), which is produced by heating limestone. The liming of acidic soils is a widespread and long-established measure to increase agricultural yields. While the liming of intensively cultivated soils in Central Europe usually aims to compensate the annual losses of base cations, there is a significant lime requirement in many tropical and subtropical regions for reducing aluminum toxicity, particularly for alleviating subsoil acidity.

The neutralization rate of lime increases with decreasing soil pH. Above pH 6.0–6.5, carbonate lime only reacts over the course of several years, depending on its grain size. The first neutralization step of $CaCO_3$ takes place in the immediate surroundings of the lime particles, and thus initially does not have an effect on the subsoil. However, dissolved Ca^{2+} and HCO_3^- can be transported downward with seepage water and, if the subsoil is strongly acidic (pH < 5), lead to an increase in subsoil pH. Ca^{2+} promotes the exchange and leaching of acidic cations (H^+, Al^{3+}) and causes an increase in the base saturation. HCO_3^- acts as a base and reacts under strongly acidic conditions with H^+ to form H_2CO_3*.

Two examples of the long-term effects of liming on subsoil acidity are shown in Fig. 5.18. The left panel shows that 4 t ha^{-1} of dolomite lime, applied in 1984 between spring (F 84) and autumn (H 84) on the surface of a strongly acidic loess Cambisol under spruce, only raised the pH value in the O horizon. Soil pH in the top layer dropped again already after 2 years (H 86). Under grassland (right panel), the rise in pH reached a depth of 20 cm after 9 years, and more than 60 cm after 23 years, although here the topsoil was then already slightly acidified again. Subsoil liming can be performed to more rapidly create better growth conditions below the plough layer. This is

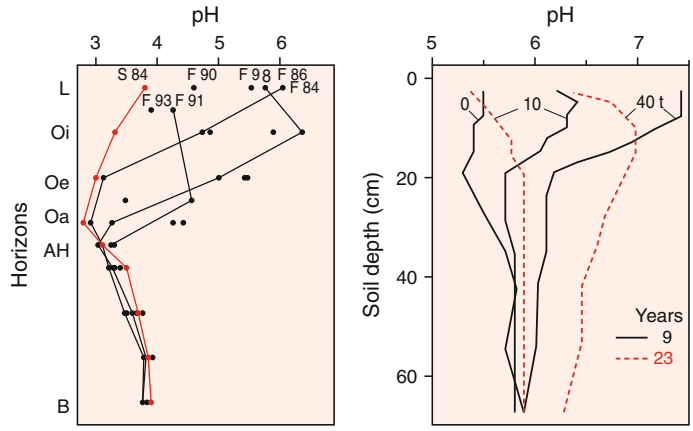

Fig. 5.18 Change in pH of two soils following lime application. *Left* Luvisol developed on loess under spruce forest after addition of 4 t ha^{-1} dolomitic lime (*S* spring, *F* Fall of the given year; after Kreuzer 1995). *Right* Fine sandy loam under grassland, 9 and 23 years after liming with 10 and 40 t CaO ha^{-1} (after Brown et al. 1956)

particularly important if the exchangeable Al content in the subsoil is too high.

The amount of lime that is required to raise a soil's pH to the desired range is called **lime requirement**. The lime requirement strongly depends on the base neutralization capacity (BNC) of the soil. This quantity can be determined experimentally by titrating the soil with a strong base (e.g. NaOH). Because this method is too elaborate for routine analysis, the lime requirement for agricultural soils is often estimated based on empirical data under consideration of soil pH, texture, organic matter content, and other factors.

In soils used for intensive agriculture, only small quantities of lime are generally required to neutralize the exchangeable Al and the strong acids added to the soil from the atmosphere (in Germany ca. 50 kg CaO $ha^{-1}a^{-1}$). In contrast, if a pH value of >6 should be maintained, the lime requirement increases exponentially, because the weak acidic groups must also be neutralized to achieve pH values >6. However, these weak acidic groups are easily protonated again, mainly by the carbonic acid produced in the soil.

5.7 Redox Reactions and Redox Dynamics

Redox reactions in soils have major effects on the chemical form and availability of nutrients, the transformation of organic matter, as well as the mobility and toxicity of many trace elements. Thus, they influence soil formation and biogeochemical cycles. The behavior of C, N, S, Fe, and Mn is particularly strongly dominated by redox processes. The behavior of several potentially toxic trace elements, such as Cr, As, Se, and U, is also strongly controlled by redox processes.

Redox processes in soils are ultimately driven by the photosynthesis of higher plants. During photosynthesis, plants make use of the sun's energy to reduce atmospheric CO_2 and produce carbohydrates, with the simultaneous oxidation of $2H_2O$ to O_2. In the process, carbon is reduced from oxidation level +4 to 0, while oxygen is oxidized from −2 to 0. If the reduced carbon compounds are added to the soil (through litter, root exudates, etc.), they are oxidized again by the

soil fauna and microorganisms to form CO_2. The organisms thereby obtain energy for their metabolism. The oxidation of carbon liberates electrons, which are transferred to O_2 (aerobic respiration) or, in the absence of O_2, to other electron acceptors such as nitrate or sulfate.

5.7.1 Redox Reactions and Redox Potential

5.7.1.1 Redox Reactions

Redox reactions involve a transfer of electrons (e^-) from one element or molecule (=electron donor or reductant) to another element or molecule (=electron acceptor, oxidant). The donation of electrons is an **oxidation**, the acceptance of electrons is a **reduction**. Because oxidation and reduction are always coupled with each other, they are referred to as **redox reactions**.

Conceptually, a redox reaction can be divided into two half reactions, one reduction reaction and one oxidation reaction. A reduction reaction (from left to right) can be written in the general form:

$$\mathrm{Ox} + m\mathrm{H}^+ + n\mathrm{e}^- \rightleftharpoons \mathrm{Red} \tag{5.80}$$

Here, Ox is the oxidized form and Red is the reduced form of an element (or molecule), and m and n are stoichiometric factors. The corresponding oxidation reaction proceeds from right to left. The equation indicates that many reduction reactions consume protons, and oxidation reactions release protons.

An important example is the reduction of Fe (III) in iron oxides (shown here simplified as $Fe(OH)_3$) with the simultaneous oxidation of organic carbon (shown here simplified as CH_2O):

$$4\mathrm{Fe(OH)_3} + 12\mathrm{H}^+ + 4\mathrm{e}^- \rightarrow 4\mathrm{Fe}^{2+} + 12\mathrm{H_2O}\ (\text{Reduction}) \tag{5.81}$$

$$\mathrm{CH_2O} + \mathrm{H_2O} \rightarrow \mathrm{CO_2} + 4\mathrm{H}^+ + 4\mathrm{e}^-\ (\text{Oxidation}) \tag{5.82}$$

Both half reactions put together result in a complete redox reaction:

Table 5.10 Redox-sensitive elements and their most common oxidation states in soils

Elements	Oxidation states (in soils)
O	−2, −1, 0
C	−4, −2, 0, +2, +4
N	−3, 0, +1, +2, +3, +5
S	−2, −1, 0, +4, +6
Fe	+2, +3
Mn	+2, +3, +4
Cu	0, +1, +2
As	−3, 0, +3, +5
Se	−2, 0, +4, +6
Cr	+3, +6
U	+4, +6

$$4\mathrm{Fe(OH)_3} + \mathrm{CH_2O} + 8\mathrm{H}^+ \rightarrow 4\mathrm{Fe}^{2+} + \mathrm{CO_2} + 11\mathrm{H_2O}\ (\text{Redox}) \tag{5.83}$$

Here, iron is reduced from oxidation state +3 to +2, and carbon is oxidized from oxidation state 0 to +4. Because Fe^{2+} is much more water-soluble than Fe^{3+}, this reaction dissolves iron hydroxide ($Fe(OH)_3$) and Fe^{2+} is released into solution. This reaction occurs under anoxic conditions in soils and is driven by iron-reducing bacteria, which gain energy from the oxidation of organic compounds and use iron as an electron acceptor.

Table 5.10 lists the most important elements involved in redox reactions and their most common oxidation states in soils. Table 5.11 shows selected half reactions relevant in soils, represented as reduction reactions. Possible redox reactions can be derived by adding two half reactions, one written in reverse direction as oxidation reaction.

5.7.1.2 Redox Potential

The **redox potential** (E) of a solution depends on the ratio of the activities of reduced and oxidized species in the solution. If the reduced species dominate, the environment is reducing and the solution can easily donate electrons to other substances. If the oxidized species dominate, the

Table 5.11 Examples of reduction reactions (half reactions) and their standard potential E_H^0 (at 25 °C and 1013 hPa) (after Essington 2004)

Oxidized form		Reduced form	E_h^0 (V)
1/5 NO_3^- + 6/5 $H^+ + e^-$	→	1/10 $N_2(g)$ + 3/5 H_2O	1.248
1/4 $O_2(g) + H^+ + e^-$	→	1/2 H_2O	1.230
1/2 $MnO_2(s)$ + 2 $H^+ + e^-$	→	1/2 $Mn^{2+} + H_2O$	1.230
$Fe(OH)_3(s)$ + 3 $H^+ + e^-$	→	Fe^{2+} + 3 H_2O	0.935
FeOOH(s) + 3 $H^+ + e^-$	→	Fe^{2+} + 2 H_2O	0.769
1/8 SO_4^{2-} + 5/4 $H^+ + e^-$	→	1/8 H_2S + 1/2 H_2O	0.308
1/8 $CO_2(g) + H^+ + e^-$	→	1/8 $CH_4(g) + H_2O$	0.172
$H^+ + e^-$	→	1/2 $H_2(g)$	0.000

environment is oxidizing and the solution can easily accept electrons from other substances. Thus, the redox potential indicates whether a substance can be reduced or oxidized in contact with the solution.

The redox potential of an aqueous solution can be measured using an inert noble metal electrode (e.g. made of Pt) as an electrical potential (in volts) relative to a reference electrode. The standard hydrogen electrode,[11] with a potential equal to zero, is the internationally accepted reference electrode. The redox potential relative to the standard hydrogen electrode is called Eh value.

The NERNST equation expresses the relationship between the redox potential Eh and the activity ratio of the reduced and oxidized species of a redox couple:

$$\mathrm{Eh} = \mathrm{Eh}^0 - \frac{2303RT}{nF}\log\frac{\{\mathrm{Red}\}}{\{\mathrm{Ox}\}} \tag{5.84}$$

Here, Eh^0 is the standard potential of the redox couple (Red/Ox) relative to the hydrogen electrode. R is the molar gas constant, T is the absolute temperature, F is the FARADAY constant, and n is the number of transferred electrons in the reaction. The standard potential can be derived from the thermodynamic data for every redox reaction. At 25 °C, the NERNST equation reduces to:

$$\mathrm{Eh} = \mathrm{Eh}^0 - \frac{0.059}{n}\log\frac{\{\mathrm{Red}\}}{\{\mathrm{Ox}\}} \tag{5.85}$$

The tendency of a solution to accept or donate electrons can also be considered as the activity of electrons, which is expressed as pe value (similar to the pH value). A low pe value means that the activity of electrons in the solution is high, and thus substances in contact with the solution will tend to be reduced. A high pe value, in contrast, indicates low electron activity and thus an oxidizing environment. The Eh- and pe values can be easily converted into one another using the following equation at 25 °C:

$$\mathrm{Eh} = 0.059pe \tag{5.86}$$

Table 5.11 shows examples of the standard potential (Eh^0) for several selected half reactions that are relevant in soils.

5.7.2 p*e*-pH Diagrams

As shown in the examples in Table 5.11, most redox reactions involve protons. For this reason, the soil's pH and pe values are closely coupled. The creation of pe-pH diagrams (or Eh-pH diagrams) is a simple way to illustrate which redox species are expected to dominate at given pH and pe values in a soil. The pe values in soils and aquatic systems can vary by several orders of magnitude, whereby the upper and lower boundaries are determined by the stability of water. Water oxidizes according to the reaction:

$$1/2\mathrm{H_2O} \rightarrow 1/4\mathrm{O_2}(g) + \mathrm{H}^+ + e^- \tag{5.87}$$

The equilibrium constant for this half reaction is $\log K_{ox} = -20.8$. This results in the relationship (assuming that the activity of H_2O is unity):

[11]Because using a standard hydrogen electrode is inconvenient, a calomel (Hg/Hg_2Cl_2) electrode or a silver/silver chloride electrode is generally preferred as a reference electrode. The measured potential can then be converted to the Eh value by adding +0.248 V (calomel) or +0.204 V (silver/silver chloride).

$$-20.8 = \frac{1}{4}\log P_{co_2} - \text{pH} - \text{p}e \qquad (5.88)$$

And in pure oxygen gas ($P_{O_2} = 1$):

$$\text{p}e = 20.8 - \text{pH} \qquad (5.89)$$

This equation shows that water is only stable at pe + pH < 20.8. At higher (pe + pH) values, water would disintegrate under formation of O_2 and H^+. Accordingly, the lower boundary of the (pe + pH) value is given by the reduction of protons to form hydrogen gas, which would also lead to the cleavage of water to form H_2 and OH^-:

$$H^+ + e^- \rightarrow 1/2H_2(g) \qquad (5.90)$$

The equilibrium constant for this reaction is log K_{red} = 0 (this reaction corresponds to the hydrogen electrode). At a relative H_2 partial pressure of ($P_{H_2} = 1$), the following relationship is obtained:

$$\text{p}e = -\text{pH} \qquad (5.91)$$

Thus, water is only stable at pe + pH > 0 and would disintegrate into H_2 und OH^- at lower values. Figure 5.19 shows the pe-pH range that is theoretically possible in aqueous systems. The pe-pH range is divided into an **oxic** (pe + pH > 14), a **suboxic** (9 < pe + pH < 14), and an **anoxic** (pe + pH < 9) range. The pe-pH range commonly measured in soils is also shown.

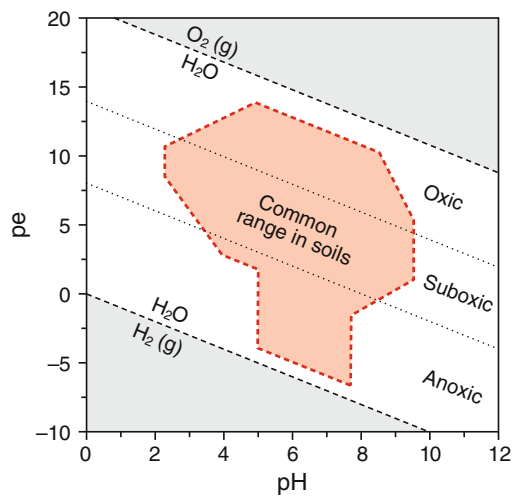

Fig. 5.19 Theoretically possible pe-pH range in aqueous environmental systems (*white area*) and common pe-pH range found in soils (*red hatched area*). The pe-pH range is divided into an oxic (pe + pH > 14), a suboxic (9 < pe + pH < 14) and an anoxic (pe + pH < 9) range. The *upper* and *lower* boundaries of the theoretically possible pe-pH range are given by the stability of water [Eqs. (5.87)–(5.91)]

The so-called rH value is also sometimes given instead of the pe + pH value. The rH value is defined as the negative logarithm of the hydrogen partial pressure p_{H_2}

$$\text{rH} = -\log p_{H_2} \qquad (5.92)$$

It is derived from the Nernst equation for the redox reaction

$$H_2 \rightleftharpoons 2H^+ + 2e^- \qquad (5.93)$$

as follows:

$$\text{rH} = 2\frac{\text{Eh}}{0.059} + 2\text{pH} \qquad (5.94)$$

and

$$\text{rH} = 2(\text{p}e + \text{pH}) \qquad (5.95)$$

The rH value represents a combined parameter for the measured pH and Eh values. It can range in value between 0 (in pure hydrogen gas) and 41.6 (in pure oxygen gas). rH values below 18 characterize strongly reducing (anoxic) conditions, and above 28 oxidizing (oxic) conditions. The suboxic range lies in between with values 18 < rH < 28. In the 1980s, rH values were introduced to the German soil classification to define redoximorphic, reductomorphic, and oximorphic soils, and were later also adopted by the WRB for the definition of Gleysols, Stagnosols, Planosols, and Reductic Technosols (Sect. 7.2.5).

In the same way as for water, the dominance fields of different redox species can be derived for all of the other redox reactions. Figure 5.20 shows pe-pH diagrams for various Fe or Mn species in equilibrium with CO_2 and H_2O. Panels (a) and (b) demonstrate that under oxic conditions, iron is present in its +3 oxidation state, which forms poorly soluble hydroxides (goethite or Fe$(OH)_3$(*am*)). Under suboxic to anoxic conditions, Fe(III) hydroxides can dissolve reductively

forming Fe^{2+}. If the pH value is high enough, mixed-valence Fe(II/III) phases such as magnetite (Fe_3O_4) or carbonate green rust (a layered Fe(II)/Fe(III) hydroxide) can be formed (Fig. 2.20). At pH > 6, the concentration of HCO_3^- dissolved in the water is high, which could lead to the precipitation of Fe^{2+} as siderite ($FeCO_3$) (green rust and siderite are not considered in Fig. 5.20).

Figure 5.20c, d show the dominance fields for Mn species in the absence (c) or presence (d) of 1 % CO_2 in the soil air. This example demonstrates that the formation of rhodochrosite ($MnCO_3$) strongly depends on the CO_2 partial pressure in the soil air.

5.7.3 Redox Reaction Kinetics

Without the activity of microorganisms, many redox reactions would not take place in soils, or only extremely slowly. A good example is the high stability of N_2 in the presence of O_2, although thermodynamically, the oxidation of N_2 to NO_3^- should be strongly favored. Even microorganisms are not able to catalyze this reaction, because the activation energy required to cleave the N ≡ N triple bond is too high. Many other redox reactions are catalyzed by microorganisms, which then use a portion of the liberated energy for their own metabolism. However, this only occurs if the reaction is thermodynamically favorable, i.e. the reaction liberates energy. Thermodynamics can therefore be used to determine whether a redox reaction can take place, and how much energy is liberated in the process. It does not deliver any information on the kinetics of the reaction.

Some redox reactions take place spontaneously, without the participation of microorganisms. For example, Fe^{2+} oxidizes rapidly in contact with O_2 and water at pH > 6 to form Fe^{3+}, which precipitates as sparingly soluble iron hydroxide. The kinetics of this redox reaction depends on the concentrations of Fe^{2+} and O_2 as well as the pH value of the solution. The oxidation rate of Fe^{2+} can be expressed with a simple kinetic equation

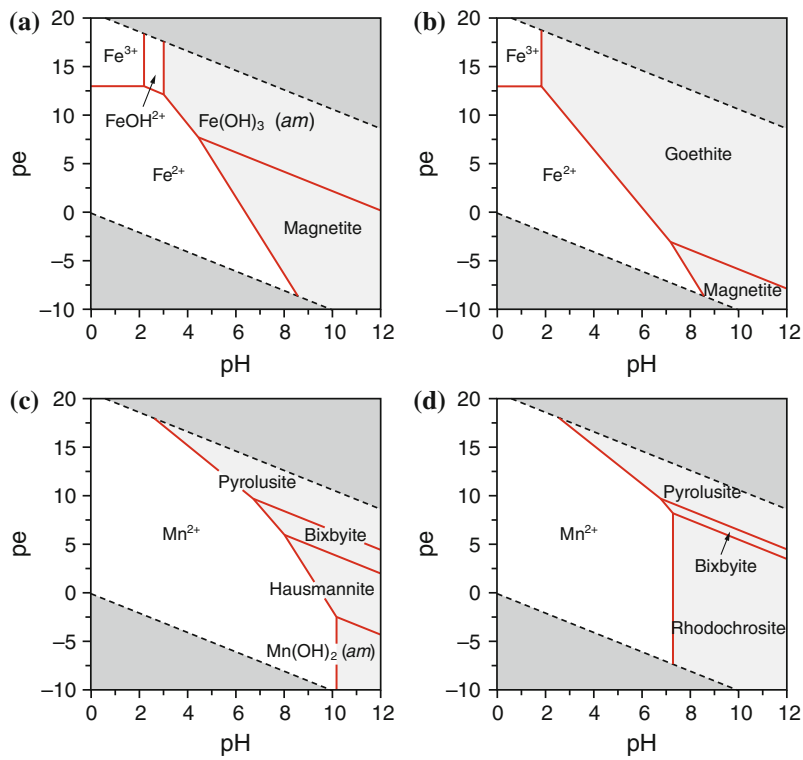

Fig. 5.20 Stability fields of Fe and Mn species as a function of solution p*e* and pH, for an ion activity of 10^{-5} M under standard conditions (1 bar, 25 °C): **a** Fe^{3+}, Fe^{2+}, $FeOH^{2+}$, Fe(OH)$_3$(*am*) and magnetite (Fe_3O_4); **b** Fe^{3+}, Fe^{2+}, goethite (α-FeOOH) and magnetite; **c** Mn^{2+}, pyrolusite (β-MnO_2), bixbyite (Mn_2O_3), hausmannite (Mn_3O_4) and Mn(OH)$_2$(*am*), and **d** Mn^{2+}, pyrolusite, bixbyite, and rhodochrosite ($MnCO_3$) at a CO_2 content of 1 % in the soil air ($P_{CO_2} = 0.01$). The stability fields were calculated with *The Geochemists Workbench*

$$\frac{d[Fe^{2+}]}{dt} = k[Fe^{2+}][OH^-]^2 P_{O_2} \quad (5.96)$$

where square brackets represent dissolved concentrations, P_{O_2} is the relative partial pressure of oxygen, and the rate constant is $k = 8 \times 10^{13}$ min^{-1} mol^{-2} L^2 (at 20 °C). This reaction takes place rapidly at neutral to weakly acidic pH values. At low pH or low O_2 partial pressures, however, the reaction is much slower.

Compared to the oxidation of Fe^{2+}, the spontaneous oxidation of Mn^{2+} by O_2 in solution is much slower and only significant at pH > 8. For this reason, Mn^{2+} is considerably more mobile in soils than Fe^{2+}. As a result, the concentration of dissolved Mn^{2+} in the soil solution is often higher than would be expected based on thermodynamic calculations. The oxidation of Mn^{2+} in soils mainly takes place autocatalytically on the surfaces of already existing Mn oxide particles. In this process, Mn^{2+} is initially adsorbed onto the surface of MnO_2. Adsorbed Mn^{2+} is oxidized by O_2 to form MnO_2 much faster than dissolved Mn^{2+}. This behavior explains why, in contrast to Fe, Mn forms very sharply defined enrichments and concretions in hydromorphic soils. Some microorganisms are also capable of catalyzing the oxidation of Mn^{2+} by O_2 to obtain energy. Thereby, they form biogenic Mn oxides that are extremely nano-crystalline and highly reactive.

The surfaces of Fe and Mn oxides as well as of iron-bearing clay minerals can participate in numerous other redox reactions and sometimes act as a catalyzer. For example, phenols and aromatic amines, as well as As(III) and Cr(III) can be oxidized on the surfaces of Mn oxides.

Because the kinetics of many redox reactions is controlled by microorganisms, which consume oxygen and catalyze reactions, the redox dynamics of soils is highly dependent on the environmental conditions. The most important influencing factors are the availability of O_2 and carbon sources (decomposable organic matter), the temperature, the pH, and the nutrient availability. Neutral soils rich in labile organic matter under warm temperature conditions exhibit the strongest redox dynamics. Under such conditions, soil microorganisms respire O_2 very rapidly, and the soil becomes anoxic after a few days of water saturation.

5.7.4 Redox Processes in Soils

Intense rainfall and/or poor drainage, groundwater rise, or floods can cause prolonged water saturation of soil pore space. With increasing water saturation, the diffusion rate of O_2 in the pores drops dramatically. The diffusion of O_2 in water-filled pores is about 10,000-fold slower than in air-filled pores. Oxygen that is still present in the soil under these conditions is consumed much faster by aerobic microorganisms and plant roots than it can be replenished through diffusion from the atmosphere. As a result, the oxygen content in the soil drops to practically zero within a few hours to days; the soil first becomes suboxic and then anoxic, and the redox potential Eh (or p*e* value) decreases.

In the suboxic and anoxic range, the soil organisms are dominated by facultative and obligate anaerobic microorganisms. These also oxidize organic substances to yield energy, however, they do not transfer the liberated electrons to oxygen as the terminal electron acceptor, but rather to other organic or inorganic compounds, which are then reduced. Under anoxic conditions, organic substances are decomposed to form CO_2 and H_2, as well as low-molecular aliphatic acids (e.g. acetic acid, butyric acid, lactic acid), polyhydroxy carboxylic acids, aldehydes, amines, mercaptans, NH_4^+, H_2S, C_2H_4 and CH_4. These degradation processes are much slower than with aerobic respiration under oxic conditions.

Analogous to a pH buffer that absorbs liberated protons and stabilizes the pH value in a certain range, redox couples can also buffer the p*e* value or the redox potential. With gradually sinking redox potential, a sequence of redox reactions sets in, which corresponds to the thermodynamic properties of the involved redox couples (Table 5.12).

If the O_2 content in a soil drops to the suboxic range, the first alternative electron acceptor used

Table 5.12 Experimentally determined redox potentials for various redox reactions (converted to pH 7)

Observed redox process	Eh (V) at pH 7
Onset of NO_3^- reduction	+0.45 to +0.55
Onset of Mn^{2+} formation	+0.35 to 0.45
O_2 no longer detectable	+0.33
NO_3^- no longer detectable	+0.22
Onset of Fe^{2+} formation	+0.15
Onset of SO_4^{2-} reduction and sulfide formation	−0.05
Onset of CH_4-formation	−0.12
SO_4^{2-} no longer detectable	−0.18

by many microorganisms is NO_3^-, which is then reduced to N_2 and smaller amounts of N_2O, NO and metastable NO_2^-. Because the gases N_2 and N_2O can escape to the atmosphere, this process (**denitrification**) leads to significant gaseous nitrogen losses from cultivated arable soils (Sect. 9.6.1.4). The trace gas N_2O is a potent greenhouse gas and contributes significantly to global warming. Smaller fractions of NO_3^- can also be reduced to NH_4^+ (**nitrate ammonification**). This process was observed in subhydric soils and in soils with waste water irrigation. However, its quantitative significance compared to denitrification has still not been sufficiently investigated.

When O_2 and NO_3^- are depleted, the redox potential drops further into the anoxic range. Various facultative (e.g. *Shewanella* sp.) or strictly (e.g. *Geobacter* sp.) anaerobic bacteria now use oxidized metal species as electron acceptors. The reduction of Mn(IV/III) to Mn(II) begins first, followed by the reduction of Fe(III) to Fe(II). This leads to a reductive dissolution of oxides and hydroxides of Mn(IV/III) and Fe(III), and to a strong increase in the concentrations of Mn^{2+} and Fe^{2+} in the soil solution and on cation exchanger surfaces. Humic substances and other organic compounds play an important role as electron shuttles between bacterial cells and oxide surfaces, and thus strongly promote the reduction of Mn and Fe oxides. The reductive dissolution of Mn and Fe oxide minerals leads indirectly to a mobilization of trace elements (e.g. As, Mo, Cd, Pb, Cu, Zn) and phosphate, which were adsorbed to these oxides. Redox-sensitive trace elements can also be reduced by bacteria (e.g. As(V) to As (III) and U(VI) to U(IV)).

A further decrease in the redox potential leads to a microbial reduction of sulfate (SO_4^{2-}) to H_2S. Many different bacterial species are capable of this, which are combined under the name **sulfate-reducing bacteria** (SRB) according to this metabolic function. Most SRB use low-molecular organic compounds (e.g. formic acid, acetic acid, butyric acid, lactic acid) as a substrate and liberate H_2S according to the reaction:

$$2CH_2O + SO_4^{2-} \rightleftharpoons H_2S + 2HCO_3^- \quad (5.97)$$

Although many SRB tolerate the presence of oxygen, their activity is strongly inhibited. For this reason, sulfate reduction can start very rapidly as soon as the conditions are sufficiently anoxic. In soils, anoxic niches where sulfate is already being reduced can occur locally, while in other areas of the soil, the redox potential is still too high. The produced H_2S either reacts with metals to form poorly soluble sulfides (e.g. HgS, CuS, CdS, PbS, FeS), or in cases of strong production, it escapes as a toxic, foul-smelling gas. Metal sulfides form via clusters and nanoparticles suspended in the soil solution, which potentially may transported with seepage water.

Finally, under extremely anoxic conditions, CO_2 is reduced to CH_4 (**methanogenesis**). This leads to the formation of fermentation gas (swamp gas), which mainly consists of methane. Methane emissions from soils (peatlands, swamps, paddy soils) play an important role in global climate change, because methane is a highly effective greenhouse gas.

5.7.5 Soil Redox Potential

The measurement of redox potentials in soils or soil samples in the laboratory encounters several problems. Because all redox couples are rarely at chemical equilibrium in the soil, and the Pt electrode is not equally responsive to all redox couples, the measured potential is a poorly defined

"mixed potential". Especially at very low concentrations of the oxidized and/or reduced species, the Pt electrode reacts only very slowly. Furthermore, several substances can poise (e.g. H_2S) or inactivate (e.g. oxide or carbonate precipitations) the Pt electrode. In this case, mechanical or chemical cleaning of the electrode must be performed regularly. The calomel electrode (Hg/Hg_2Cl_2), used as a reference electrode, can also be destroyed by H_2S as a result of the formation of mercury sulfide. For this reason, in samples containing sulfides, the reference electrode has to be protected from contact with the sample using an electrolyte bridge. Redox potential measurements in the field also often exhibit strong fluctuations, because the redox conditions in soils can exhibit strong spatial heterogeneity. Other systematic errors may occur because traces of oxygen are carried over when inserting the electrodes (especially in wet soils), or due to poor or lacking electrode contact (especially in dry soils). Redox potential measurements in soils should therefore be interpreted qualitatively. Nevertheless, they can provide valuable information on the redox dynamics in soils, and are therefore used in field and laboratory experiments together with other measurements.

Well-drained, strongly acidic soils have the highest redox potentials (up to +0.8 V). The lowest values are found under anoxic, neutral to alkaline conditions (up to −0.35 V). The redox potential of soils can vary strongly during the course of the year, especially in soil horizons influenced by groundwater or stagnant water, which are periodically wet. Here, in addition to the temperature, the redox dynamics also depends strongly on the soil's degradable organic matter content. When humus-rich Ah horizons are water-saturated, the redox potential decreases within a few hours, because microorganisms rapidly consume oxygen and the soil becomes anoxic. In contrast, microbial activity is much lower in subsoils with low organic matter contents, and the redox potential therefore drops more slowly and less strongly at water saturation. Cool temperatures also slow down the redox dynamics due to the lower microbial activity. In Reductosols, reduction takes place in unsaturated soils, because of leaking **reductive gases** (CO_2, CH_4) from post-volcanic mofettes, from landfills, or damaged gas pipelines preventing atmospheric O_2 from entering the soil (Sect. 7.5.1.16).

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6 Physical Properties and Processes

Soils are natural entities and as such, each soil is characterized by typical physical properties, with color (Sect. 6.8) and texture (Sect. 6.1) being the most readily visible. Therefore, they are important components of any soil description.

Beside both of these properties, the next parameter to be defined is the spatial distribution of the particles, being either homogenous or aggregated. Thus, structure is the next physical property that can generally be exhaustively documented by morphological description.

All other physical properties such as the stability, and therefore load-bearing capacity for trampling and wheeling, the pore size distribution and thus root penetration, as well as the water and air storage capacity, and temperature, i.e. the primary growth conditions for all plants, are correlated in different ways with the above-mentioned morphological properties. However, the correlations are often not very close when the soil primary properties are clearly altered by soil development and land use. For this reason, special measurements are required in most cases.

This applies particularly to movement and associated transport processes. These complex processes depend on the climate and weather conditions, and are therefore often seasonal. They influence the water and air balance of any soil, and non-stationary and periodically occurring processes are much more frequent and exceed the existence of continuous measurements within the scope of these regimes.

Correlations between the properties of all three groups are therefore of great practical significance. They enable statements without laborious and time-consuming measurements. This applies both to use-relevant properties and to the design of computer models for the representation of process cycles. In both cases, the results depend on the understanding of the type and extent of the correlations.

6.1 Texture and Packing

The material constituting the solid phase of the soil does not usually lie on the surface of the lithosphere as a continuum, but rather is in granular form. This applies not only to the inorganic components, which consist of rock fragments or mineral particles, but also to the organic components, which consist almost exclusively of or are derived from more or less broken down and decomposed plant material.

The texture and porosity resulting from the packing of these particles create space within the soil volume for water and air, as well as for roots and soil fauna. For this reason, these soil properties not only influence all living processes in the soil, but also the interactions between the solid, liquid and gaseous phases, as well as any transport and dislocation.

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6.1.1 Particle Formation

When solid rock is exposed to changing climatic conditions through geological processes, such as volcanoes, erosion by wind and water, retreat of water or ice, and changing environmental conditions, the internal stress conditions also change. This leads to tensile and shear failure fractures and the formation of a **crack network**. A previously continuous emerging rock mass thus soon becomes a collection of fragments and particles. During the course of further physical weathering (Sect. 2.4.1), the rock fragments continue to be crushed and sorted depending on the type of parent material, weather and climatic conditions as well as transport processes. This leads to the formation of various distributions and mixtures of particles of different sizes, the diameter of which can vary by several orders of magnitude. A comparable size distribution of the discrete particles can also be documented for organic soil components, resulting from the decomposition of plant debris mainly through the feeding processes of different soil-dwelling organisms, ranging from rodents to arthropods (e.g. mites). These organic particles often have much more irregular shapes than mineral or rock particles. In addition to such fragments and decomposition products, **new formations** also occur in soils in the form of inorganic or organic components. With increasing size of these new formations, their fraction in the overall texture decreases. New formations do not always occur as discrete particles. They may also be formed as a film or coating on larger particles and only become free particles during further soil development.

Such unconsolidated particles are also described using the term **primary particle**, in order to clearly differentiate them from aggregates, i.e. units consisting of adhering primary particles. **Aggregates** can occur in all sizes and exhibit different stabilities. For the assessment of the particle size distribution, it is therefore important to consider the degree to which the aggregates were broken down into their primary particles before or during the analytical process. Because of the mentioned varying strength, the proper recording of primary particles always represents difficulties, which can only be avoided by observing the conventional laboratory pretreatments e.g. of the organic matter or carbonates.

Particles with a diameter <2 mm are of special significance for soil development and use. On the one hand, significant amounts of water can be held between them against the force of gravity, which than also influences the fraction and quantity of air. On the other hand, the extent of chemical adsorption and exchange processes depends on the available mineral surface per unit mass. This, in turn, increases with decreasing particle size.

6.1.2 Particle Size

Both the crushing of coarse fragments into smaller ones but also the formation of new and coarser particles result in a great variation in the scale of the occurring sizes. They may vary from the meter range to beneath the resolution limit of an optical microscope. In order to have a standard index for this wide range, the median (of the logarithm) of the equivalent diameter of the primary particles is generally used for characterization. The **equivalent diameter** is an auxiliary value that enables the assignment of a diameter both to individually tangible particles and to those that can only be seen under the microscope. It is thus a convention.

For particle separation by sieving, the particle diameter is defined by the diameter of the holes or mesh of the sieve as the boundary between two particles size classes, especially when the particles are not spherical. In the range of particle separation by sedimentation, the equivalent diameter corresponds to double the radius of a sphere that settles just as fast as the corresponding primary particle during sedimentation assuming spherical form. This single parameter enables the measurement of particles across the range of all existing shapes and dimensions. The particle size scale can then be represented as a continuum. Due to its large span from 10^0–10^{-9}, it is depicted on a logarithmic scale.

Since digits do not illustrate the equivalent diameter very well, simple names, some of which are colloquial, are used to designate the main particles fractions. The fraction limits used here are defined by convention (Fig. 6.1).

6.1.3 Particle Classification

In most cases, the size of the primary particles, represented by the equivalent diameter, is used for their classification.

6.1.3.1 Particle Size Fractions

In many countries, a logarithmic scale is used for the classification of equivalent diameters into fractions. The fraction limits suggested by ATTERBERG are based on the digit 2. According to this convention, first the soil skeleton (coarse soil) with equivalent diameters >2 mm is separated from the fine soil with diameters ≤2 mm. In Germany, the fine soil fractions for sand, silt and clay are further classified by dividing the scale sections based on the digit 2 in the middle of the logarithmic scale, i.e. at the digit sequence 63. The resulting fraction boundaries are shown in Fig. 6.1. The figure demonstrates that e.g. the USA does not adhere to the convention of the equidistant logarithmic interval (0.5 as the difference between the digits lg 2 = 0.3 and lg 6.3 = 0.8 etc.) for the fine earth range at the transition from silt to sand (at 50 µm). The boundaries also vary in the range of the skeleton. Nonetheless, all classification systems share the same boundary for the clay fraction beginning at ≤2 µm; for soil evaluations, however, the smallest particle size is <10 µm (see Sect. 11.2).

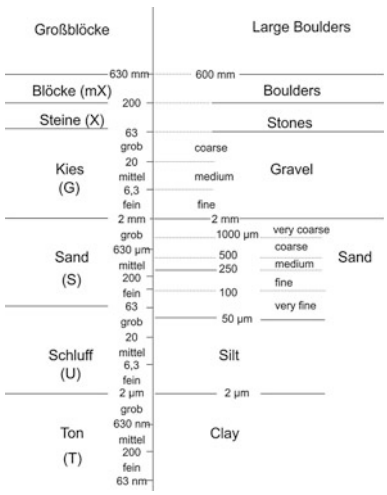

Fig. 6.1 Classification of particle size fractions. German (*left*) and American nomenclature (*right*)

6.1.3.2 Mixtures, Particle Size Distributions

The particle mixture existing in a soil can cover a wide or narrow range on the size scale shown in Fig. 6.1. Their sizes can be mixed, or more or less well-sorted. This data is best shown by means of a **cumulative particle size distribution curve** (Fig. 6.2). This continuous curve is obtained by connecting the points representing the experimentally determined cumulative fractions that are bigger or smaller than a given equivalent diameter. This representation reflects the character of a particle size distribution better than a histogram drawn from the analytical data. Smoothed cumulative curves also offer the possibility to convert the percent fractions from other classification systems to standard values, as shown e.g. in Fig. 6.1.

Examples of conventional classifications for the fine earth particle mixture are the triangle diagrams shown in Fig. 6.3 (for the German), and in Fig. 6.4 for the FAO and the World Reference Base (WRB) classification systems. They are based on the agreement in the definition of the upper limits of the clay and sand fraction shown in Fig. 6.1. Within these fractions, however, the classification does not concur. In Germany, the classification shown in Fig. 6.3 is defined by a

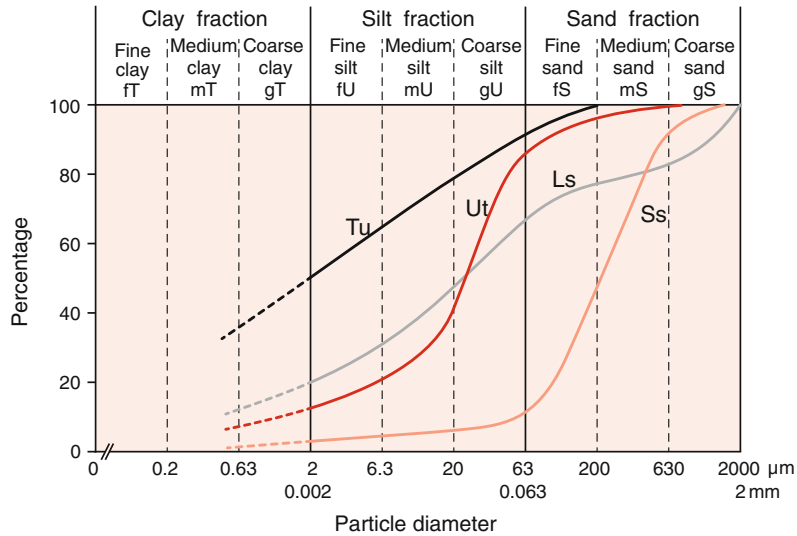

Fig. 6.2 Cumulative particle size analysis curves for the fine earth (<2mm) taken from soils consisting of sand (Ss), loess (Ut), glacial loam (Ls) and clay-rich mud (Tu)

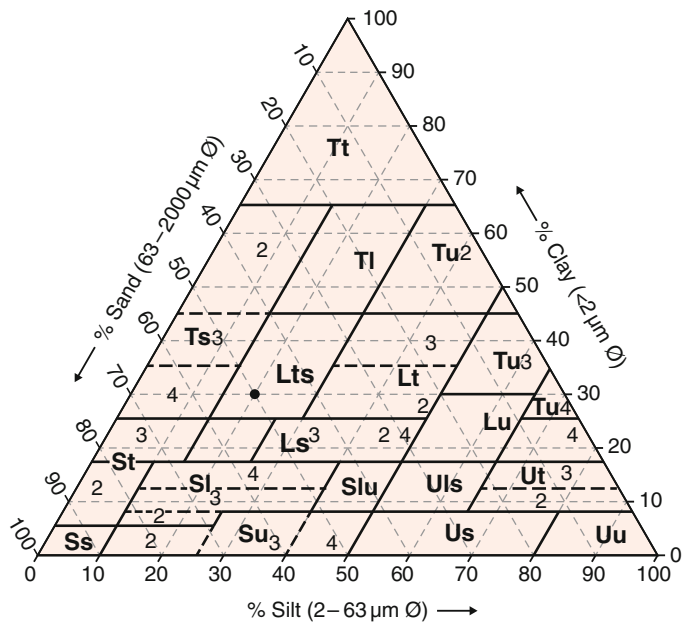

Fig. 6.3 Soil textures of fine earth in the triangle coordinate system. *S, s* sand, sandy; *U, u* silt, silty; *T, t* clay, clayey; *L, l* loam, loamy. The numbers *2*, *3*, *4* within the respective field indicate the proportion of the secondary fraction characterized by the adjective. The marked point *bullet* (•) corresponds to fractions of 50 % sand, 20 % silt and 30 % clay

German Standard 4220 but also introduced in Europe as DIN—ISO. In addition to the designations listed in Fig. 6.1, the term "loam" also appears in the texture triangle (Figs. 6.3 and 6.4). It does not represent an inherent particle size fraction, but rather a mixture (of sand, silt and clay).

In German, the term **soil texture** was introduced for the particle size distribution of fine earth. It is based on the designation of the texture mixtures in the country's soils evaluation in 1934, where it is only defined by the % fraction <10 µm, as it still is today. The German

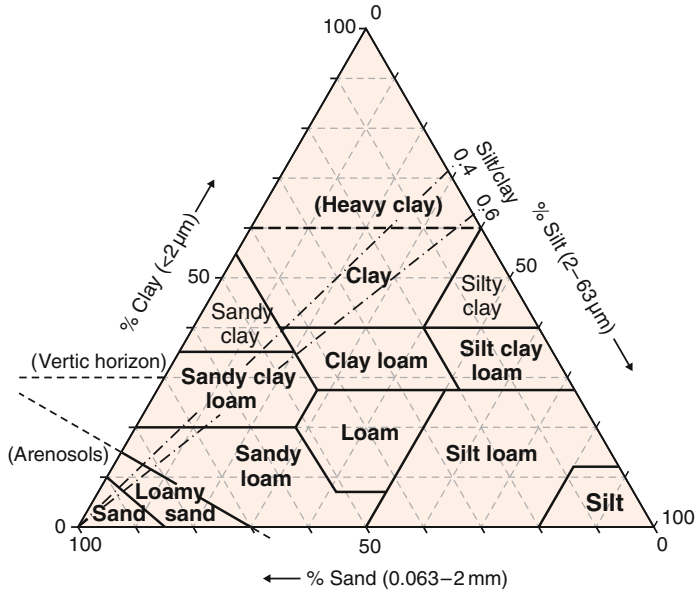

Fig. 6.4 Soil textures of fine earth according to the FAO and the World Reference Base (WRB)

mapping instructions (5th Edition) make a distinction between a total of 21 different groups, from pure sand (Ss) through to clayey clay (Tt).

6.1.3.3 Determination of the Particle Size Distribution

The proportions of the individual fractions are generally determined for the purpose of drawing a cumulative particle size distribution curve. Depending on the conditions, a varying number of fractions can be used. This curve is generally drawn for the fine earth fraction (Ø < 2 mm) (Fig. 6.2). In skeletal soils, however, the percent fraction of gravel must also be considered.

Before the fine earth is analyzed, readily soluble salts (including gypsum) must be removed with water because they inhibit dispersion; carbonate/lime is often destroyed using hydrochloric acid, and organic matter is oxidized using hydrogen peroxide. In special cases, the iron oxides are also removed using a Na-dithionite/citrate/hydrocarbonate extract. The aqueous solution is then agitated with a dispersion agent such as sodium metaphosphate, because phosphate complexes Al, Ca and Mg ions that have a coagulating effect, which are then replaced by strongly peptizing Na ions.

Other methods are also used in addition to the preparations described here, depending on the purpose of the investigation. For example, the lime may not be destroyed if the lime particles exist as separate constituents of the texture range.

In the fine earth fraction, the proportions of the sand fractions are determined by **sieving**. The proportions of the silt and clay fractions, in contrast, are determined by **sedimentation**, usually using the pipette or areometer methods. These methods involve the calculation of the **sedimentation velocity** (v), which depends on the particle size (radius r), the difference in density between the particles (ρ_S) and water (ρ_w), as well as the temperature-dependent viscosity of water (η) and the acceleration (g), according to the equation by Stokes (1845):

$$v = \frac{2 \times r^2 \times (\rho_F - \rho_w) \times g}{9 \times \eta} \qquad (6.1)$$

The equation only applies for spheres and is therefore, strictly speaking, only directly applicable for sands. The finer the particles, the more they deviate from a spherical shape, and in clay minerals, they ultimately reach a completely platy shape. For all shapes other than spheres, a so-called equivalent radius is determined as the

average radius of the particles, and this is set to be equal to the radius of the sphere.

The density of quartz is usually used as the density of the mineral particles ($\rho_s = 2.65$ g cm^{-3}) because this mineral is common in soils, provided that the soils do not consist of e.g. basalt, limestone, high iron oxide contents or humic material.

It is very time-consuming to perform a complete texture analysis. Alternative methods involving the use of gamma radiation or laser technology are used just as estimation methods. The latter are mainly used within the scope of field work. A **finger test** can be performed on a moist sample to identify texture criteria such as plasticity, rollability, smearability and coarseness. The clay fraction can be easily formed and has a shiny surface due to the squeezed-out water, and at the same time, it has a smooth smeared surface due to the alignment of the clay platelets. Silt is less deformable; it is floury and becomes easily dusty. Its smeared surface is coarse. Finally, sand cannot be rolled and deformed, and its grains are visible. In humic samples (to be described with the color), the humus content must be subtracted from the value estimated for the clay fraction. Experienced soil surveyors are capable of estimating the fractions of these three soil components with ca. 5 % accuracy in the range up to 20 % clay. If the clay fraction is more than 20 %, the estimates are less accurate. Thus, in many cases it is possible to use a finger test to assign the soil texture to a soil type, i.e. a section of a soil texture triangle as shown in Fig. 6.3, with high reliability.

6.1.4 Particle Properties

The particles (primary particles) of the inorganic components generally determine the soil's character. Only in cases with high organic matter fractions, as they are observed in e.g. humus rich soils or moors (Sect. 7.5.4), the character of the mineral particles is masked by their properties.

6.1.4.1 Composition and Shape

While the primary particles in block, stone, gravel and coarse sand fractions are generally rock fragments, mineral particles dominate the finer sand, silt and clay fractions. Here, the proportion of new formations from the clay mineral and oxide groups is the greatest. In terms of the shape and the variation spectrum of the shapes, the roundness of the particles in both the skeletal fraction and in the silt and clay fractions decreases, while a spherical shape is most common in sands from sedimentary rocks. In the gravel and stone range, very sharp-edged shapes can occur (=debris, grit), while boulders and pebbles can be very rounded. The particles also approach the shape of the minerals from which they are formed. For this reason, the clay fraction is characterized by its irregular shapes, and many clay minerals by a pronounced platelet shape because they are layered silicates (Sect. 2.2.3). Irregular shapes also characterize the fine particles in strongly humified peat.

6.1.4.2 Surfaces

The surface area and the mass unit are closely related to the degree of roundness and the particle size. Already the division of the mass of a sphere into always more and smaller spheres leads to a considerable increase in the surface area (Table 6.1). Any deviation from a spherical shape increases the surface area of a body in relation to its volume. Thin platelets represent the furthest deviation from a sphere. For this reason, they have the largest surface area related to their mass (or their volume). The size of the platelet diameter, which is measured using the surface area, is not as important as its thickness. Because the similarity to a sphere decreases from sand through silt to clay, the increase in surface area per unit of mass is much greater in natural soils than shown in Table 6.1. If the platelets are thin enough, it can reach ca. 1,000 m^2/g of clay. The surfaces of the mineral particles in the sand and silt fractions are generally not completely exposed. They are often

Table 6.1 Relationship between particle size, grain number, and total surface when dividing a sphere with a radius r = 1 cm into spherical particles

Sphere radius	Number of spheres	Total surface area
10 mm	10^0	1.26×10^1 cm^2
1 mm	10^3	1.26×10^2 cm^2
0.1 mm	10^6	1.26×10^3 cm^2
0.01 mm	10^9	1.26×10^4 cm^2
1 µm	10^{12}	1.26×10^5 cm^2
0.1 µm	10^{15}	1.26×10^6 cm^2

covered with thin films of fine material, such as newly formed minerals or their precursors. In the A horizon, these films often consist of organic material, which in turn can have significant seasonal effects on the wettability of particles and aggregates. In the clay fraction, accessibility of the surfaces is impeded by the formation of microaggregates. This is exhibited e.g. by the fact that textural analysis performed using only water as a dispersing agent only records part of the material belonging to the total clay.

6.1.5 Common Particle Distributions

The texture of a given soil is the result of interactions between the parent material and its development, weathering and rounding and where applicable, the size and mineral type sorting due to transport by flowing water or by wind. As a result, some textures occur more often than others, and the spatial distribution is also subject to physical laws.

6.1.5.1 Reasons

Particle mixtures that are transported by wind or water are more strongly **sorted**, i.e. they have a narrower concentration of the diameter around an average value, than those flowing in the presence of large amounts of water or sliding down a slope (e.g. mudflows). Sediments transported by ice are also **unsorted**, unless the glacier carried material that was already previously sorted.

As a result, well-sorted textures are more often found in landscapes where the arid climate promotes transport by wind, i.e. in deserts (cold and hot deserts), and also areas with extensive water flow events, such as floodplains, in the tidal zones of oceans, and in wadis in hot deserts. Another correlation is the fact that individual particles of the silt fraction are most easily carried by wind and can be transported over long distances, because they can remain in a suspended state for a long time at the frequently occurring wind velocities. For this reason, silt-rich eolian deposits (loess) on continental surfaces are the most common and their texture provides a uniform parent material for soil development.

Coarser particles are less frequently found over large areas, because neither the water nor the wind velocity is sufficient to initiate more extensive or long-distance transport. Desert crusts and gravel layers, originating from deflation, washing out of fine fractions or through downward movement of coarser particles (cryoturbation and peloturbation), are generally very thin, as suggested by their names. Clays are also seldom extensively transported by wind, and if they are, then usually in the form of aggregates that would be assigned to the silt fraction. Transport by flowing water, in contrast, leads to large-scale clay accumulations, because clays are more strongly dispersed in water, i.e. they are displaced without restriction to the aggregated state.

These regularities cause some textures to occur more often than others (Fig. 6.5). The texture triangles show that sands are the fraction that is purest, i.e. is the most well-sorted (up to >95 %). Silt-rich sediments, as they are found in loess or in marshes and floodplains, hardly ever contain less than ca. 10 % clay. Clay contents of more than 80 % are also rare, and the rest of the texture then consists of silt. Clay-rich textures are not only found in fresh sediments and in weathered clay rocks (clay-schist series), but are also observed as a product of the weathering of limestone, if the non-carbonate residues accumulate. These mainly belong to the clay fraction, because the coarser grains are seldom transported into the range of lime deposition.

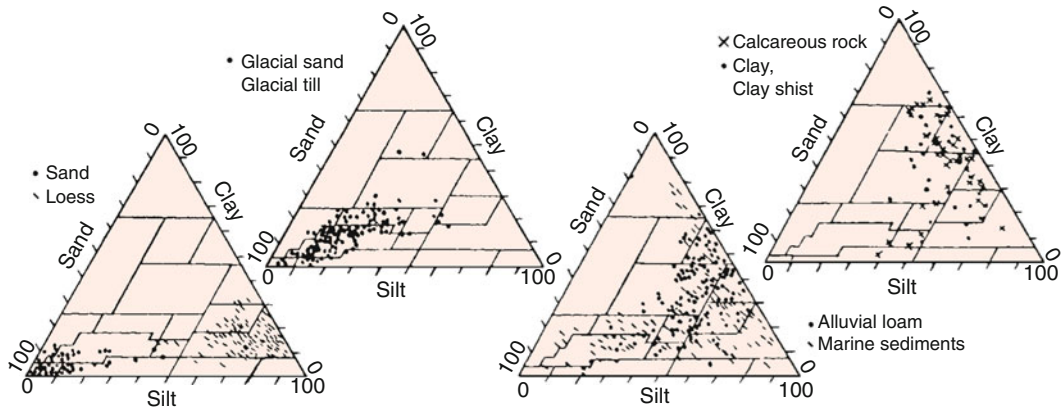

Fig. 6.5 Texture of common soils developed from different parent rocks from Central Europe (from Hartge and Horn 2014)

6.1.5.2 Landscape-Related Occurrences

The described correlations cause the occurrence of specific textures to be roughly determined by the geological and climatic history of a landscape and the influenced geomorphological forms.

This includes the observation that the character of a hard sedimentary rock in young landscapes determines the texture of the weathering material and thus the nature of the soils. Soils developing from the weathering of sandstone have high sand fractions, while the weathering of schist results in high clay fractions. Sites where the parent material for soil formation is located near the weathering site due to gravitational mass movement (landslides, solifluction) generally have a particularly wide spectrum of grain sizes. This is true for sites close to mountains, but also for areas affected by former glaciations. In contrast, more strongly sorted textures are always found in floodplain landscapes and also in mudflat and sander sediments. The sorting increases with the distance from the weathering site, i.e. in rivers, towards the lower reaches of the waterways. In principle, the average grain size decreases in the same direction. For this reason, finer textures are more often observed at the lower reaches of rivers and streams than at their origins. Parallel to this, the texture close to the river, in the banks, is always coarsest and becomes finer with increasing distance from the riverbed, because only here does the current allow the finer particles to settle (see Sect. 8.3). The widespread distribution of loess-like textures has already been mentioned. They are formed in areas with climates where the substrate is rarely wetted so that menisci are formed, i.e. if it is dry or cold. In parent rocks from old geological surfaces, the results of the above-mentioned processes can be so altered by the further course of weathering at the site that the correlations described here are no longer observed.

As a general rule, it can be assumed that most soils fall into the wide range of loams and loamy soils. This can be seen in the frequency distribution curves in Fig. 6.5, but also in the frequency with which loamy soils are found in data compilations. As a result, the classification of this texture range is particularly well differentiated (Figs. 6.3 and 6.4).

6.1.6 Packing of the Primary Particles

Because of the varying particle size distributions and the diversity of shapes of the primary particles, the solid phase is not able to completely fill the space, even at the highest packing densities. The remaining interstices are called **pores**. Together, the solid particles and pores form the **matrix**, where water and air are stored and flow,

and where all chemical and biological processes, but also leaching and accumulations take place. For this reason, the porosity as well as the physical laws governing its development and changes describe soil properties that significantly influence almost all processes in all soils.

6.1.6.1 Bracing and Contact

A central point of the packing of primary particles is the mutual bracing in the overall structure. This takes place at the contact points between the particles. The closer these particles are packed, and thus the higher the soil density, the more there are points of contact, in principle on every grain. The more intensive the bracing due to more contact points within the soil volume, the greater the soil's resistance towards further compression or displacement.

This relationship is so universal in soil science terminology that it is used as a generalizing contrast to a loose soil for both 'more compact' (=compaction) and 'more dense' soils (=consolidation, stabilization). However, this wide-spread simplification neglects the fact that although an increase in the number of contact points is a common cause for an increase in density, it is not the only reason. A selective increase in the strength at a given number of contact points is the alternative. Examples for this are the formation of hard pans in Podzols, the formation of bog iron ore in Ferric Gleysols, the formation of loess puppets in Chernozems, the formation of calcrete in Calcisols or the formation of duripans in Durisols (see Sect. 7.2.6).

The correlation between the number of contacts per sphere and the mass per unit of volume and thus with the void ratio is particularly evident with same-sized spheres (Fig. 6.6). The volumetric void ratio in this figure is based on the volumetric ratio of the solid particles, i.e. the volume of the spheres, because it does not change. For this reason, the void ratio is plotted on the ordinate. The graph shows that the total volume increases with a reduction in the number of contact points per sphere. In a soil where the solids cannot deflect to the side, which is generally the case in large-scale load changes, the height of the packing increases. Changes in the

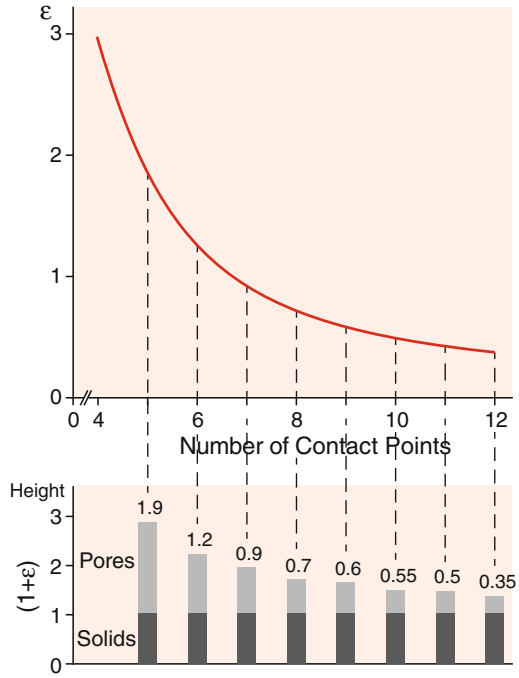

Fig. 6.6 *Top* Correlation between the number of contact points and the void ratio with same-sized spheres. *Bottom* Height difference based on the same total volume of the spheres depending on the number of contact points (after Hartge and Horn 2014; values from von Engelhardt 1960)

number of contact points not only also lead to changes in strength, but also to changes in the height of the soil surface.

In the case of ideal rigid spheres, the contact surfaces are infinitely small. With irregularly shaped primary particles, in contrast, more extensive contact surfaces can also occur. This may potentially prevent direct grain-to-grain contact, because water films remain between the mineral particles that would be expelled with true point contact. This affects the strength of the soil when subject to changes in the applied stress (Sects. 6.3.3 and 6.3.4).

Because the soil mineral particles beneath the gravel fraction are rarely loaded to their break point under the loads occurring in the topmost 5–10 m, configurations that develop during sedimentation cannot be easily changed at a later time. The most dense orderly packing, as shown in Fig. 6.6 for same-sized spheres with 12 contact points each, is therefore never reached under

natural conditions, even if during the glacial periods, glaciers with a thickness of several hundred meters not only planed the subsoil smooth, but also the ground moraines became more intensely compressed due to shearing. After melting, during which a slight relief occurs and platy structures are formed, glacial till still exhibits ca. 30 % pore volume and thus less than 12 grain contact points.

6.1.6.2 Packing Parameters

Depending on the required information, various methods are used to characterize the packing state of a soil, which differ mainly in their reference basis.

If the focus is on the total soil volume (Vt) and the change in the pore ratio (Vp) is based on this, it is referred to as **porosity** or the **pore volume** (n or PV) (Fig. 6.7).

$$PV = n = \frac{Vp}{Vt} = \frac{Vp}{Vp + Vs} \tag{6.2}$$

If the focus is on the change in volume in the overall system, then the solid particle volume (Vs) is used as a reference basis. This correlation parameter is called **void ratio** (ε or PZ).

$$PZ = \varepsilon = \frac{Vp}{Vs} \tag{6.3}$$

Both the porosity as a decimal (e.g. 0.4) or as a percent (e.g. 40 %) and the void ratio can be calculated using the **bulk density** of a sample (ρ_B), because this is the easiest method and is least prone to error. The equations used for this purpose are:

$$n = 1 - \frac{\rho_B}{\rho_F}; \tag{6.4}$$

$$\varepsilon = \frac{\rho_F}{\rho_B} - 1 \tag{6.5}$$

The bulk density of the sample (ρ_B) can therefore also be directly used as a measurement for the packing. This is then referred to as the bulk density or **soil density** (in contrast to the particle density ρ_s), where the mass of the soil dried at 105 °C is related to the total volume.

$$\rho_B = \frac{m_f}{Vt} \tag{6.6}$$

Here, m_s is the mass of the solids contained in a volume Vt.

If the mass of the moist soil is related to the total volume, it is called the **wet density**. In this case, the total mass includes the mass of the water (m_w) contained at that moment ($m = m_s + m_w$).

6.1.6.3 Soil Pore Ratios

The size of the pore volume (or the void ratio) depends on the texture and grain shape, the soil organic matter content, and on the soil development. Initially considering the most dense packing with spheres of the same size, regardless of

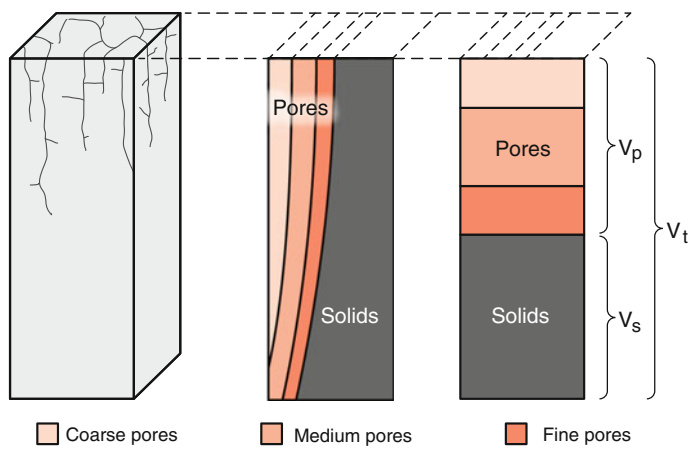

Fig. 6.7 Fractions of the pore space in the total volume as a basis for the calculation of pore volumes (=porosity) and void ratio; V_p = pore volume, V_s = solid volume, V_t = total volume

the sphere size, a pore volume of just under 26 % is obtained, a void ratio of 0.35, and with quartz, a soil density of ρ_B = 1.96 g/cm^3. If the packing is less well-arranged, the sample's pore volumes are larger. Thus, when spheres of the same size are filled (e.g. glass beads) into a vessel, pore volumes of 38–42 % (ρ_B = 1.65–1.54 g/cm^3) are obtained. The pore volumes or soil densities observed in sandy soils below the Ah horizon lie in the same range. If this is compared to packing with spheres of different size, the pore volume decreases as the difference in size of the spheres increases. Deviations from the spherical shape, e.g. towards a more platy form, usually lead to an increase in the pore volume (card-house structure). In general, an increase in pore volume is observed with decreasing particle size (Table 6.2), which is partly due to increasing deviation from the spherical shape, and partly due to the increasing effects of surface forces.

This is particularly true for the finest particle size fraction, clay. If its generally platy particles were all aligned in the same direction, its pore volume should be much smaller than that between the spherical sand particles. In reality, however, clayey soils almost always have greater pore volumes (Table 6.2). This is due to the irregular, card-house-like packing of the clay minerals, where the surface forces overshadow the mass-related forces. Freshly deposited clayey sediments, in which the interstitial spaces between the particles are filled with water, have pore volumes of 70–90 %. Due to the 'flocculating sedimentation', the salt concentration in this water as well as the type of exchangeable cations further increase the pore volume.

Table 6.2 Variation of the bulk density, pore volume and void ratio in mineral soils (C content up to 2 %)

	Bulk density (g cm^{-3})	Pore volume (PV) (%)	Void ratio (ε) (–)
Sand	1.16–1.70	56–36	1.27–0.56
Silt	1.17–1.63	56–38	1.27–0.62
Loam	1.20–2.00	55–30	1.22–0.43
Clay	0.93–1.72	65–35	1.85–0.54

However, this large pore volume in clays is not stable. If the particles move closer together when water is removed from the overall system or if the overlying layers press them together (Sect. 6.2.2: shrinkage), the pore volume is reduced to 40–50 %. Even in this range of magnitude, however, the pore volume in clayey soils is never as stable as that in sandy soils, but rather can increase again with additions of water due to swelling.

The pore volumes in other textural classes, e.g. in silty soils, lie between those of sandy and clayey soils (Table 6.2). This is especially true for loess soils, which are important in agriculture. The main exceptions are soils where the interstitial space between large particles can be filled to a vast extent with finer particles. As a result, the bulk density increases in more poorly sorted textures. This is observed e.g. in glacial loams, where this effect is even intensified when the alignment of the texture is improved by high pressure under the ice. For this reason, ground moraines are often more densely packed than push moraines, where the finer particles are washed out by secondary melt water outflow and the degree of sorting is increased. In ground moraines, the measured pore volumes range between 26–0.30 % (ρ_B = 1.96–1.78 g cm^{-3}; ε = 0.35–0.49). Bogs represent the other extreme, with pore volumes of up to 95 % (ρ_B = 0.1 g cm^{-3}; ε = 9.77; ρ_S = 1.4 g cm^{-3}). Soils from volcanic ashes and tuffs (Andisols), which are mainly found in Chile, Japan and New Zealand, have pore volumes of 70–80 % (ρ_B = 0.8–0.5 g cm^{-3}; ε = 2.3–4.3).

The pore volume (PV) and void ratio (ε) can be determined through sampling with a cylinder of known volume and separately calculating the volume fractions of water and air using Eqs. 6.1.2 and 6.1.3 in Sect. 6.1.6.2. The volume of water is obtained by drying the soil at 105 °C ($\rho_W \sim$ 1 g cm^{-3}), and the volume of air can be directly measured using e.g. an air pycnometer.

6.1.6.4 Pore Shapes

The shape of the pores in a subsoil consisting of densely packed sand can be described using linked tetrahedra and octahedra with the convex

surfaces curved towards the middle of the pore. These pores are called **primary pores** or also texture-related pores.

It is difficult to describe the shapes of primary pores in clayey soils, because they depend on the orientation of the clay platelets, i.e. the type of card-house structure (Fig. 6.10), and on the mutual distance (Figs. 6.15 and 6.16). The development of the card-house structure depends on the composition of the exchangeable ions, the salt content of the soil solution and the extent of the maximum previous drainage.

In addition to these texture-related pores, another group is found in soils, the **secondary pores**. These mainly include the shrinkage cracks, root and animal tunnels (earthworm burrows), as well as irregular voids that are formed e.g. through loosening and rummaging by animals, windthrow or soil tillage (Fig. 6.16).

These secondary pores are often characterized by strongly pronounced continuity and, compared to the primary pores, a significant size (equivalent diameter >50 μm). Their proportion and their vertical length often have a strong effect on the soil water and air regimes. Secondary pores also differ from primary pores in that they can be relatively easily destroyed, because the edges of the primary particles are only supported by other particles on one side. This is even truer for extensive pores, i.e. cracks, than for tunnel-shaped pores. The secondary pore system is often the **hollow mold matrix** of the aggregates; in coherent soils, it is the worm and/or root tunnels. The extent of the development of the secondary pore system can therefore also be described by the type of aggregates (Sect. 6.3.1). It generally decreases in the soil profile from top to bottom. This is clearly expressed by the distribution of the hydraulic conductivities, where the influence of the primary pore system increases with increasing depth (Fig. 6.35). Thus, in soils with aggregated structures, there are two interconnected pore systems: a coarser secondary pore system and a fine primary pore system.

6.1.6.5 Pore Size Distribution

Like for the texture, the pore size distribution also represents a continuum that is divided into conventionally defined ranges. The classification used in this book is based on papers by F. Sekera and M. De Boodt (Table 6.3). The boundaries between the pore size ranges are based on characteristic parameters of the water regime. The equivalent diameters of 50 and 10 μm correspond to the drainage boundary at different matric potentials at field capacity (e.g. pF 1.8 and 2.5) and 0.2 μm is the drainage boundary at the permanent wilting point (pF 4.2) (see Sect. 6.4). This classification shows that water in the fine pores is generally not plant-available, although certain desert plants (halophytes) are still capable of extracting moisture out of fine pores up to a pF value of 6.5. In contrast, the water in the medium-sized pores is plant-available. The coarse pores are generally empty of water in terrestrial soils, and therefore their proportion is decisive for the degree of soil aeration. This is particularly true for pores with >50 μm diameter, which are also called large coarse pores. The pore size is also important for root growth and microbial activity, since root hairs (diameter >10 μm) are only able to penetrate coarse pores, while fungal mycelia (diameter ca. 3–6 μm) and bacteria (diameter 0.2–1 μm) can also live in medium-sized pores. However, the fine pores are not accessible to microorganisms. In

Table 6.3 Division of the pore size ranges according to the equivalent diameter and the matric potential (hPa, pF) as a threshold value for the drainage of cylindrical pores

Pore size range	Pore diameter (μm)	Matric potential (hPa)	pF
Wide coarse pores	>50	>−60	<1.8
Fine coarse pores	50–10	−60 to −300	1.8–2.5
Medium-sized pores	10–0.2	−300 to −15000	2.5–4.2
Fine pores	<0.2	<−15000	>4.2

addition to the classifications mentioned here, there are also other systems.

The pore size distribution of the primary pores depends on texture and particle shape, and for the secondary pores, on soil structure and thus on soil development. For this reason, the coarse pore fraction is generally greater the coarser the texture, i.e. the more sandy or gravel-rich the soils. In contrast, the fine pore fraction is greater the finer the soil texture. In sandy soils, the coarse pore fraction dominates with 30 ± 10 %, and decreases with increasing clay content (Table 6.4). In clayey soils, it is sometimes only of 2–3 %, and just like with silty and loamy soils, it is strongly dependent on soil structure. In contrast, there is a close correlation between the fine pore fraction and the clay content, which is reflected in the pore volume, even if it is less pronounced. In extreme cases such as freshly deposited clays, it can be of 70 % and more. The mesopore fraction generally correlates closest with the coarse silt content (20–63 μm) and reaches a maximum of 15 ± 7 % in silty soils (loess soils). The relationship between the coarse pores and the texture is not as close, because they include the secondary pore fraction, which is hardly texture-dependent.

Especially in sandy soils, an increasing soil organic matter content leads to an increase in the medium-sized and fine pores. Their extent depends on the form and degree of humification of the organic matter. Soils with high organic matter contents, especially moors, usually have very high pore volumes. However, their coarse pore fraction decreases if the degree of humification of the organic matter increases, and the fine pore fraction increases at the same time.

Because of the water contents, the pore size distribution is calculated at different matric potentials. The physical law is described by the capillary rise equation, i.e. the **law of capillarity** or the **Young-Laplace Equation**:

$$r = \frac{2 \cdot \gamma \cdot \cos \alpha}{h \cdot \rho_w \cdot g} \tag{6.7}$$

Here, r is the capillary radius, γ is the surface tension of water, α is the wetting angle, h is the height of the capillary rise, ρ_w is the density of water, and g is the acceleration of gravity. Because the formula actually only applies to cylindrical pores, an equivalent diameter is defined similar to that used for determining the particle sizes (Sect. 6.1.2). In doing so, all pores are included whose capillary rise is equal to that in cylindrical capillaries with a radius r. The height of the capillary rise (h) is generally determined using the pressure required to drain these capillaries. In principle, the same methods are used as for the determination of the binding strength of various water fractions in the soil (cf. matic potential/water content curve; Sect. 6.4.2.3). In addition to assuming that the menisci are circular, the conversion to capillary radii also requires assuming that the soil has a rigid pore system. However, this depends on the mechanical, hydraulic and chemical tension situation (Sect. 6.3.3), and must be defined specifically. Because every pressure can be assigned to a specific pore diameter, providing that the sample can be completely wetted: $\cos \alpha = 1$ and the chemical composition of the soil solution is known, the water loss between two pressures corresponds to the volume of a specific pore size range. If the pressure is expressed as **pF = log cm**

Table 6.4 Total pore volume and the pore size distribution in mineral soils (C content up to 2 %) and organic soils

	Pore volume (%)	Wide coarse pores (%) pF < 1.8	Medium-sized pores (%) pF 1.8–4.2	Fine pores (%) pF > 4.2
Sand	46 ± 10	30 ± 10	7 ± 5	5 ± 3
Silt	47 ± 9	15 ± 10	15 ± 7	15 ± 5
Clay	50 ± 15	8 ± 5	10 ± 5	35 ± 10
Half-fen	70 ± 10	5 ± 3	40 ± 10	25 ± 10
Bog	85 ± 10	25 ± 10	40 ± 10	25 ± 10

water column or **log hPa**, the correlations between the pore diameter and pF shown in Table 6.3 are obtained.

6.1.7 Temporal Changes

The particle size distribution is one of the soil properties that changes relatively slowly. Still, it must not be neglected that this soil characteristic is also subject to changes governed by physical laws. The same is also true for the packing of the primary particles into aggregates. However, the changes here take place much faster, which are the regular results of pedological and also anthropogenic processes. In contrast to textural properties, structural properties have a more short-lived character.

6.1.7.1 Textural Changes

Changes in texture through translocation in soils (turbations) or material transport within the soil take place more rapidly than changes in the size of individual particles due to progressive weathering. The same is true for the new formation of primary particles. The mechanisms within a soil that change the texture are particle segregation (separation) and particle mixtures. The former occurs at the soil surface as a result of erosion events, if no further transport has taken place. In the soil profile, downwards clay migration is the most important form of segregation, which ultimately leads to the formation of Luvisols (Sect. 7.6). Particle segregation can also occur through the freezing of water (upward movement of stones due to freezing, **cryoturbation**), still taking place today as a long-term process in glacial till landscapes, or resulting in the formation of stone garland or stone ring soils in Arctic regions. Deeply humic and intensely aggregated Vertisols can form as a result of strong changes in volume in intensely swelling clay minerals where there are regular shrinkage/swelling cycles, leading to high swelling pressures (**peloturbation**).

Especially in thin-layered deposited sediments, the particle mixtures are changed by root and animal activity. This also includes the mixing by endogeic earthworm species, which hardly carry any soil material to the soil surface, while other species make burrows with less mixing. This **bioturbation** thus also changes the particle mixture and often creates gravel layers in the subsoil. Among the earthworms, the endogeic species that consume soil along with their food cause more mixing than the deep-burrowing worms, which only build their living burrows once in a lifetime. Tropical earthworms are particularly active (up to 27 kg m^{-2} a^{-1}). Ants, and in warm climates also other invertebrates such as termites, contribute similarly to bioturbation (see Sect. 4.1). The same is true for rodents (hamsters, European ground squirrels, gophers) in steppe soils. Another form of turbation is windthrow in forest climates, which is so important that it was given a special term, **arboturbation**. This arboturbation plays a decisive role in the formation of *Stagnic Albeluvisols*.

6.1.7.2 Changes in the Packing

Changes in the packing represent either an increase or a decrease in the proportion of pores. Increases are generally associated with a rise in the soil surface as well as a reduction in the number of contact points per primary particle. A reduction in the pore volume generally leads to a lowering of the soil surface and an increase in the number of contact points per primary particle (Fig. 6.6).

Under natural conditions, without any anthropogenic influences, every soil formation is initially associated with a rise in the soil surface, and therefore a loosening of the initial packing. This rise does not affect all parts of the soil profile to the same extent, rather its effect decreases with increasing depth of the observed zone in the profile. This is caused on the one hand by decreasing bioturbation and/or cryoturbation intensity with increasing depth, and on the other, by the decreasing load of the soil horizons to be lifted when moving towards the soil surface. Because soil heaving is associated with a reduction in the number of contact points, it simultaneously leads to a decrease in the stability, i.e. of the strength towards increasing loads. This pedogenic heaving is clearly visible when the subsoil has a high density, as is the case in

most terrestrial soils. This limitation is particularly striking in soils originating from glacial till, where the soil was loosened only to a maximum depth of 2 m in more than 10,000 years. This is then followed by a layer with a high bulk density, which can be derived from the former glacier thickness, and has a higher strength (=precompression stress due to former loading). The value of the preload is therefore also used to reconstruct the glacier thickness (see Sect. 6.3.2.2).

Human activity on the soil surface always leads to a compression on the long term, which is associated with **lowering** of the soil surface. This is true for all forms of soil management (agriculture, forestry, pasture) (see also Sect. 10.7.2).

The extent of pedogenic **loosening**, as well as pedogenic (during weathering such as decalcification, podzolization and clay migration) or anthropogenic **subsidence** generally cannot be directly observed in the field. However, it is usually clearly discernible when the void ratio for a depth of up to ca. 1 m is plotted against the soil mass overlying the corresponding reference depth (=load). On a semi-logarithmic representation, this results in a straight line for virgin (normal compacted) soils, and a broken line for soils that have been used. Figure 6.8 shows examples of these packing curves for a Cambisol under forest or under agricultural use. In an "unused" state under forest, intense bioturbation (also in association with arboturbation) leads to a very loose packing, represented by the packing curve with a strong negative slope. With agricultural (field) use, in contrast, a corresponding strong compression takes place, because especially in ploughed topsoils, the loosened soil is less stable due to reduced support of the primary particles and aggregates, and is thus very susceptible to compaction.

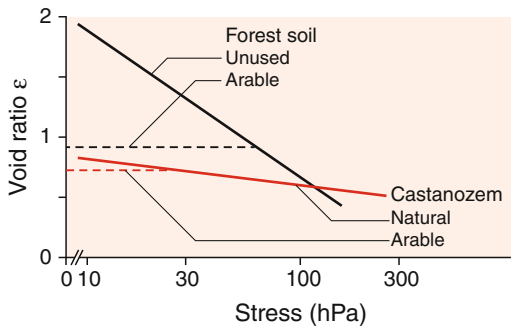

Fig. 6.8 Packing curves: correlation between void ratio and normal stress of the soil for two normal i.e. virgin soils (virgin compaction state of the profile) and two soils under agricultural use (pre-compacted state of the profile)

The other example shows Castanozems in short grass steppes. Here, the negative slope of the packing curve is much lower, not only because there is little pedoturbation in the arid climate, but also because simultaneously the more intensive desiccation results in more significant contraction of the particles and thus contributes to aggregate formation. Accordingly, there are a greater number of contact points with aggregates and primary particles, and the strength increases. In this case, agricultural use does not result in much change.

6.1.8 Correlation Between the Solid Phase and Other Soil Properties

Because of the close relationship between the soil's water holding capacity and its texture, packing and stability, it is also possible to use this data to draw conclusions on the characteristics of the soil water and air regimes, and on its mechanical strength. Because in many cases, this is the only source of data on the water regime or on the large-scale mechanical stability, and also often represents a procedural simplification, numerous mathematical approaches exist that are called **pedotransfer functions**.

6.2 Interactions Between the Solid and Liquid Phases

Contiguous phases generally do not react neutral to each other, rather there is always attraction or repulsion reactions taking place. In the case of attraction, the mobile phase is adsorbed to the solid phase. This is mainly true for water

molecules, which are preferentially adsorbed onto mineral surfaces due to their polarity. As a result, the particle surfaces in soils (apart from the exceptions: the topmost cm of soils in extreme aridic deserts, are so-called "puffy" (these are soils containing organic matter, or drained moors, where peat mineralization takes place. The drained moor particles react therefore hydrophobic with very reduced swelling potential.

Generally, the first layers of water molecules are firmly bound to the particle surfaces, whereas the further layers are less firmly bound with increasing distance.

As a result, the first water molecule layers can only be displaced at punctual sites through grain-to-grain contacts with minimal area; this is hardly the case with extensive contact areas, as they are found in fine-grained and clay-rich substrates. Here, the water films are contiguous. This has effects on the changes in volume caused by water additions (=swelling) or desiccation (=shrinkage).

Thus, swelling processes depend on the properties of the clay minerals, their state of flocculation, or the stress release of the aqueous phase. Shrinkage processes depend on the wettability of the particle surfaces and on the surface tension of the soil water. The consistency of a soil, in turn, depends on the one hand on the texture, and on the other, also on the state of flocculation of the clay particles. Especially with sudden changes in the ambient conditions, e.g. if there are sudden changes in pressure in the soil water, or if changes in pressure are caused by compression of the granular packing, the flocculated soil structure can collapse or also liquify.

6.2.1 Flocculation and Peptization

The processes of flocculation (=coagulation) and peptization affect particles of **colloid size**. In chemistry, the boundary between coarsely dispersed and colloid-dispersed substances is drawn at a diameter of 0.1 μm. In soil science, however, the range of the colloid fraction in soils is combined with the range of the clay fraction, because soil particles with a diameter of up to 2 μm also exhibit colloidal properties.

This is amongst others due to the particle shape in the clay fraction. The thinner the clay mineral platelets, the more the properties caused by the mass are overshadowed by the properties related to the surfaces. Therefore, the colloid-like behavior becomes more obvious.

In a soil suspension, the particles are subject on the one hand to gravity, which causes sedimentation, and on the other, to the effects of diffusion due to Brownian molecular motion, which counteracts the settling. If an electrolyte-free, strongly diluted clay suspension is left to settle, the clay particles can remain in suspension for a long time (days or even weeks) before they flocculate. Under these conditions, the collisions between the particles caused by Brownian motion only seldom result in adhesion of the particles to each other, because only high-energy collisions (high kinetic potential) enable the particles to approach enough to penetrate the relatively large thickness of the electrical double layer (Sect. 5.3).

The frequency of adhesion of two particles after a collision caused by Brownian motion is greater if (a) the electrical double layer becomes thinner, i.e. the salt concentration in the outer solution increases, and/or if (b) the pulse intensity of the collisions increases, i.e. with increasing temperature in the system. The process involved in the formation of larger units from adhering primary particles is called **flocculation** or **coagulation**. The newly formed larger units (flakes, coagulates) sink more rapidly out of the suspension to the ground, because they are less affected by Brownian motion than the individual particles.

When the salt concentration in the soil solution decreases, the flocculated state is lost again. The primary particles can then be easily separated again by light kneading or stirring. This

separation process with the reestablishment of the non-flocculated, i.e. suspended state, is called **peptization**.

Because the flocculated particles are irregularly attached to each other, sediments that are formed from flocculated suspensions are more voluminous than those originating from non-flocculated (peptized) suspensions. They have a larger pore volume and therefore inhibit the percolation of water less than sediments from non-flocculated deposited particles. For this reason, layers of non-flocculated deposited clay can be used e.g. to seal irrigation channels. Inversely, the separation of non-flocculated colloids from water is impeded by the formation of a poorly permeable sedimentation layer e.g. on the soil surface.

Flocculated and peptized soil particles behave differently due to the varying nature of the linking of their individual particles under different types of loads. In a flocculated state, the free mobility of individual particles is smaller than in a peptized state. Their dislocation during the course of soil surface sealing is therefore smaller. However, the **plastic deformability** at the same moisture content is greater in a flocculated state than in a peptized state, because the open structure of the flakes contains more readily mobile water.

Due to the friction to be surmounted during particle displacement, kneading stress often initially results in high resistance, which rapidly decreases with progressive deformation through the "lubricating effect of water" The resistance threshold caused by the reversible disruption of weak links through kneading, stirring or shaking is called **thixotropy**; the resulting flow of soil is called **liquefaction**. Especially in the building sector, this liquefaction is of special importance considering the total loss of stability exhibited by some soils; in agriculture and forestry, the vibrations caused by harvesters on moist soils can lead to extensive liquefaction and thus transform the soil structure into a soupy state. Also to be mentioned in this context, the procedure involving simple knocking on a soil auger to determine the height of the effective capillary fringe in the soil is based on the visual effect of the soil flowing back together in the sampler (=thixotropic behavior).

6.2.1.1 Energetic Interactions Between Soil Colloids

Soil colloids interact through their adsorbed cations, adsorbed water, and direct contact, whereby electrostatic interactions take place between positively and negatively charged sites on the surfaces. Above the (pH-dependent) isoelectric point, the charge is always negative on the edges of clay minerals and on humic substances, and below this point, it is always positive (see Sect. 5.5), so that corresponding interactions can be expected. Attraction and repulsion forces can occur between soil colloids.

The **repulsion** between two approaching clay particles is based on (a) the same electrical charge of the counterion, (b) the binding strength of the adsorbed molecules in the ambient medium and (c) the concentration and composition of the solution within the electrical double layer. As a result of the strong osmotic pressure gradient, the soil solution tries to dilute the solution in the double layer. This causes neighboring particles to be pressed apart. The strength of osmotic forces is demonstrated e.g. by the swelling and the swelling pressure of strongly drained clays.

Two particles become **attracted** to each other when they separated by a distance of less than about 1.5 nm. This is caused by various forces (see organo-mineral compounds, Sect. 3.2): (a) Van der Waals forces between molecules and atoms, (b) formation of bonds through chain molecules (see polyelectrolytes, Sect. 5.4), (c) Coulomb forces between positive and negative surface charges, (d) boundary surface forces between non-miscible components (e.g. water/air meniscus forces). When the particles are closer than ~ 1.5 nm apart, the diffuse layer overlap and they now belong to both particles. The attraction forces outweigh the repulsion forces as long as the repulsion forces don't increase again significantly if the particle distance becomes even smaller (and thus also with positive potential), due to irregularities on the particle surfaces that are approaching each other (Born repulsion). All factors that reduce the thickness of the electrical

double layer therefore promote the formation of flakes and larger aggregates. The two main factors here are the concentration of the solution and the valence of the adsorbed cations. Figure 6.9 shows the effect of the salt concentration on the potential occurring when colloids approach each other. Here, the potential is the work or energy that must be expended to force the particles to approach against the repulsive forces. The figure shows (a) the individual curves for the positive potentials caused by repulsive forces (dashed curve above the abscissa), (b) the individual curves for the negative potentials caused by attractive forces (dashed curves below the abscissa), (c) the resultant obtained by adding the positive and negative potentials for the individual particle distances. If the observations are based on respectively the same particles, the potential curves can also be considered as **energy curves**. The slope of the curves for the different particle distances is a measurement for the effective attractive or repulsive forces. Their size and orientation depending on the distance from the particle surface is also shown in Fig. 6.9 (dotted curve). The increasing attraction below a distance of ~1.5 nm is defined by the intersection of the resultant with the abscissa. However, if the distance becomes even smaller after crossing the minimums (for the potentials or forces), the particle repulsion resulting from irregularities (BORN repulsion) once again leads to increasing repulsive forces or positive potential values. Furthermore, the figure demonstrates that the course of the potential curves depends on the salt concentration. At **low** salt concentrations, the potential, i.e. the energy required to approach even closer, initially increases almost exponentially as the particles approach. The curve becomes flatter with the increasing effect of attractive forces as the particles approach closer. The energy contributions required to approach closer become smaller and smaller, and reach a value of zero at the maximum of the curve. This energy barrier, or the distance at which this maximum energy contribution is required, must be crossed if the particles are to unite and form

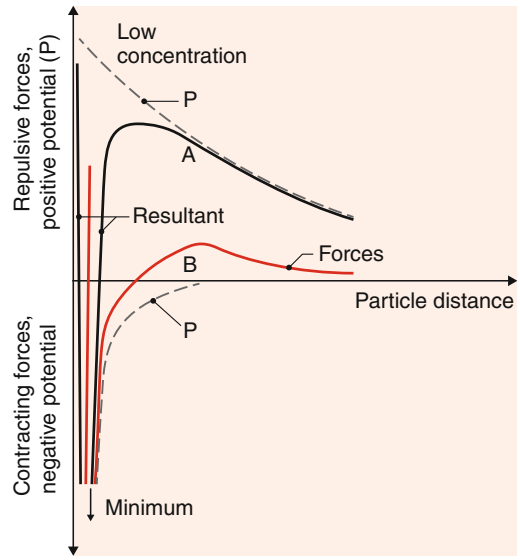

Fig. 6.9 Schematic representation of the potentials (*P*), the potential cumulative curve (=resultant), and the forces between two particles in a suspension as a function of the particle distance (after van Olphen, modified)

flakes. The figure also shows that the repulsive force reaches its maximum (Point B) at the particle distance where the slope of the potential cumulative curve is the greatest (Point A). When the maximum potential is reached, the repulsive force is equal to zero (intersection of the forces curve with the abscissa). The particles attract each other as they approach further. This rarely occurs at low salt concentrations, so that flocculation only reaches a greater extent after weeks or months. Soles with such properties are called **stable**. With increasing salt concentration, the attractive forces dominate at every particle distance, except with maximum proximity. Therefore, there is no energy barrier to surmount. The flocculation rate reaches its maximum at high salt concentrations. The increase in the flocculation rate, both with a rise in the salt concentration and under the influence of polyvalent cations (compared to monovalent), is due to a decrease in the thickness of the diffuse part of the double layer (see Chap. 5). In this case, it is referred to as **rapid flocculation**.

6.2.1.2 Effect of Exchangeable Cations and Valence on Flocculation

The flocculation sensitivity of exchange media, i.e. the tendency to change over to a flocculated state, increases with the valence of the sorbable cations; for negatively charged exchange media in the sequence: $Me^{+} < Me^{2+} < Me^{3+}$ – (Me = metal ions). If e.g. an Na^{+}—saturated clay mineral is suspended in water, a very stable sol is formed. The peptizing effect of Na^{+} ions is used for texture analysis (Sect. 6.1.3.3). In contrast, sols from exchange media that are saturated with polyvalent cations, e.g. with Ca^{2+} or Al^{3+}, are very instable and flocculate within a relatively short time. Flocculation is accelerated when a saline solution is added to the sol. At high salt concentrations, flocculation takes place very **rapidly**, regardless of the valence of the exchangeable ions and of the cations in the solution. At low concentrations, as they are found e.g. in soil solutions in the field, flocculation takes place slowly, but it is strongly influenced by the valence of the ions.

(a) **Particles with negative charge (cation exchange media)**
According to the rule by Schulze-Hardy, the flocculating effect of electrolytes that do not react chemically with the colloid is greater the higher the valence of the counterions, i.e. in the case of clay minerals, that of the cations. Investigations on various colloids (arsenic(III) sulfide, silver iodide, gold) delivered the following **flocculation values**, i.e. the salt concentration at which rapid flocculation of the sol begins, for

Monovalent cations	25	to	150 mmol L^{-1}
Divalent cations	0.5	to	2 mmol L^{-1}
Trivalent cations	0.01	to	0.1 mmol L^{-1}

Particularly high salt concentrations are required for flocculation in soils with high Na saturation (Table 6.5). Na-rich soils are therefore only flocculated in the presence of relatively high salt contents in the soil solution, and easily change over to a peptized state in case of desalination. In this state, in turn, they have a high swelling capacity. In contrast, drainability and infiltration are strongly impeded due to the often relatively dense packing. For this reason, in soils with high Na saturation, an attempt is made to substitute Na^{+} with Ca^{2+} (structural amelioration of saline and sodic soils). Compared to cations of different valence, cations of the same valence exhibit only very small differences in the flocculation values. It was often observed that they increase according to the **lyotropic series** (=Hofmeister ion series, see Chap. 5):

Table 6.5 Flocculation values for an aqueous suspension of a Na and a Ca montmorillonite after the addition of NaCl and $CaCl_2$ (after O'Brien)

Clay mineral	NaCl (mmol L^{-1})	$CaCl_2$ (mmol L^{-1})
Na montmorillonite	12–16	1.2–1.7
Ca montmorillonite	1.0–1.3	0.09–0.12

$$Li^{+} < Na^{+} < K^{+} < NH_4^{+} < Rb^{+} < Cs^{+}$$
$$Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$$

For cation exchange media, the **valence of the anions of salts** only has a very slight effect on the flocculation values, provided that the anions do not chemically react with the particles. Therefore, with the same cation, chloride, nitrate and sulfate have very similar flocculation values. Already because of its very low concentration in the soil solution, the flocculating effect of phosphate ions is of minor importance.

(b) **Particles with positive charge (anion exchange media)**
For positively charged colloids and thus anions as counterions, e.g. with Fe and Al oxides below their point of zero charge, the valence of the anions is decisive for flocculation, for example in acidic Ferralsols. The Schulze-Hardy rule also applies to anions. As was proven for sols of Fe and Al oxides, for the same cation, divalent anions such as SO_4^{2-} have 60–80 times the flocculating capacity of

monovalent anions (Cl^-, NO_3^-). The effect of OH^- ions can hardly be observed separately in soil colloids, because the addition of soluble hydroxides leads to chemical reactions. Thus, in clay minerals, Al ions are precipitated and the pH-dependent charge increases.

6.2.1.3 Effects of Polymers on Flocculation and Dispersion

In principle, the state of flocculation of fine-grained soil particles, i.e. the clay fraction, is affected by anionic or cationic polymers (macro molecules with a molecular mass >1000, mostly organic compounds, e.g. polyacryloamide) in the soil solution in the same way as by the much smaller inorganic ions. Both adsorption on the solid surfaces or desorption can occur.

Anionic polymers have various arrangement possibilities. Depending on the concentration-related supply, chain-like polymers can form closely arranged packets consisting of extended chains or more widely spaced packages with tangled chains. If a polymer consists of a hydrophilic and a hydrophobic part, the former extends into the aqueous phase, while the latter is adsorbed to the solid boundary surface.

Despite the fundamental broad diversity of phenomena, there are also laws governing polymers. The chain length has a significant effect on the adsorption strength: the longer the chain, the stronger the tendency to be adsorbed. As a result of this, under otherwise identical conditions, shorter chains that are already adsorbed can be substituted by longer chains. Because of the size of the molecules and the relatively slow diffusion compared to ions, this process takes place much more slowly with polymers than with ions.

Polyelectrolytes, in addition to the chain length, the charge density on the polymer chain—in combination with the charge density on the surface of the adsorbent, i.e. the mineral surface—as well as the ionic strength of the solution play an important role. Chains with low charge density in solutions with high ionic strength have a neutral character. In contrast, with a dense arrangement of the charges—especially if the solution has a low ionic strength—the adsorption behavior is so strongly affected by the surface charges of the solid phase that unequal charges attract, while equal charges promote **displacement** from the surface. Strong hydrophilia or hydrophobia can easily compensate the charge effects, so that in boundary cases, anion polyelectrolytes can be adsorbed to negatively charged particles.

The presence of polymers in the soil, or if applicable, an artificial input of polymers, can therefore influence the flocculation and dispersion state of soils and therewith the stability of aggregates, especially in the micron range. Examples for the diversity of effects are the flocculation intensities towards smectite. Here, the flocculation mechanism caused by cationic polymers is based on charge neutralization, and is stronger the higher the charge of the chain. Nonionic polymers have a flocculating effect due to the formation of bonds. Flocculation was even triggered with anionic polymers. The obtained flocculated states reduce crust formation and thus promote infiltration. The effect of organic synthetic aggregate stabilizers and so-called **soil conditioners** is also largely based on their flocculating capacity.

6.2.1.4 Flake Structure

When platy particles unite to form flakes, three different types of contact can occur: surface-to-surface, surface-to-edge, and edge-to-edge (Fig. 6.10). With surface-to-surface flake formation, thicker platelets are formed through parallel agglomeration, while a void-rich **card-house structure** is formed in the case of surface-to-edge and edge-to-edge agglomeration (Fig. 6.10c, d). The formation of a card-house structure results from the presence of positive charges on the side edges of the octahedral sheets, which are neutralized by the negative charges of the other clay mineral. Furthermore, bonding between two clay minerals can also occur through cations that are bound to the surface of the exchange medium. As a bond between the two surfaces, polyvalent cations (e.g. Ca^{2+}, Al^{3+}) have a higher linking capacity than monovalent cations, because they are not capable of shielding the negative charge of the surface as completely (a divalent cation must shield two negative charges, see Sect. 5.5). Surface-to-edge-type flakes are mainly found in

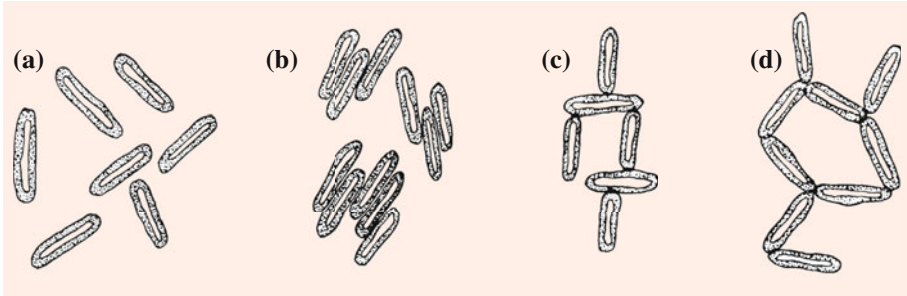

Fig. 6.10 Aggregate formation of minerals: **a** peptized, **b** aggregated surface–surface, **c** aggregated surface–edge, **d** aggregated edge–edge (*dotted* water shell of the double layer)

the acidic range, while surface-to-surface-type flakes dominate in the alkaline range, because the positive charge on the side edges decreases with increasing pH. Rod-shaped particles can be considered as platy particles.

6.2.1.5 Effect of the Electrokinetic Potential

Flocculation was formerly often explained with a decrease in the zeta or electrokinetic potential. The **zeta potential** is the electric potential that is established in the boundary area between the double layer of an exchange medium and the surrounding solution when applying an electric field across the solution (electrophoresis). In doing so, part of the cations are stripped from the diffuse area of the double layer on the cation exchange media (e.g. clay minerals), so that the particles adopt a negative charge and migrate towards the positive electrode. The zeta potential can be calculated from the **electrophoretic mobility** of the particles. The magnitude of the potential is considered as a measurement for the repulsive force between two particles. The zeta potential of the particles drops under the influence of an electrolyte addition to the solution, and when it falls below a so-called 'critical potential' the sol flocculates. However, because it is not known which part of the cations in the diffuse part of the double layer is stripped during electrophoresis or how the thickness of the double layer is changed, the zeta potential cannot be assigned to a specific distance from the surface within the double layer.

6.2.2 Shrinkage and Swelling

Shrinkage and swelling are caused by interactions between the solid particles and the surrounding water. They are associated with the wettability, the extent of water adsorption on the solid particles, and the surface tension of the water. Another factor influencing the respective behaviors with changes in the moisture content is the previous history: Shrinkage is never completely reversible, unless there is an input of kinetic energy. This leads to the destruction of soil aggregates formed by shrinkage, the spacing of the individual particles increases, and the accessibility of the particle surfaces for reattachment of water is improved. As a result, the course of shrinkage and swelling must always be analyzed with reference to the respective previous packing and/or maximum desiccation, including the bonding stability caused by flocculation or peptization. The formation and destruction of structure in cold and hot deserts can also be considered in the same way, since temperature-dependent changes in the water vapor saturation deficit also cause contractions and associated approaching of the soil particles or swelling due to e.g. dew formation. The degree of shrinkage here also depends on the area-dependent menisci forces acting between the

particles through the pore filling. Finally, the process of freeze-drying as the most extreme form of desiccation through the loss of any contracting menisci forces between the soil particles, leads to complete homogenization, i.e. disaggregation.

6.2.2.1 Shrinkage

On the one hand, shrinkage is caused by the cohesion and surface tension of water, and on the other, by the adhesion between water and the solid primary particles. It begins as soon as a water-saturated layer of primary particles looses water. As a decrease in volume/moisture content, it is always the primary process of structure formation.

When coming to rest after transport, the moist primary particles are initially loosely deposited, as described in Sect. 6.1.6, and are only then pressed together by the weight of the overlying subsequently deposited particles.

However, as soon as water is removed from such a packed soil volume, the particles assume a more dense packing, because the water between the soil particles reduces its surface area with a decrease in volume. At first, the volume of the water-saturated and still homogenous soil decreases by the same amount as that of the water. This shrinkage range is called **normal** (or **proportional) shrinkage** (Fig. 6.11). It can be perceived visually through the constant 'dark' soil color during desiccation, because the particles approach closer to each other and lead to additional contact points (cf. Sect. 6.1.6.1). This increases the resistance against further approaching of the particles. For this reason, with further water loss, the water surfaces surrounding the saturated bodies until now must enter the space between the primary particles, i.e. the soil pores.

In this state, a greater volume of water is now being extracted from the soil than can be compensated by further approaching of the primary particles. This shrinkage phase is called **residual shrinkage** (Fig. 6.11). It is associated with drainage, and the soil seems lighter in color due to the soil pores beginning to be filled with air. During this process, the stronger the water menisci are pulled into the pores due to progressive water loss, the stronger the vacuum effect in the remaining water and thus its contracting effect. However, the force that can build up during the process not only depends on the pressure difference between the water and the atmosphere, but also on the surface area of the pore space that is still filled with water, through which the forces act (see Sect. 6.3.2.3).

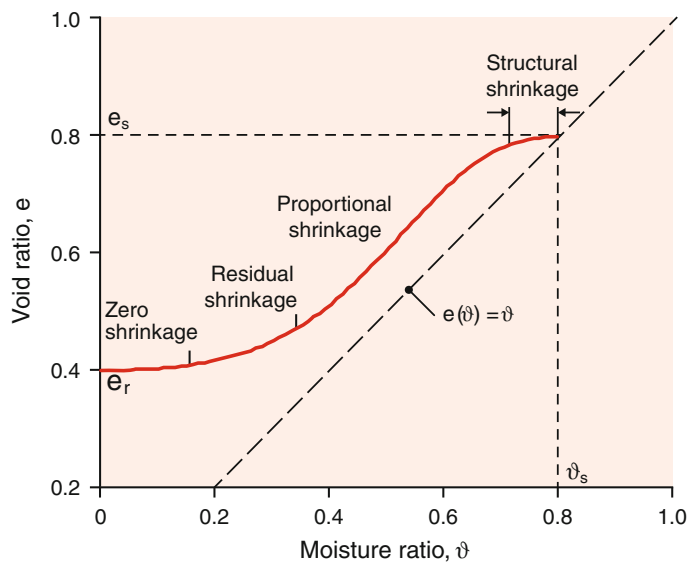

Fig. 6.11 Shrinkage curve pattern in soils

This correlation explains why moist sands initially shrink when drying and temporarily have a higher strength due to the particles being pressed together, and then rapidly fall apart again with further desiccation. In contrast, when shrinkage occurs due to progressive desiccation, the strength of silts continues to increase over a greater matric potential range. Still, if they are not also fixed by adhesive substances, the individual grains can be easily separated by rubbing. Clays only reach very high strength with greater degrees of desiccation (e.g. 'adobe' = air-dried bricks). Therefore, with respect to the extent of the change in volume, the role of shrinkage processes becomes greater the finer or more clay-rich the soil.

The change in volume as a result of meniscus tension is isotropic. However, the soil can only freely follow this tension in a vertical direction. Horizontally, further approaching of the particles is impeded by friction on the substratum or by the water still remaining in the lower parts of the sediment. This is why the soil volume tears apart during desiccation.

The developing **shrinkage cracks** are important morphological soil characteristics (Sect. 6.3.1). The first cracks run down the soil body perpendicular to the depth (=tensile cracks). Coarse prismatic structures or (in saline soils) columns are therefore the first aggregates to form in a homogenous environment. Repeated wetting and drying cycles cause a stronger approaching of the particles, until no more cracks can be formed that are respectively perpendicular to each other. At the same time, the prismatic or columnar structures become smaller, and more energy-efficient shearing soil movement lead to the formation of polyhedrons. These are finally transformed by further shear rounding of the edges into subangular blocks with rough surfaces. Further progression of this process would ultimately lead to the formation of a sphere as the smallest free enthropy shape.

However, this consecutive direction of formation is altered if a change in the texture or layers occurs, because it influences the contraction situation. Thus, in drying puddles for example, cracks formed in the most recent, finest sediments are not able to spread in depth into the underlying sandy part due to a lack of contraction. As a result of this, the shrunken zone bursts like a skin and the edges of the scales formed through the network of cracks are bent upwards, thus approaching the lowest-energy state, the sphere. The contracting vacuum in the water body of a shrinking soil can be measured using the difference with the atmospheric pressure (δp). Its dependence on the texture-related pore size (equivalent radius$r$) and the surface tension of water (γ) can be described as follows:

$$pL - pW = \delta p = 2\gamma/\mathrm{r} \tag{6.8}$$

The contracting force (F) is calculated according to:

$$F = \delta p \cdot A \tag{6.9}$$

Here, A is the effective surface area. This area increases with increasing meniscus curvature, i.e. with decreasing pore size or more intense approaching of the particles, as long as the pores are still water-saturated and the menisci are not yet pulled into the pores (proportional shrinkage). With the onset of drainage, the contracting force becomes smaller when the effective pore surface area decreases. Otherwise, if the effective pore surface area decreases less strongly than the matric potential becomes more negative, it leads to an increase in the contracting force. This is especially true for clayey soils or more densely packed aggregates. However, both cases are called **residual shrinkage**, regardless of the changes in stability due to desiccation (see Sect. 6.3.2.3).

When drainage has progressed to the extent that only ring-shaped water menisci exist between the primary particles, the effect of the two opposing curvatures of the water menisci (surface shape of these rings) must be taken into account. The equation describing this state is:

$$F = A \cdot \gamma(r_1 - r_2)^{-1} \tag{6.10}$$

Here, r_1 is the radius of the water meniscus between the particles and r_2 is the curvature of the water meniscus. The equation also demonstrates that a very narrow, almost rod-shaped

collar cannot have a contracting effect. This explains the trickling of sand, which occurs earlier the more the grains are well-rounded and sorted, and therefore the more spherical and uniform they are in size, because the contact zones are then more punctual (e.g. dune sand).

The terms 'normal or proportional shrinkage' and 'residual shrinkage' sufficiently describe the shrinkage process, as long as dehydration is continuous or only interrupted by stagnations. However, if a shrinkage process is interrupted by intermittent water additions and the tensile effect of the menisci is relieved, the soil starts partially reswelling. When drainage resumes, these 'youngest' water fractions are removed first, but as a result of previous (pre-)drying, no appreciable reduction in volume occurs. This range of shrinkage is called **structural shrinkage** (Fig. 6.11). The range of drainage where this takes place increases the stronger the previous desiccation and formation of aggregates under the respective chemical and biological boundary conditions. The decrease in volume only changes over to proportional shrinkage (also with stronger desiccation) when the previous desiccation is exceeded and/or when there is a change in the chemical and biological boundary conditions, while residual shrinkage primarily involves a decrease in moisture content. Structural shrinkage and also the reswelling can be defined as processes taking place within the range of a precompression stress and of preshrinkage. They indicate the comparability of hydraulic and mechanical processes in terms of the structural development and mechanical strength. While repeated wetting and drying within the range of structural shrinkage does not lead to an appreciable reduction in the pore volume (represented as void ratio), every desiccation exceeding this range results in new proportional shrinkage, which runs along the 1:1 line in Fig. 6.11.

6.2.2.2 Swelling

When a dried soil is re-wetted, the inward curves of the menisci are relieved. The tensile stress decreases, and depending on the resulting combination of forces, the cracks will be more or less closed again. However, a fully reversible increase in volume corresponding to that prior to the shrinkage process generally does not occur. The horizontal expansion dominates instead (i.e. swelling is initially defined as horizontal anisotropic). Under natural conditions, the increase in volume normally only reaches the state of isotropy (i.e. horizontal and vertical motion take place equally). Considerable vertical lifting of the soil through swelling only takes place when the swelling pressures are big enough to compensate for or even surmount the compacting soil pressures. Such lifting processes are observed e.g. in Vertisols, which contain a high fraction of strongly swelling clays (smectite, vermiculite). In these clay minerals, swelling pressures >0.4 MPa have been measured. Gilgai and crab holes also develop in connection with alternating swelling and shrinkage (Sect. 7.2.6).

However, complete reswelling until the initial shrinkage line is reached (analogous to the initial compaction, see Fig. 6.21) generally does not occur without additional mechanical forces applied. Because the surface tension of water only provides a contracting force, the shrinkage is only reversible if one or several other mechanisms push the particles apart again. This swelling is a result of the deposition of water on mineral surfaces and on adsorbed cations. In principle, it is a precursor of dispersion. Because the clay fraction has the greatest surface area in soils and contains most of the exchangeable cations, swelling increases with increasing clay contents in the soil. Among the clay minerals, the swelling capacity for the same particle size decreases in the sequence: smectite ~ vermiculite > illite > kaolinite as a result of the decreasing surface area.

The hydration capacity of the adsorbed cations also has a strong effect on the swelling capacity. Swelling decreases in the valence sequence $Na^+ > Ca^{2+} > Al^{3+}$. Swelling is promoted by a reduction in the salt concentration in the soil solution, because this increases the hydration of the adsorbed cations. Substrates that have lots of space for adsorbed water as a result of their low packing density and those that only have a low surface area are also not capable of swelling. This can sometimes be observed in shrunken fresh

sediments of silt-rich material (loess) and in limnic sediments such as Limnic Subaquatic Fluvisol and lacustrine organic sediments.

The significance of the time factor for reswelling is clearly demonstrated in marshland soils. Here, after a summer of intensive in-depth desiccation, the reswelling until the next vegetation period is so minimal that the air and water regimes are regulated through the secondary pores due to the remaining structure. This may result in particularly high yields even if the following growing period is extremely wet. The swelling state of a clayey soil is therefore generally not at equilibrium with the water supply, but rather is influenced by the strongest previous shrinkage and the duration of the later water supply. This explains why shrinkage in many terrestrial clay soils is initially hardly visible, because they are still in the range of structural shrinkage (see Fig. 6.11).

The mechanical work required for the soil to freely swell again after prior shrinkage is provided by a change in load due to wheeling or trampling, but also by the impact of drops during precipitation. Already the slight deformations caused by the latter facilitate the access of water to the adsorption sites and promote the accretion of water layers around the clay platelets in the topsoil. This process becomes more intense the more the clay platelet surfaces become accessible during the course of constant displacements. For this reason, landslides on slopes with clay-rich material are always associated with swelling processes. Because of the more viscous consistency, they start with slow "soil creep" When the consistency has become soft enough and at the same time, the accessibility of the soil surface for water was improved by shearing, then the sliding velocity becomes faster. Large-scale hillside sliding and/or shear induced ground breaks are the visible results of these initially "microscopic" changes in the menisci forces. On the other hand, the **swelling pressure** builds up if swelling is impeded. This is generally the case in deeper soil horizons, because the respective overlying mass must be lifted. The osmotic interactions must also be taken into account, since the swelling pressure is higher with high Na saturation than with high Ca saturation, and the respective maximum decreases with increasing soil water content. Finally, in addition to the surcharge of the overlying layers, the swelling pressure in the soil profile also depends on the **shear resistance** in the surroundings. Greater amounts of swelling can therefore be observed in smaller than in larger soil samples.

Under field conditions, the swelling pressures in soils of Central Europe hardly exceed 2 MPa. The values are lower in wet i.e. waterlogged soils. The strong adsorption forces involved in the adsorption of the first unimolecular water films on mineral surfaces only produce a low swelling pressure, because the existing low bulk densities provide enough volume for the water films and there is no spatial resistance. The strongest effect of swelling pressure on the soil structure is observed with the **self-mulching effect** in smectite-rich Vertisols (Sect. 8.4.2).

6.2.3 Wettability

The wettability of a soil with water is the macroscopic visible result of the combined effect of various surface energies occurring where the solid surfaces of soil particles meet the soil solution and the soil air. Due to the great variety of possible substance combinations in the soil solution and on particle surfaces, there is a great range of observable phenomena. It can be measured overall using the wetting angle that is formed between the soil solution and the solid surface (Fig. 6.12).

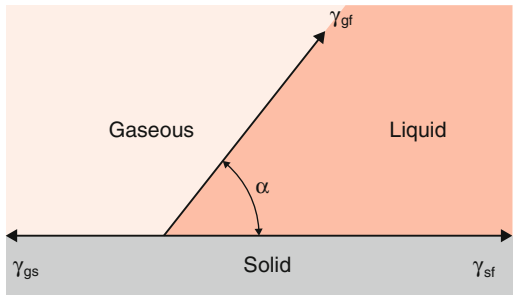

Fig. 6.12 Wetting angle (α) resulting from the equilibrium between the surface tensions of the gaseous–solid (γ_{gs}), solid–liquid (γ_{sl}) and liquid–gaseous (γ_{gl}) phases

The wetting or contact angle (α) is the result of the relative size of three boundary surface tensions, i.e. it depends on the ratio of the cohesive forces (attraction of the water molecules to each other) and the adhesive forces (attraction of the water molecules to the particle surfaces). The lower the adhesion, the lower is the wettability and the greater the contact angle. It can be described as follows:

$$\cos\alpha = (\gamma_{gs} - \gamma_{sl}) \cdot \gamma_{gl}^{-1} \qquad (6.11)$$

Here, the subscript s is for solid, l for liquid, and g for gaseous. Only one of the three involved boundary surface tensions can be directly measured, that is the surface tension of the soil solution against the atmosphere (γ_{gl}). The angle is a quantitative thermodynamic parameter only in ideal systems, but due to the many influences in soils (chemical heterogeneity, roughness, dissolution effects, swelling etc.), it can often only be used for relative comparisons among themselves. It is still a relevant phenomenon, because soil properties such as the susceptibility to slaking and thus crust formation, infiltration and wet aggregate stability, and impeded resaturation of desiccated humus-rich topsoils all depend on the wettability. Depending on the composition of the surface films on particles or on other aggregate-sized units, they inhibit wetting over a long period of time. They can therefore not only serve for characterizing soils or land uses, but also give an indication of a season dependence of the pore size distribution or matric potential/water content relationship for the previous desiccation, and thus also for the decomposition-dependent changes in the wettability of the organic matter. It can be clearly seen that in most soils, there is no unrestricted wetting (documented with an angle of 0°), but rather values are generally measured that deviate up into the >90° angle range. The most important parameter affecting the wettability of soils are the organic components and their amphiphilic properties, whereby here also, the extent of previous desiccation has a significant effect on the wettability. In this context, it is also comparable to a hydraulic preload. In general, the wetting angles of soil particles towards water are higher in the presence of organic matter than those of pure mineral surfaces, which do not exist in the field. Depending on the method used, the contact angles in arable soils are between 0 and 60°, up to 80° in grassland, and up to 130° in the humus-rich soil horizons of forests, especially under acidic coniferous forests. It is often difficult to assign the angle to individual substance components. In general, the formation of new substances in soils (humic substances), as well as components of plant origin or from microorganisms such as fats and waxes, can cause hydrophobicity. Because the wetting angles affect the height of capillary rise, it also affects the water holding capacity, and therefore the effective pore size distribution (see Sect. 6.4.2.3) and the infiltration. The hydrophobicity varies during the year, rising during dry periods and dropping again during the winter months. However, complete wettability of soils is rather the exception.

The wettability also plays an important role in the cracking of aggregates caused by trapped air escaping during sudden wetting. The high surface tension of the water makes the trapped air strive to achieve a spherical shape. If the structure of the surrounding soil particles is loose and is or becomes soft due to the infiltrating water, it cedes and spherical (vesicular) pores are formed (cf. Sect. 8.6.7). If the soil structure does not allow such escaping, the aggregate breaks apart when its resistance is lower than the force that was introduced by the contraction of the meniscus to form a sphere. The size depends directly on the wetting and is greater the more complete the wetting, and therefore the smaller the wetting angle. For this reason, synthetic aggregate stabilizers often have hydrophobic components.

6.2.4 Cohesion, Consistency and Hydraulic Pressure Head

The water menisci that are formed at the contact points between primary particles are the decisive factor for the behavior of the respective soil towards kneading and compacting loads. The same is true for the films that surround the

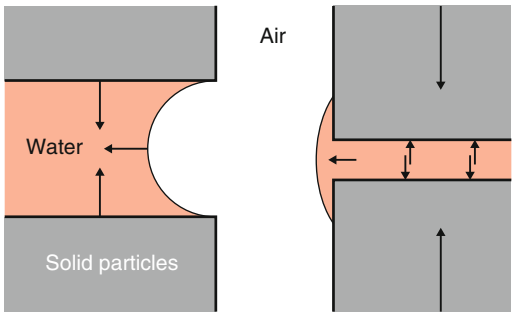

Fig. 6.13 Schema of the meniscus effect. *Left* Contracting meniscus pull (concave curvature) stabilizes; *right* meniscus pull destabilizes when the solid particles are compressed (development of convex curvature)

particles in the clay fraction. They also come together and form menisci around the contact points, which initially have very small curvature radii. The effect that free organic particles have on the cohesion between coarser primary particles can also be attributed to changes in the curvature radii of water menisci.

Menisci where the contracting pulling force depends on the developed vacuum (pore water pressure, matric potential) exist at all water contents, from air dry under field conditions through to saturation. In the latter case, the menisci curvature in the respective pores can be relieved by a very small addition of water. If this small addition of water produces plane menisci, the contracting effect and therefore the cohesion between the primary particles then disappears (Fig. 6.13).

The same effect also occurs if an aggregate or a soil section e.g. is temporarily compacted by vehicle wheeling. The primary particles are then pushed together and the existing water is left with a reduced pore space. This always leads to a flattening of the meniscus curvature, a reduction in cohesion, and increasing water saturation.

Because an addition of water always results in stress release, it can result both in an increase in volume on principally non-swelling material (e.g. loess) and in shear fractures. Depending on the approach, the decrease in cohesion can be described as a loss in stability, but also as a change in the consistency.

The significance of this correlation for the behavior of soils leads to the classification of the **consistency** into ranges as shown in Table 6.6. They are divided according to the limits named after their author, Atterberg (**Atterberg limits**). The amount of water that a soil must absorb to change from a hard to a soft plastic or liquid consistency (Table 6.6) is greater in more finely-grained soils, and therefore the higher the clay content. Finely dispersed org. matter acts in the same way. While there are no menisci to support the soil structure at water contents above the liquid limit, they do exist at water contents below the liquid limit. Finally, at the plastic limit, despite the increasing contracting pressure of the menisci, the water content has become so low that the total force produced over the cross-sectional area of the rolled-out soil (a cylinder half the

Table 6.6 Consistency of clay-rich soils depending on the water content (Atterberg limits)

Water content	Soil properties	Consistency	Consistency limits
High	Aqueous suspension, flows together	Thin fluid Semi-liquid	
			Liquid limit
↑	Sticks to the working tools, smears when working	Soft plastic Ductile	
			Plastic limit
Low	Optimally workable Hardly workable, hardened	Friable Hard	

thickness of a pencil is produced) is insufficient to prevent the soil roll from falling to bits.

As already mentioned, the menisci curvatures can also be flattened by pressing the primary particles together, i.e. by compacting the structure. When the compression has progressed far enough to press the water out of the pores surrounding the soil body, the contraction switches over to dilatation (=swelling). The menisci are now curved outwards and press the soil particles apart (Fig. 6.13). In doing so, most of the stabilizing mechanisms become less important if the developing excess water pressure is not lowered by discharging the surplus, before any further mechanical deformation occurs through shear stress.

This mechanism is at the origin of the complete **wettability** of fine-grained soils due to repeated traffic or vibrations in a wet state (thixotropic effect). In coarse-grained soils, e.g. sands, in contrast, the water generally flows out fast enough during compression so that the other stabilizing mechanisms cannot be overridden. Only in exceptional cases can the water pressure cause changes in the position of the primary particles relative to each other.

Shifting sands that lie in water represent one of these exceptions. They loose their bearing capacity under local loads because the water-filled pressurized total package is so big that the 'local' overpressure acting through the larger soil volume cannot be relieved fast enough through flowing. Another case is the situation on fresh slopes, where sliding occurs because large amounts of water can be suddenly supplied from inside the soil body under exceptional weather conditions. The one-sided stress on the grains, caused by the lack of support on the slopes, is enhanced by the pressure gradient of the flowing water and carries the suspended soil particles.

6.3 Soil Structure

Section 6.1 discusses the texture, packing and the resulting void shapes under the aspect of the particle diameter and shapes, and the pores produced by these solid bodies. Aggregate formation, in contrast, due to the organized juxtaposition of particles, leads to the formation of larger discrete units based on natural, largely uninfluenced by humans, physical, chemical and biological processes such as swelling and shrinkage, energetic interactions between soil colloids, flocculation and peptization depending on the valence and concentration of the ions, or also after the intestinal passage in worms. Structural formations affected by anthropogenic influences are observed in conjunction with soil loosening or compaction practices. Chemical processes, such as redox reactions, can also be affected by structural formation. The structure also influences filtering and buffering functions, plant growth, yields, and even the overall soil development.

6.3.1 Structural Morphology

Because the soil structure can exhibit a great diversity of shapes, which can be observed in all scale ranges from the visual identification in the profile down to the submicroscopic range, the morphological description is of great importance. As a result, various identification or classification systems have been developed. These include systems based on purely morphological classification, which can be used in all scale ranges. Other systems that include soil genetic elements are generally more scale-dependent, but contain more detailed information. The following description of the macrostructure is largely based on a classification by Mückenhausen.

6.3.1.1 Macrostructure

The structural shapes that are visible with the naked eye are called macrostructure. A comparison of natural soil structures demonstrates that in some cases, the individual particles easily fall out of the structural association, and in others, in contrast, only bigger or smaller peds can be detached. These properties of the soil structure result in three main groups, which can also be clearly distinguished in the field: single grain, coherent and aggregate structure.

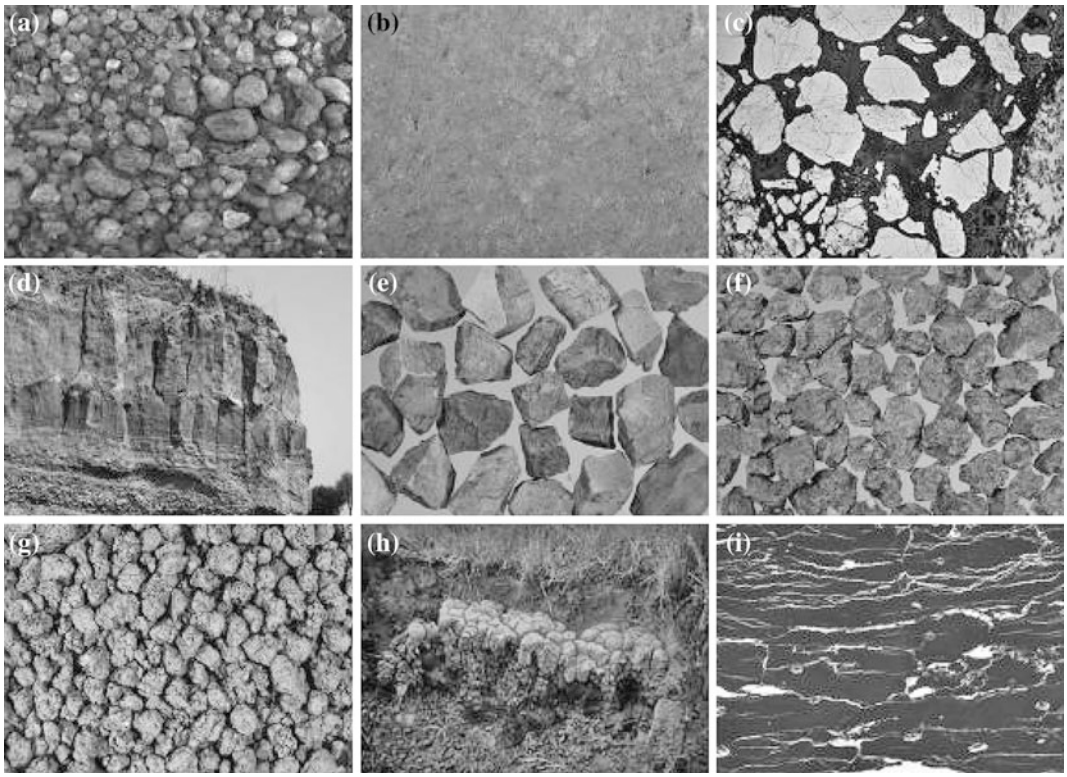

Fig. 6.14 Development of structural forms beginning from a single grain structure due to swelling and shrinking, biological processes and anthropogenic loads. **a** single grain structure, coarse sand; **b** coherent structure, loess; **c** massive structure, mainly coarse sand coated with iron oxides **d** prismatic structure, loess; **e** polyhedral structure, Bt horizon of a loess Luvisol; **f** subangular blocky structure, Bv horizon, loess; **g** crumbly structure, Ap horizon, loess; **h** columnar structure, **i** platy structure, plow pan in loess (*Images* R. Tippkötter, H.H. Becher)

(a) **Single grain structure**
In a single grain structure (Fig. 6.14), the primary particles (mineral and organic particles) **do not adhere** to one another. Their position relative to each other depends on the particle shape, grain size, the friction at the contact points, and the prior loosening and compaction processes. The most dense packing, in the sense of an orderly sphere packing, is never reached. At medium water contents, the water menisci produce cohesion between the particles; however, it is lost both when drying out and during flooding. As a result of these packing properties, steep slopes and profile walls trickle easily until the natural slope angle is established. Single grain structure is found in sands and gravels that are poor in clay and iron oxides, as well as in freshly deposited silt-rich sediments and in coastal mudflats.

(b) **Coherent structure**
With a coherent structure, the primary particles are held together by cohesive forces and form a **structureless mass** even after drying (Fig. 6.14). Slopes and profile walls therefore do not trickle, but rather remain more or less as steep walls.
Coherent structures are found in silty, loamy and clayey soils, particularly in freshly deposited and not yet shrunken soils. A special type of coherent structure is found in sandy soils, where the primary particles are cemented at the contact points by coatings of iron oxides, carbonates or organic substances. This form of coherence is called **massive structure** (Fig. 6.14), and is found as a hardpan in

Podzols, bog iron ore in gley soils, silcrete in Durisols, plinthite in Plinthisols and as calcrete in Calcisols (see also Sect. 8.4).

An important source of coherence in soils is the contraction of particles due to **water menisci**. For this reason, the extent of coherence strongly depends on the fraction of water-filled pores in the soil, i.e. on the water content. This is most pronounced in fine-grained soils, where the coherence varies greatly at different water contents. However, the coherence caused by water menisci is easily reversible. Once they have been broken, massive structures loose their coherence and turn into single grain structures if the primary particles are in the sand fraction size range, because the coherence caused by menisci then remains low.

(c) **Aggregate structure**

In an aggregate structure, parts of the soil matrix are clearly delimited from their surroundings and form **separate bodies**—the aggregates. The shapes and sizes of the aggregates differ greatly depending on how they were created, as well as their degree of development. Aggregation can be so strongly pronounced that fine-grained soils assume the properties of coarse-grained soils (development of pseudo-sands or gravels), which is significant for drainage, erodibility, the air and hydraulic conductivity.

Aggregate structures develop both from soils with coherent and single grain structures. The shape of the aggregates is characteristic for specific horizons and also for specific development types, whereby a distinction is generally made between separation structures and biological structures (Fig. 6.14).

Separation structure

Prismatic structure. Prismatic structures are vertically stretched aggregates that are delimited by 3 to 6 usually **rough lateral surfaces**, with a diameter often varying in a wide range between 10 and 300 mm (Fig. 6.14d). The prismatic **separation** develops through shrinkage and swelling as the first form of aggregate formation. With increasing profile depth, there are less shrinkage cracks and the diameters of the prismatic structures increase, whereby their mechanical strength decreases.

Prismatic structures are characteristic for all soils with pronounced swelling and shrinkage behavior. They are observed in Luvisols, Pelosols, in stagnic horizons of clay-rich Stagnosols, as well as in the groundwater fluctuation range of clay-rich Gleysols and marshes.

Columnar structure. Columnar structures contain vertically stretched aggregates with 4–6 sides, which, contrary to prismatic structures, have rounded edges and have a cap-like rounded top surface (Fig. 6.14h). Columnar structures are characteristic for strongly swelling Solonetzes due to their high Na-saturation, whereby the top surfaces can form a plane at the base of the Ah horizon. Columnar structures are also sometimes found in the knick horizon of Umbric Gleyic Fluvisols, or in Gleyic Salic Tidalic Fluvisols and in saline soils at the edges of roads (due to the spraying of salt in the winter).

Polyhedral structure. Polyedrons are aggregates with main axes of about the same length, mostly sharp edges and smooth surfaces, which do not meet at right angles (Fig. 6.14e). At comparable clay contents, the frequency and intensity of swelling and shrinkage as well as the organic matter content affect the aggregate size and the bulk density and pore distribution inside the aggregates. As a result, polyhedral structures are mainly found in clay-rich soils, such as in Pelosols, as well as in Bt horizons of Luvisols and Vertisols degraded Chernozems.

Subangular blocky structure. Repeated shearing in the soil due to partial and varying swelling and shrinkage intensities as well as biological processes, not only further reduce the size of the polyhedrons, but also **rounds** their edges, while the surfaces simultaneously become rougher. The removal of small soil volumes on the surface of the polyhedrons associated with this process is caused by varying residual and proportional shrinkage behavior, which is due to varying degrees of desiccation in the millimeter range.

Subangular blocky aggregates usually have a diameter of ca. 5–30 mm (Fig. 6.14f) and are found

in surface soil horizons and in horizons with intense and frequent swelling/shrinkage processes.

Prisms, polyhedrons and subangular blocky aggregates are therefore separation structural forms that build up on each other, and become continuously smaller in the upper profile zone as a result of repeated wetting and drying, while becoming more stable in the process.

Platy structure. Horizontally bedded platelets (Fig. 6.14i) develop as a result of **compression**, especially with repeated rapid alternation of the load. The thickness of the platelets is of ca. 1–50 mm. Especially in surface soils, platy structures can also be formed through freezing and thawing due to the volume expansion of water by up to 9 % during the transition to ice. Comparable structural forms are observed e.g. also in C horizons in glacial regions, such as the young moraine region of Schleswig Holstein. In addition to the formation of ice, platy structures can also be produced through biological compressions, e.g. under the root balls of large trees that are subject to strong wind pressure. On the microscopic scale, platy structures are found in the direct surroundings of growing plant roots or earthworm burrows. Platy structures of anthropogenic origins are found under wheel tracks or in ruts, trails, in plough soles and other hard layers caused by tillage, whereby their thickness depends on the intensity of the mechanical loads.

Fragmented structure

Fragments such as clods and peds are **irregularly** and artificially shaped aggregates produced as a result of soil tillage in Ap horizons with coherent or aggregate structures.

a) **A ped structure** is formed from aggregates with rough surfaces. It is mainly formed due to the tillage of soils with moderate clay contents at optimal soil moisture (diameter of the peds <50 mm). The goal of soil tillage is to produce a ped structure, and in addition to the generally existing integrated natural structure, it is an important aspect of field cultivation measures.
b) **A clod structure** is mainly produced with the tillage of loamy and clayey soils that are too wet or too dry. The clods have a larger diameter than the crumbs and are often smeared at the surface.

Repeated homogenization of the A horizon, e.g. through rotary hoes, results in rounded spherical roll aggregates that are not very stable even though they are dense. These are also produced by recultivation measures, due to the rolling movement associated with the relocation of soil material during transport on conveyor belts at moderate water contents.

Biological crumbly structure (Fig. 6.14). Crumbs are produced under the influence of high levels of **biological activity** with simultaneous high organic matter contents and intensive rooting. They are generally rounded and irregularly shaped, have a diameter of ca. 1–10 mm, and have a high porosity. The individual soil particles are often connected by small piles of earthworm fecal pellets and by actinomycete filaments, and cemented by bacterial mucus.

The crumbly structure is particularly characteristic for topsoils under grassland and for A horizons with high biological activity and mull as a humus form. If the crumbs are cemented together, this structure is also called **sponge structure**.

Earthworm cast structure. Earthworm cast aggregates consist of fine soil particles that are cemented together by the mucus substances from the intestinal flora of worms (e.g. earthworms, see Sect. 4.1.2). They have high organic matter content and form irregularly shaped, often globular heaps with a size of up to several cm. In Ah and Ap horizons of sandy soils, which consist mainly of fecal pellets from oribatid mites, Collembola and Enchytraeidae, fine coagulates are often found that fill the voids between the sand grains, and are connected partly with the latter by roots and fungal hyphae.

6.3.1.2 Microstructures

Because of the wide range of the particle size scale, several orders of magnitude must be treated separately in the classification of the soil structure. For this reason, since the research

performed by Kubiena (1958), the size range that can only be described using a microscope is treated separately from the previously described structures that can be described with the naked eye. A distinction is therefore made between the **macrostructure** that is identifiable in the field, and the **microstructure** that can only be seen through a microscope.

Investigations on the undisturbed microstructures often require extensive preparation. Investigations using optical microscopes require **soil thin sections** with a thickness of ca. 20 µm, or block-shaped polished sections, where the soil sample is bedded in liquid synthetic resin after gentle drainage, and is ground and polished after the resin has hardened. The reconstruction in layers using polished sections delivers initial spatial impressions of the soil structure.

Using computer tomography (CT) from the medical sector, undisturbed soil samples are scanned in layers with a resolution of ca. 1 mm and represented up to a minimum pore cross section of ca. 40–70 µm. It has recently become possible to represent undisturbed soil structures in two and three dimensions using the computerized synchrotron or microfocus tomography (µCT) with a resolution of ca. 1–5 µm, enabling a clear and quantitative representation of the functions and morphology of the coarse mesopores or medium-sized pores.

The scanning electron microscope (SEM) shows both the soil surface and the voids directly in three dimensions, whereby the resolution of the microscopic features is much higher than with any other technology, reaching into the nanometer range.

In the micron range, many pedological and also physical and biological processes can be recognized by their micromorphological characteristics, which cannot be recorded using macroscopic observations. The **solid phase** and **voids** always serve as important differentiation criteria, which are described using the size, occurrence, sorting, shape, surface properties, and orientation. This also enables the analysis of weathering and degradation processes on primary particles and displacement sequences and biogenic processes such as the formation of aggregates from earthworm and Enchytraeidae excretions. Modern digital image analysis methods used in micropedology not only enable quantitative statements on the pore distribution and continuity as well as the phase composition in the pore system, but also on spatially effective hydraulic flow functions.

Recent developments in micropedology attempt to record the mutual influences of the soil physical and microbiological processes on a microscopic scale. Thus, on the one hand, the physically possible microhabitats of fungi, Archaea and bacteria are determined, where colonization in the structural interspaces is potentially possible e.g. based on the size, air and water supply. At the same time, modern methods used in molecular microbiology, such as FISH or DNA analysis, can provide information on metabolic products that have a stabilizing effect on the structure (Fig. 6.15). In addition, the effect of filamentous microorganisms such as fungi and Actinomycetes on the stability of aggregates is not to be underestimated. They connect individual particles or whole aggregates, go through aggregates like a reinforcement, and can also protect larger aggregates from external influences like a net (Fig. 6.15).

6.3.1.3 Crack and Channel Systems

Cracks result from pressure and tensile stress in the soil, which was relieved by brittle fractures. Because cracks and channels are only formed during pedogenesis, they are sometimes collectively referred to as **secondary pores** (also: structural pores) compared to the texture-related **primary pores**. The position of cracks relative to one another is typical and allows interpretations on their development.

Tensile cracks (Fig. 6.16a) are formed by shrinkage when a coherent matrix cannot follow the contraction. Because stress cannot be transferred beyond the cracks, a new tension system builds up after fissuring, which is also why it is sometimes referred to as stress release cracks. In an ideal system, the next generation of cracks therefore always begins at a right angle to the previous cracks. Because the first cracks in a homogenous layer of sediment are in the vertical direction, they

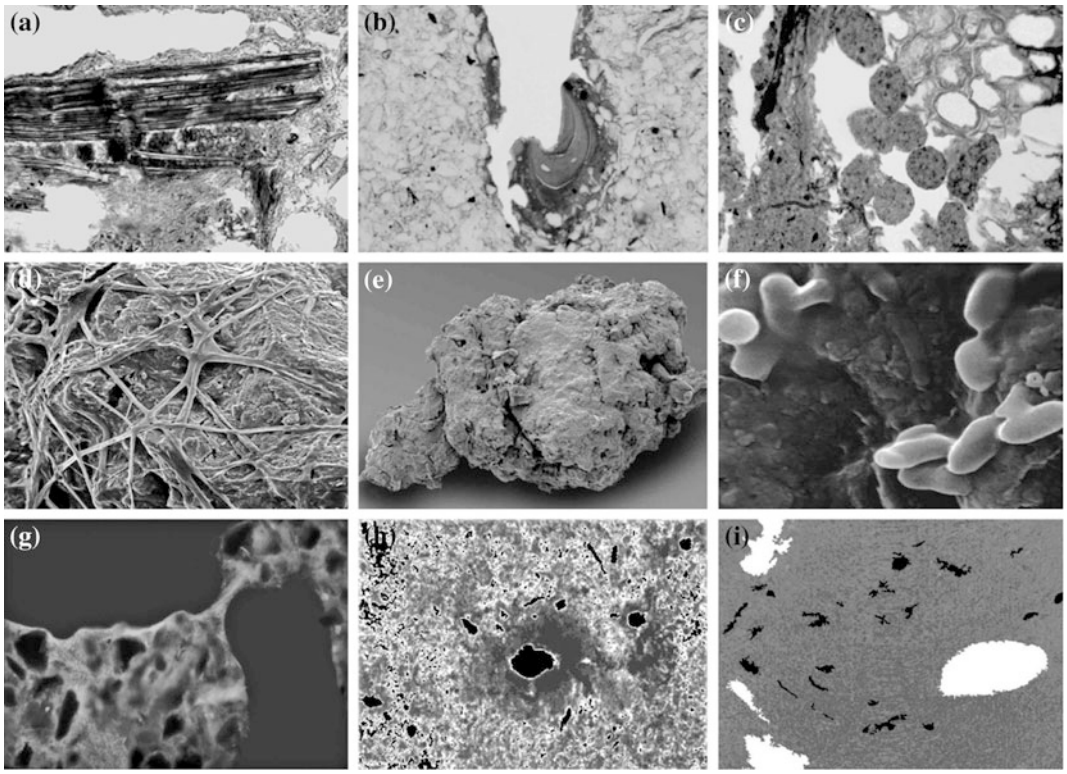

Fig. 6.15 Micropedological processes and characteristics in undisturbed soil layers. **a** Weathered biotite; **b** clay illuviation in a macropore; **c** fecal pellets of Enchytraeidae; **d** fungal hyphae stabilizing a microaggregate; **e** crumbly structure; **f** bacterial colony with exudates on a pore surface; **g** bacterial colonies between aggregates; **h** compaction in the area surrounding former fine roots (*pores are black*); **i** digital pore size analysis (*Images* R. Tippkötter, T. Eickhorst)

form a system consisting of long vertical aggregates (**prismatic structure**), appearing at the soil surface under homogenous soil conditions as a rectangular system, or as a polyhedral system under heterogeneous texture situations. Due to the younger generations of horizontal cracks, the prismatic structure is fragmented into smaller aggregates during pedogenesis.

Shear cracks are produced particularly during further pedogenesis or when there are varying water contents in the soil (swelling states), which can lead to tension = negative stress. With the cracks from the previous generation, they form angles that deviate by the amount of half the angle of internal friction at the moment of crack formation of 45°. Shear fractures generally only occur after the initial shrinkage (Fig. 6.16b). For this reason, the proportion of non-right-angled edge angles on polyhedrons and as a result, also on subangular blocky aggregates, is greater the further the course of soil development, i.e. the more shrinkage and swelling cycles have taken place since the initial shrinkage.

Coherent soils are often interspersed with cylindrical **tunnels** produced by animal or root tunnels. The more or less vertical earthworm or taproot tunnels reaching down to a depth of up to >1 m are particularly striking. Fine (<1 mm diameter) pores with irregular branching are often found in coherent soils, especially those consisting of silts. These 'needle pores' are mainly typical for loess that is not kneaded or flooded. The cylindrical pores in the subsoil represent effective conductors for rainwater. If they have a diameter of several millimeters, they also act as the most important air channels.

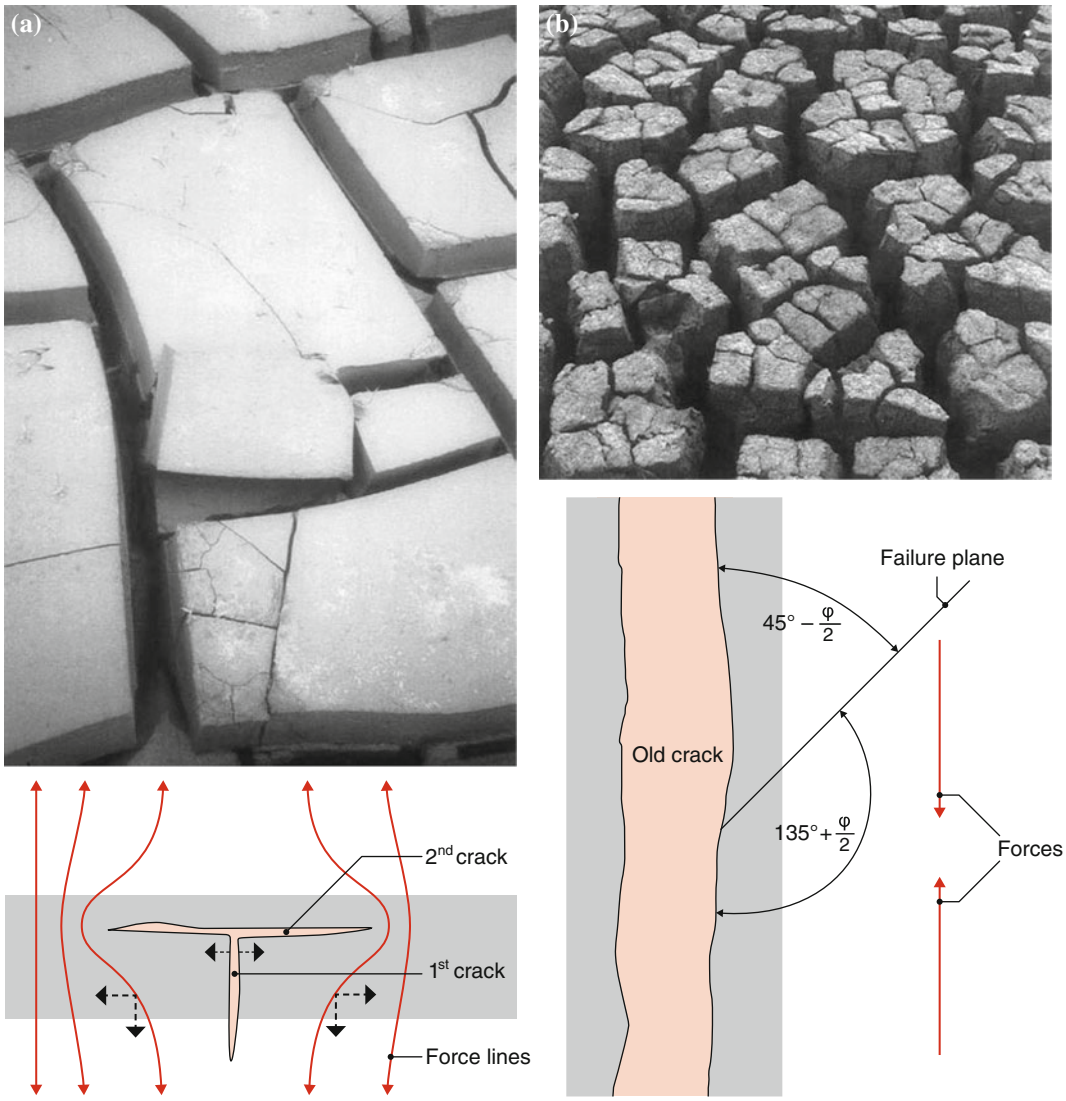

Fig. 6.16 Development of aggregates through the formation of a system with 3 generations of tensile cracks (**a**) and through shear cracks that are not perpendicular to each other (**b**)

6.3.2 Stresses and Deformations

6.3.2.1 Forces on the Grain

The external forces acting on each and every primary particle in the soil can be summarized in four simplified groups:

- Weight forces,
- Cohesion and adhesion,
- Forces transferred by neighboring solid particles (=surcharge) and
- Forces transferred by movement of the soil solution (hydraulic stress, see Sect. 6.2.4).

The combinations of orientation, contact point and magnitude of the forces result in a system of forces, the simplest case being a central system as shown in Fig. 6.17. Its resultant mobilizes counterforces that can be divided into a **tangential** and a **normal** component for each contact point between two particles.

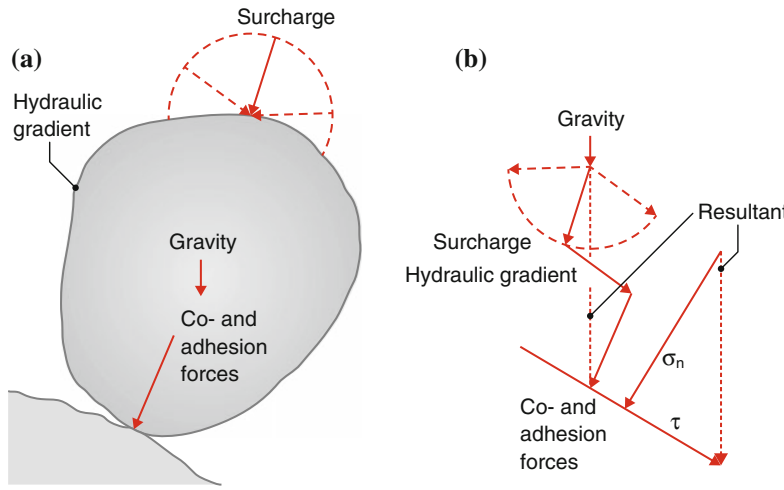

Fig. 6.17 Schema of the forces acting on a soil particle or aggregate: visual depiction (**a**) vector representation (**b**) (τ = shear resistance, σ_n = normal stress)

Depending on the extent of these counterforces, the system is either more or less stable if there are changes in each of the four components involved. If there is a displacement of the particles relative to each other because the size of the mobilized counterforces was exceeded, it is generally associated with a change in volume and therefore a change in the number of contact points between the particles. The **reaction force** (=counterforce) also consists of a tangential component (τ, shear resistance) and a normal component (σ_n), which is induced by the adjacent particles. The latter is called supporting force (abutment load).

6.3.2.2 Forces and Stresses in the Soil Profile

The forces acting on each individual particle also act within the entire soil profile. The fraction relative to a unit of area is called **stress**, as opposed to external pressure acting on the system.

In terms of the overall soil profile, the **weight force** (gravitation) is the most important component. Evenly directed towards the center of the Earth, it causes every horizontal layer in a profile to be under stress, induced by the weight of the overlying soil layers. Because every overlying load must be carried by the underlying zone, it becomes compressed and the pore volume filled with air and water is reduced, since under normally occurring pressures, the solid particles cannot be compressed due to their own comparatively high strength. At the same time, the particles are pressed together and the number of contact points with neighboring particles is increased for each individual particle.

The total load on each horizontal layer in the soil body, relative to the unit of area, is called **vertical stress** (σ_z). It results from the depth (z), the bulk density of the soil (ρ_B), and the acceleration of gravity (g):

$$\sigma_z = z \cdot \rho_B \cdot g \tag{6.12}$$

The increase in vertical stress with profile depth is the reason for the higher densities observed in subsoils (cf. Fig. 6.8).

(a) **Laterally unlimited load**
The weight of the 'hanging' soil zones on any given section from the horizontal layer can be assumed to be equal within the boundaries that are of interest here. Therefore, the settling behavior can be represented by the experimentally measurable correlation between load and volume, whereby lateral deflection is either neglected or defined. In simplified terms, information is obtained on the inherent stability of soils by using a uniaxial pressure test with inhibited lateral expansion (=compression test, e.g. using soil cylinders) or using the much more elaborate triaxial test with defined lateral counterpressure.

The resulting **stress-strain curve** (also called compaction curve) depends on the friction, the cohesive and adhesive forces in the solid phase, and how these are affected by the soil water content. It represents a material constant (Fig. 6.18a). The stress-strain curve also delivers information on the load history of the investigated soil. A distinction is made between two states:

1. **Virgin (or normal) compaction**: This state of compaction corresponds to the current existing load and/or the corresponding drainage (=matric potential or negative pore water pressure). Any additional load on the soil causes a further change in height with an associated reduction of the pore space, the void ratio and an increase in the bulk density. A semi-logarithmic plot shows this virgin compaction as a straight line. After stress release of the load, the soil remains mostly **plastically deformed**, because the mutual friction resistance caused by the displacement of the primary particles lead to an increase in the number of grain-to-grain contacts.
2. **Overcompaction**: If, in the time period before the measurement of the current compaction, the soil was more strongly mechanically or hydraulically loaded and thus stabilized than at the time of the measurement, more negative matric potential values (=more negative pore water pressure) and/or the actual stress applied must exceed the former maximum stress in order to reach the virgin compaction range. Up to the former load/desiccation, not only is the height reduction minimal, but the soil surface rises again after stress release by the amount of the **elastic deformation**. The reaction of this stress or pore water pressure range is defined as elastic because the internal soil strength is not exceeded. Furthermore, the unloading and loading branch shows a clear hysteresis effect.

It must be pointed out that non-compacted soils do not exist in the gravitational field of the Earth, but **normal compacted** ones, as well as no "over-loosened" soils do exist. The virgin compaction line (= normal compaction in Fig. 6.18a) represents the outer stability boundary condition. Overcompaction or recompaction (also called **precompaction**) lie on the unloading and the secondary compaction branch. Depending on the load history, various vertical stresses/tensions can cause this branch to merge into the virgin compaction branch. The stress on the confluent point of the recompaction

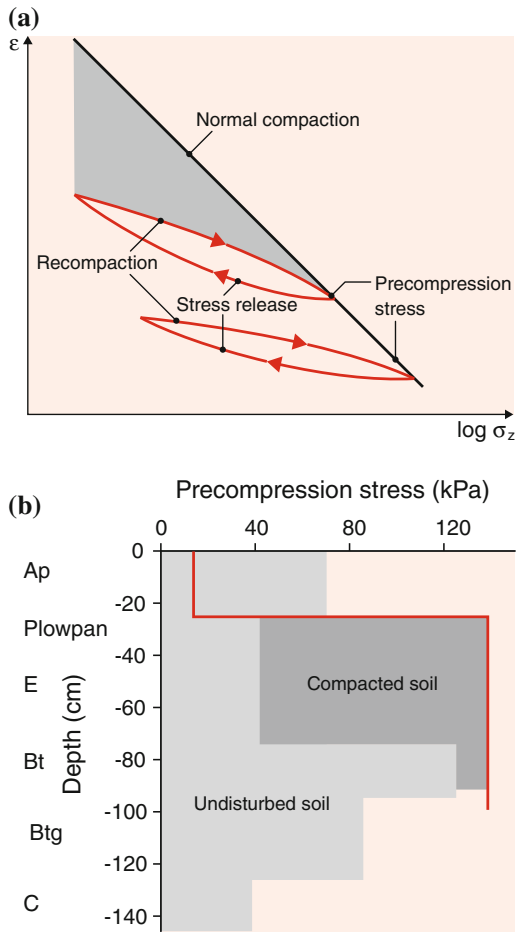

Fig. 6.18 **a** Schematic representation of a stress-strain curve with recompaction and virgin compaction branches. The course of the curve during the unloading and subsequent reloading shows the hysteresis effect in terms of the change in height. The *shaded area* identifies the maximum possible reloosening. **b** Depth distribution of the preload in a loess Luvisol under natural conditions and modified by plowing

branch into the virgin compaction branch indicates the highest (formerly acting) load and is called **precompression**. However, the origin of such precompression stress can only be determined if information is available on the geological history (e.g. load or height of glaciers, advance processes, etc.), the hydraulic (e.g. drainage, shrinkage, aggregation) or the present mechanical load conditions (e.g. due to agricultural and forestry machinery, animal trampling). For a loess Luvisol, for example, the natural soil development for the clay-depleted E-horizon with coherent structure results in low precompression stress values, as well as higher values caused by aggregation in the Bt horizon, characterized by clay deposition with associated polyhedral structure. The intense compression underneath the load areas, induced by harvesting, wheeling and soil tillage practices, may also result in a higher precompression stress, and is detected by only a slight decrease in compression with depth over large soil depths (see Figs. 6.18b and 10.20.).

Because the transition between the two sub-branches cannot always be precisely detected from the course of the stress-strain curve, different methods have been developed for this purpose. The most commonly internationally used method was developed by Casagrande based on the inherent strength value of the precompression stress which can be read directly using a graphical interpretation method to analyze the curvature of the stress-strain curve. In principle, the packing curve shown in Fig. 6.7 is also a 'stress-strain curve of the soil profile', because here also, a distinction is made between the virgin and the overcompaction line.

Changes in the load not only affect the vertical stress components, but also have an effect on the other stress or tension (=pore water pressure) vectors in the soil, because soils are not rigid and exhibit plastic behavior with loading/unloading. A portion of the total load is transferred in a horizontal direction rather than in the vertical (σ_z = greatest principal stress). This amount of stress is called horizontal stress ($\sigma_{x,y}$) or smallest principal stress. The ratio between the vertical and horizontal stress in a three-dimensional space is described by the deviator stress at rest and has values between 0.2 and 0.7 in normally compacted soils. In originally over compacted soils that were later unloaded, the originally acting stress then remains as a mechanical preload due to the predominant effective plastic deformation in the horizontal plane in the original state, while in the vertical plane, none of the stress caused by the former load is measurable after unloading. As a result, the original vertical principal stress becomes the smaller stress, and in contrast, the original horizontal principal stress has higher numerical values. In this case, the reciprocal reference system is therefore used to calculate the deviator stress at rest. The propagation or transfer of the forces differs depending on the direction. Stresses and deformations are therefore corresponding **tensors**.

Under a vertical load on virgin compacted soils, the increase in stress is lowest in the horizontal plane. It is considerably smaller than in the vertical plane. The removal of a soil layer has the same effect by reducing the vertical stress component, and the horizontal stress is only reduced by such a small amount that the remaining stress can be greater than the remaining vertical stress. Such a stress distribution is also called an over-compacted state. This state can be demonstrated by pressing soil into a tube that is open at the bottom (sampling ring) and compacting the soil from the top before lifting the ring. This behavior is caused by the higher force acting on all contact points between the primary particles as a result of the increased load during compression. The resulting higher force

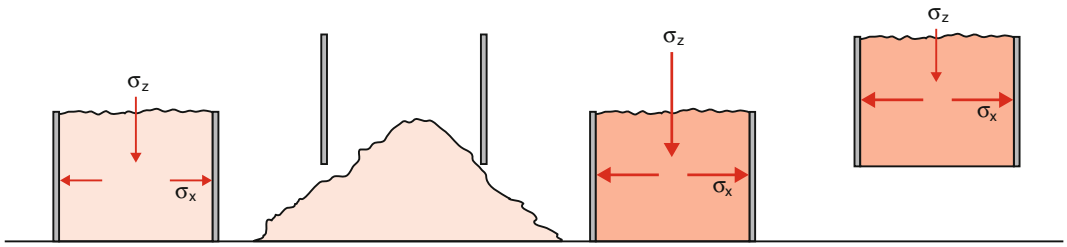

Fig. 6.19 Development and effect of pre-compaction. Soil that is poured into a cylinder slips out again when it is lifted. After a temporary increase in the vertical stress (σ_z), the irreversible part of the horizontal stress (σ_x) holds the soil in the cylinder

fraction on the horizontal plane can only be reduced again if the particles are lifted again by the amount of the plastic deformation that occurred during compression, i.e. when the deformation (compaction) caused by the load is reversed (Fig. 6.19). Such loosening and therefore lifting of the soil can only be accomplished by animal activities or root pressure (bioturbation), by windthrow (arboturbation), by the formation of ice and thawing (cryoturbation), swelling and shrinkage, or abrupt changes in temperature in a small area (see Sect. 6.3.4). These processes are grouped together under the term **pedoturbation** (cf. Sect. 7.2.6). Within the scope of human influences, loosening is mainly accomplished through ploughing, cultivating or special subsoiling. However, these measures can only achieve the state of the virgin compression line at most. This is shown with the hatched area in Fig. 6.18a.

(b) **Laterally restricted load**

The laterally restricted load represents a special case in the pressurizing concept for soils. These are defined as loads that only cover part of the existing soil surface. This includes loads from trampling by people and animals, traffic loads, and the foundations of all types of buildings. The laterally restricted load was already reduced to a punctual load for mathematical calculations a long time ago (Boussinesq 1885). The greater the load and thus the stress in the compressed soil body, the more contact points between the particles must be produced to obtain the required bearing capacity. This is partly accomplished by distributing the force onto a greater area in the soil, and partly by increasing the resistance and thus the number of contact points per unit of volume through local compaction. The distribution and thus the relief of stresses in the soil under a load can be given for a plane by a group of equipotential lines (=lines with the same pressure). Depending on the design of the measurement setup, the resulting **pressure bulbs** (Fig. 6.20) either give the vertical stress components (σ_z) or the principal stresses (σ_1: highest = vertical; $\sigma_{2=3}$: lowest = horizontal principal stress in normally compacted soil). The shape of the

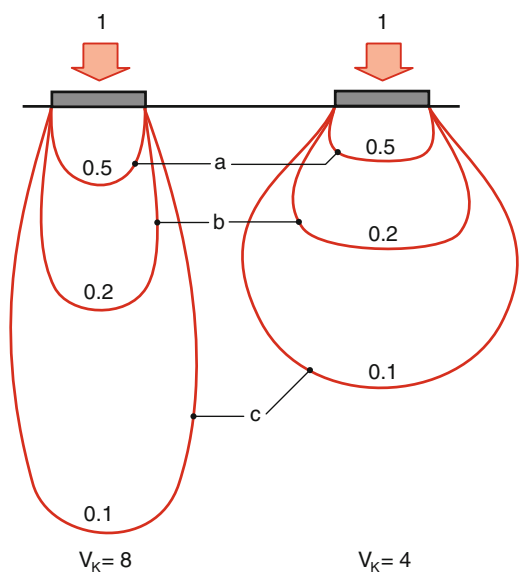

Fig. 6.20 Pressure bulbs: lines of equal vertical stress (*a–c*) in a soft soil (*left*) and a hard soil (*right*)

bulbs shows the stability of a soil layer. The softer the soil, the closer the equipotential lines run to the perpendicular plane but reach deeper into the soil, while in hard soils, the stresses are concentrated closer underneath the load and reach further into the horizontal plane. Their shape is described by the concentration factor values, which become greater the more narrow the equipotential lines (factors according to Fröhlich, mathematical method according to Newmark, among others) As a result, they are smaller for aggregated soils than for soils with coherent or single grain structures, just as they are smaller in dry than in wet soils, smaller in compacted than in loose soils, and lower in soils with high organic matter contents than in samples without any humus. In addition, they depend on the load area at a given pressure, they are smaller at pressures below the precompression stress than in the virgin (i.e. normal) compaction range, and thus serve as a measurement for the state of soils. In general, due to the law of conservation of energy, the length of the equipotential lines increases proportional to the reduction in pressure, and thus e.g. the 0.1 equipotential line is 10 x longer than the pressure curve with the number 1 in a 2-dimensional space.

6.3.2.3 Effect of Water

In Fig. 6.17, three functions of water are shown that have an effect on the stability:

1. It transmits the hydraulic pressure through its movement. This phenomenon plays an important role on all banks and slopes, and is covered in detail in studies on soil mechanics and foundations.
2. It creates buoyant forces when the pore space is completely filled with water (=water-saturated state), which affects the weight components of the solid particles.
3. It is part of the cohesive and adhesive forces when the pore space is partly filled with water (unsaturated state).

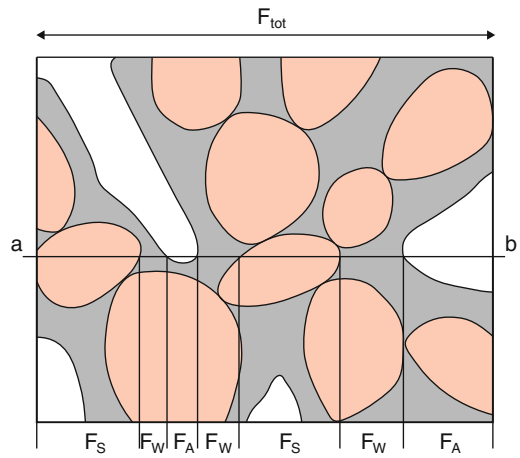

Fig. 6.21 Transmission of stresses (F) over the different parts in the plane a–b in the solid (subscript S), liquid (water = W) and gaseous (air = A) phase

In a virtual plane through a soil where the pore space is only partly filled with water (unsaturated state), there are area fractions from all three soil components: solid particles, water bonds, soil air (Fig. 6.21). These three phases transmit the stresses arising in the represented soil section to different extents. For this reason, the total stress depends on the proportions of the three components.

Thus, in the case of the plane a–b shown in Fig. 6.21, a force (F) is transmitted over an area (A) by the following components:

$$F = p_S \cdot A_S + p_W \cdot A_W + p_A \cdot A_A \qquad (6.13)$$

Here, $p_{S,W,A}$ is the pressure in the solid particle fractions, the water and the air, and A is the corresponding area fraction.

Of these three components, only the stresses in the solid phase are capable of developing an appreciable and longer-term effective shear resistance with an increase in load. The stress fractions in the two other components are marginal because they can quickly dissipate, so that the stress here cannot accumulate as strongly, which retards the deformation and the decrease in volume. This is generally accepted for the air phase, whereas in the water phase, the comparatively slower water flow velocity caused by viscosity may lead to longer-lasting positive pore water pressures under

a sudden increase in load, which may retard the corresponding settling but does not increase the shear resistance between the particles.

As a result, in terms of long-term soil stabilization, the effect of pressure on the water fraction decreases the stability if a hydrostatic pore water pressure (p_W) is produced, whereby although the total stress (F/A) increases, the fraction contributing to the shear resistance does not (p_S is equal to σ'). In soil mechanics literature, these effects are summarized in the effective stress equation (according to Bishop):

$$\sigma = \sigma' + u \tag{6.14}$$

Here, σ is the total stress (F/A), σ' is the effective stress, and u is the pore water pressure. The air fraction is neglected because it generally immediately escapes at the moment the load is exerted. It only plays a role in rare cases, if e.g. air is trapped in pores due to flood irrigation or refilling from a great height during recultivation. Thus, the effective stress σ' between the particles at a given total stress in a saturated state (=two-phase system: solid, liquid phase) depends solely on the pore water pressure. In the case of positive pore water pressure ($+u$), the strength decreases, whereas the effective stress increases with negative pore water pressures ($-u$), i.e. matric potential and its amount (=the water tension) (equal to ψ_m see Sect. 6.4.2).

In a three-phase system (solid, liquid, gaseous phase), however, the water menisci only have an effect in the water-saturated pore space.

$$\sigma' = \sigma - \chi u \tag{6.15}$$

The fraction of the water-filled pore space in the total pore area on the observed plane is defined by the factor χ as a normalized parameter, where $\chi = 1$ in a water-saturated state, and $\chi = 0$ at complete desiccation.

As a result, there can always be an increase in soil strength due to more negative pore water pressure values (matric potentials), if the reduction in the χ factor caused by the decrease in the water-filled pore space induced by desiccation is lower than the corresponding reduction in the matric potentials. The change in the stability of sands is a typical example, where their state passes from flowing (instable; $u \geq 0$) at water saturation, through load-bearing (stable, $u < 0$) to trickling (without stability, no effective water menisci force between the particles) with further desiccation.

Equations 6.14 and 6.15 also show that every increase in the total stress, e.g. due to compaction at a given effective stress leads to an increase in the water pressure by increasing the matric potential. This makes the soil look wetter after compression.

The stability-reducing effect of water is particularly significant if there is trampling or vehicle traffic on a virtually or completely saturated soil. If the load passes so quickly that the water cannot escape, an increase in strength due to compaction is prevented, but this phenomenon (which practically corresponds to aquaplaning) also results in a temporary rigid and thus load-bearing soil system due to the incompressibility of water. However, it must be considered that this strength is actually only maintained depending on the hydraulic and the mechanical conditions (see Sect. 6.4.3), and is completely lost under any shearing soil movement, as it inevitably occurs under e.g. driven tires, wheels, tracks or also the hooves of animals, or even additional homogenization. Any shearing deformation inevitably pushes particles and the water phase against each other, which may cause sinking and at the same time homogenization by kneading of the soil and the pore system.

If there is no support at the sides and/or if there are additional effective vibrations in the soil, the suddenly occurring (over)pressure of the pore water can lead to a characteristic mass movement, as it is observed on slopes, walls of drainage ditches, and hillside cuts for canal and road structures. It is the result of a change in the components of the force system (see Fig. 6.17).

6.3.3 Soil Structural Stability

A soil structure is considered to be stable if the position of the primary particles relative to each other is maintained when there is a change in stress or tension. This general statement is also true for aggregate structures that are changed or destroyed by tillage measures (e.g. seedbed preparation). However, the behavior towards changes in structure due to stress -related deformations in the overall soil profile is also included in the term stability (**structural stability**). As a result of these very singular aspects, very different empirical methods have been developed, which often no longer reflect the basic similarities. This is especially true with the use of "indirect" methods (e.g. wet sieving, Atterberg method, Proctor test, or penetration resistance). However, reproducible and quantifiable results are mainly obtained from methods where the reasons for the stability, which are responsible for the preservation of a given packing are quantified using the mobilized counterforces against an acting load. This approach uses the **Mohr-Coulomb Equation**

$$\tau = \tan\varphi\ \sigma_n + c \qquad (6.16)$$

Here, τ is the shear resistance, σ_n is the normal stress, φ is the angle of internal friction, and c is the cohesion (Fig. 6.22). For noncohesive soils, e.g. sands, the equation is reduced to

$$\tau = \tan\varphi\ \sigma_n,$$

while the shear resistance for pure water is calculated using

$$\tau = c$$

Here, c corresponds to the surface tension of water.

The Mohr-Coulomb failure line is simultaneously the tangent on the Mohr's circles. These are calculated based on the two principal stresses σ_1 (greatest principal stress) and $\sigma_2 = \sigma_3$ (smallest principal stress) respectively in pairs in the state of the fracture.

The center of the Mohr's circle is then calculated as $(\sigma_1 + \sigma_3)/2$ with the radius $(\sigma_1 - \sigma_3)/2$ (Fig. 6.22).

As a result, the **shear resistance τ** is the reaction force that can be mobilized by the soil under loads. If it is exceeded, fractures and thus slipping occur. The soil is then considered to be instable under the load. The equation shows that the stability is always defined by two soil properties: the angle of internal friction φ and the cohesion c, whereby the respective normal stress σ_n (=load) on the contact points of the particles determines the maximum mobilized resistance. Figure 6.17 also shows that there are only two points that lie perpendicular to each other on the plane where the resultant cannot be divided into normal stress and shear stress components, but rather only the two principal stresses (σ_1, $\sigma_{2=3}$) come into effect.

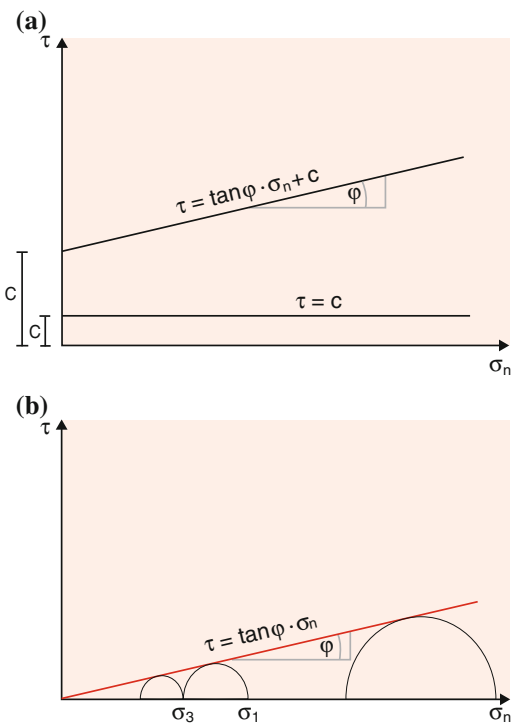

Fig. 6.22 Mohr-Coulomb failure lines for aggregated soils and aqueous suspensions (**a**), cohesionless/substrate (**b**) (schematic). **b** Shows the Mohr circles, for which the failure line represents the envelope curves

6.3.3.1 Stabilizing Substances

The stability of the soil structure, and therefore especially the stability of the secondary pores, is promoted by various substances with particle-binding effects, such as organic substances, aluminum and iron oxides, calcium carbonate, and to a lesser extent also magnesium carbonates, silicic acid, and in arid areas, especially gypsum and water soluble salts, etc. Their effect is particularly important in the upper soil horizons, because here the soil particles can be more easily pushed up against each other than in the C horizon, and because the soil here is subject to special loads due to the impact of raindrops and desiccation, tillage and traffic. The effect of particle-binding substances can be considered as an increase in the shear resistance both between the primary particles and also between the aggregates. The different possibilities for binding individual particles to form aggregates are represented schematically in Fig. 6.23.

(a) **Organic substances**

Organic matter has a very strong effect on the stability of aggregates in the topsoil. This is demonstrated by the fact that e.g. the most stable aggregates generally have a higher C content than the rest of the soil, and that the fraction of smaller and more stable aggregates (>0.5 mm) increases with long-term organic fertilization.

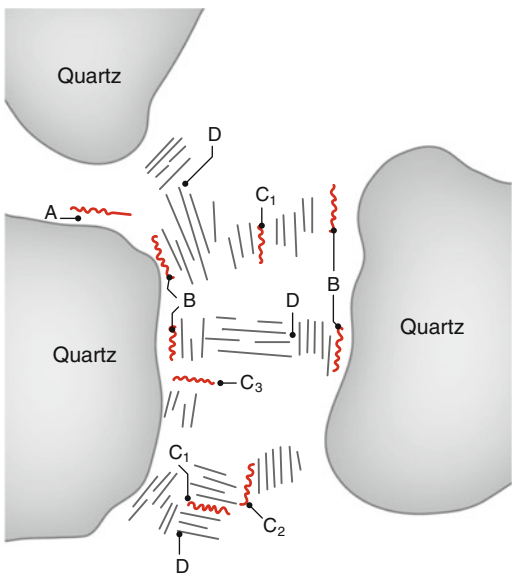

Fig. 6.23 Model of the arrangement of clay mineral packages, organic matter and quartz in a soil aggregate (after W.W. Emerson)

The organic matter added to the soil in the form of **vegetation residues** and **organic fertilizers** indirectly promotes aggregate formation by increasing the microbial activity. Some of the organic compounds originating from the intermediate products from the microbial decomposition and metabolic products of the microorganisms (mucus), mainly polysaccharides and polyuronides, are capable of binding inorganic particles. However, since these compounds are also not resistant and are decomposed again by the microorganisms, their maximum stabilizing effect is only of short duration.

The effect of organic substances is not limited to aggregate formation in a more specific sense of the term. In sandy soils, the accumulation of only a few percent organic matter is already associated with an increase in the shear resistance. The shear resistance at a given load correlates with the reduced pore volumes due to the accumulation. The stabilizing effect on the soil structure, resulting from the accumulation of organic substances under grassland, lasts several years in cultivated soils after they have been ploughed.

Because organic matter also serves as food for smaller soil fauna, a high organic matter content in the soil also results in a higher population of smaller animals, especially **annelids (earthworms** and **Enchytraeidae**). When they have been hydrophobized by intermediate desiccation, the fecal aggregates from these animals are particularly resistant to the silting effect of water, due to the simultaneous intake of organic and inorganic substances and the mechanical rearrangement in the intestinal tract.

Fungal hyphae, Actinomycetes, bacterial colonies and root hairs also have an aggregating effect (see Sect. 6.3.1.2, **biological structures** according to F. Sekera).

However, their effect only lasts as long as their habitat in the soil provides the conditions they require for their activities. Interference with the air and water balance as well as major changes in the soil chemistry can lead to population dynamics that are detrimental to aggregate stability.

(b) **Oxides, carbonates and salts**

Fe and Al oxides can bind soil particles together. This either leads to a structure consisting of small (mm range) loosely packed aggregates, or the texture analysis with H_2O reveals an increase in the silt or sand fraction, which indicates particularly high stabilization. Pseudosand is typical for many Plinthisols and Ferralsols.

Higher additions of Fe and Al lead to the development of hard cemented forms, such as the more or less rounded concretions in the mm to cm range, or whole banks consisting of more or less continuous parts such as bog iron ore and plinthite crusts (ferricrete). Their structure leads to the conclusion that Fe and Al in the pore system preferentially crystallize as oxides around the contact points of the mineral particles. In this way, they cause an enlargement of the contact areas, which explains the cementation.

Similarly, cementation also takes place with silicon oxides (silcrete, duripan) or carbonates (calcrete). In arid climates, cementation also occurs due to the precipitation of gypsum or even more readily soluble salts (cf. Sects. 6.3.4.2, 7.2.4.3–7.2.4.5).

The formation of small, loosely packed aggregates are mainly attributed to electrostatic, but also to non-electrostatic interactions between very small positively charged oxide particles and negatively charged clay minerals (**aggregation**).

(c) **Cation composition and soil solution**

The effect of exchangeable cations on the structural stability is based on their flocculating and peptizing effect (see Sect. 6.2.1). However, this effect in soils cannot be observed separately from the salt content of the soil solution (exchange equilibrium), because the salt content required to maintain the flocculated state is lower the stronger the flocculating capacity of the exchangeable cations (Na < Ca < Al). For this reason, soils with high **Na saturation** are only found in a flocculated state if they contain a considerable amount of readily soluble salts, e.g. young marsh or saline soils. If the salts are washed out, the aggregates disintegrate and the secondary pores disappear, as is the case with e.g. the transformation of Solonetz into Solonchak.

With **Ca saturation**, the salt content required in the soil solution to maintain the flocculated state is much lower than with high **Nasaturation**. The salt concentration increases with the Ca saturation of the soil, the CO_2 partial pressure of the soil air, and the input of strong acids through precipitation. It reaches a maximum in soils containing $CaCO_3$ with high biological activity. High Ca saturation also leads to increased aggregate stability as a result of the formation of Ca bonds between clays and humus particles, and also has an indirect effect through increased biological activity. If the Ca saturation drops, there may be clay migration beneath the range of the carbonate buffer because of increasing degradation of the aggregates.

The conversion of CaO to $Ca(OH)_2$ is an important effect in loamy and clayey soils, as it desiccates the soil. However, the resulting 'desiccation' disappears again when $CaCO_3$ is formed due to CO_2 influx but the released water can spread into the matrix again. Because of the previous desiccation, associated with the formation of secondary cracks due to an expanded structural shrinkage range, the subsequent reswelling is less intense.

In mineral soils, the **Al saturation** increases below pH 5. As a result of the strong aggregating effect of Al ions, the structural stability in very acidic loamy and clayey soils is generally better than in soils with Ca saturation. However, because high Al

saturation is detrimental to plant growth, the stabilizing influence of Al can hardly be used in practice.

(d) **Inorganic fertilization**
Some readily soluble inorganic fertilizers have a direct effect on structural stability by increasing the salt content in the soil solution. An example of this is the favorable effect of high additions of gypsum (ca. 2500–5000 kg ha^{-1}) on the structure of some loamy and clayey soils. An indirect effect of inorganic fertilizers on structural stability is caused by the increase in yields, and thus the larger amount of vegetation residues and the induced biological activity.

(e) **Synthetic stabilizers**
The soil structure can also be stabilized by synthetic compounds. Their functional groups (−COOH, −OH, $-NH_2$) are capable of adhering mineral particles together in a way similar to the polyuronides and polysaccharides formed by microorganisms. Of the numerous compounds that are used for stabilization, polyacrylic acid and polyvinyl acid derivatives are most commonly used. Synthetic stabilizers are used e.g. to preserve a prepared seedbed and to stabilize soil surfaces at risk of erosion, e.g. sand dunes.

6.3.3.2 Sealing, Kneading and Crust Formation

On the one hand, seedbed preparation results in a loose packing, but at the same time, it also leads to a stability situation approximately comparable to the virgin compaction. Under these circumstances, the packing is very sensitive towards any loads. This is especially true when loads are applied in a wet state, or, like with the impact of raindrops, are associated with the addition of water. The effect of the **raindrops** is particularly significant on small aggregates, because the amount of water from one drop increases the water saturation and the matric potential more strongly in an exposed aggregate than in a closed soil layer. In this respect, larger clods or aggregates are much less at risk.

In this way, the impact of raindrops provides both the additional water and the mechanical stress. Both are required to enable local swelling through to dispersion. The resulting suspension seeps into the subsoil, whereby the solid particles are filtered out and form a more densely packed sedimentation layer, which inhibits further infiltration. This process is called **dispersion or soil surface sealing**.

During this **soil surface sealing**, the wetness in the still intact aggregates increases continuously and their stability decreases. When the soil surface is inclined, surface runoff and thus erosion take place (see Sect. 10.7.1). The same **dispersion** effect occurs when on a wet soil, another **mechanical load**, e.g. footsteps or traffic, produces the required movement of the particles. Here also, this results in homogenization and thus a reduction in the infiltration capacity. In contrast to the impact of raindrops, which only has an effect on exposed aggregates, the deeper effect of kneading does not form crusts. **Kneading** is caused by tillage under conditions where the forced deformation causes positive pore water pressures in the soil (shiny smear zones). In the absence of anthropogenic interference, homogenizing kneading is caused by wind-induced movement of roots of trees, animal migration, and by the tracks of animals at water sources.

Crusts formed on agricultural soils interfere with soil aeration, and if they harden due to desiccation, they inhibit the germination of crops as a mechanical obstacle. This is especially true if they form only few shrinkage cracks that are far apart, i.e. especially in fine sandy and silt-rich material and in Na clays.

For this reason, in arid regions using furrow and surface flooding irrigation, it is important to regularly break these crusts through tillage measures. In soil zones that were homogenized by kneading, as well as in crusts, the initial desiccation produces a wide-meshed network of cracks. This is why tillage then produces coarse clod structures.

6.3.3.3 Hydraulic Pressure, Solifluction

The stability of any soil structure depends on whether the water is supporting the respectively

existing state, or if it is causing change. As soon as the water pressure approaches the atmospheric pressure and causes the effect of the menisci on the effective tension to decrease, the effect of a hydraulic gradient gains in importance. This gradient not only has an effect on the water in the pores, but also on the solid particles surrounded by water. If they are weakly supported in the direction of the hydraulic gradient, they are finally removed and carried away due to the shear strain from the resulting flow of water. This phenomenon is called **pressure head** (Fig. 6.17), and it leads to fractures and sliding where water begins to emerge out of slopes because its pressure has reached or even exceeded that of the atmosphere. This can be observed on a large scale on cliff lines with unconsolidated rock (e.g. coast of the Baltic Sea in Germany), on road cuts, at the edges of drainage ditches, and with the disintegration of coarse clods (plough clods) following persistent precipitation.

Soil flow and **solifluction** on slopes (Sect. 7.2.7.1) are caused by the same hydromechanical processes as the pasty deflection of the soil during kneading. In all cases, the hydraulic gradient carries solid particles along, so that they are put into motion together with the water, if the friction caused by their weight on the base or on the contact points between the particles is reduced by the buoyancy process in water.

Finally, clay migration (Sect. 7.2.3) in a profile is also the result of a hydraulic pressure: the transportation and subsequent deposition of dispersed particles in the pores between the larger primary particles is significantly dependent on the strength of the hydraulic or matric potential gradients occurring during precipitation events.

6.3.3.4 Determination of the Structural Stability

The stability of a soil structure, i.e. the immobility of the soil particles in terms of their position relative to each other, depends on many forces and can also be modified in many ways. A change in any one of the forces shown in Fig. 6.17 has an effect on the entire system, and as a result, also affects the shear and normal components on each of the contact points between two particles. Due to this complexity, it can hardly be expected that the 'stability' phenomenon can be sufficiently observed in all of its aspects using one single method. For this reason, soil science has always used a multitude of empirical, i.e. indirect methods, each of which measures specific aspects from the overall complex using relative numbers (e.g. percent). However, their results are generally not comparable, because they attack the system at different points.

Instead, basic research methods in soil mechanics use clearly defined, i.e. direct measurement methods (e.g. shear tests or similar, dimensions: pressure, stress), which can also be used to quantify the soil's inherent stability. References to corresponding specialized literature are provided. Visual descriptions of the crust can be used for the assessment of the **dispersion stability** of aggregate complexes. In the lab, the '**wetstability**' is determined for comparative assessments. Sieving methods (wet sieving under water), irrigation methods (drop impact), percolation methods (dispersion through flowing water) and the stability measurement (kJ) with ultrasonic tests are used for this purpose. For microaggregates in the fine sand and silt range, changes in aggregation are determined using **turbidimetry**.

Without taking account of the packing state the correlation between the loss in stability of the substrate (**plastic deformability**) and the water content is often determined using the **consistency limits** according to Atterberg (Table 6.6). The plastic and liquid limits are the water contents at which, under standardized conditions and using fully homogenized material, the soil can be kneaded without breakage or viscous flow occurs.

The water content between the two limits: the **plasticity index** provides a basis for comparison of the sensitivity of different soils with regard to changes in stability caused by additions of water. Here, the change in the thickness of the electrical double layer of the clay particles is decisive. For this reason, the plasticity index increases with increasing clay fraction and decreasing valence of the adsorbed cations.

These indirect methods are all basically only indicators for the physical parameters 'internal

friction' and 'cohesion', which, depending on the respective normal stress, result in the shear resistance. These parameters change as a result of the complexity of the system, so that a simple characterization using standardized shear tests do not allow any universal conclusions. It will always be necessary to vary the conditions for the determination of the shear parameters according to the specific investigation.

6.3.4 Biological, Climatic and Anthropogenic Effects on Soil Structure

The correlation between the load and the compaction state characterized by the stress-strain curve (Fig. 6.18a) suggests that a typical depth-dependent course of the pore space fraction can be assumed for a soil profile. This correlation can be given by the change in the bulk density (ρ_B), the pore volume (PV) or the void ratio (ε) as a function of depth (z).

$$f(z) = \rho_B, PV, \varepsilon \qquad (6.17)$$

Because changes in volume in the soil only have an effect in the vertical plane, they are associated with changes in the height of the soil surface. For this reason, any compaction is simultaneously associated with a subsidence or a lowering of the soil surface, and every loosening with a rise in the soil surface.

However, this is not clearly shown if the assessment is based only on the pore volume or the soil density. In contrast, when the height of the upper edge of the soil above a reference level is observed, it can be clearly seen that the solid fraction remains constant, but the void ratio changes. This correlation is shown in Fig. 6.24 using the example of cultivation throughout the season. The tillage sole (bottom edge of the furrow turned by the plough) is the reference level. Because the solid fraction in the Figure forms an unchanging bar, it is often used as a reference basis instead of a level. The change in the pore space is then represented by the void ratio (ε) (Sect. 6.1.6.2).

6.3.4.1 Structure of a Soil Profile as a State of Equilibrium

As a result of the stress situation described in Sect. 6.3.2, the overall volume of a soil represents an **equilibrium** between the forces of subsidence (or compaction) and loosening (or heaving). Because these forces act on different areas in the profile, their effects and thus also the equilibrium situation differ. For this reason, the change in volume in the overall observed soil volume (Fig. 6.24) only provides a lump information.

The packing curve (Fig. 6.25) provides detailed information on the state of compaction of a cultivated site. With a representation on a log-normal coordinate system, the deviation of

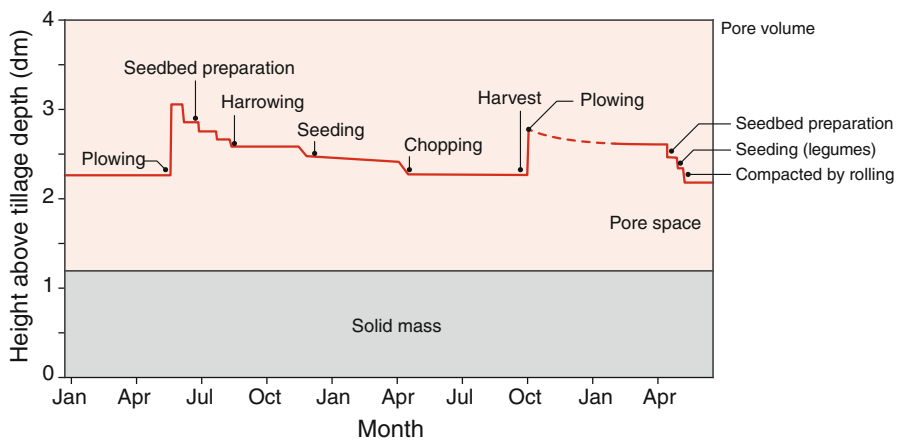

Fig. 6.24 Change in the level of the soil surface and the pore volume due to crop cultivation methods (after Andersson and Hakanson, simplified)

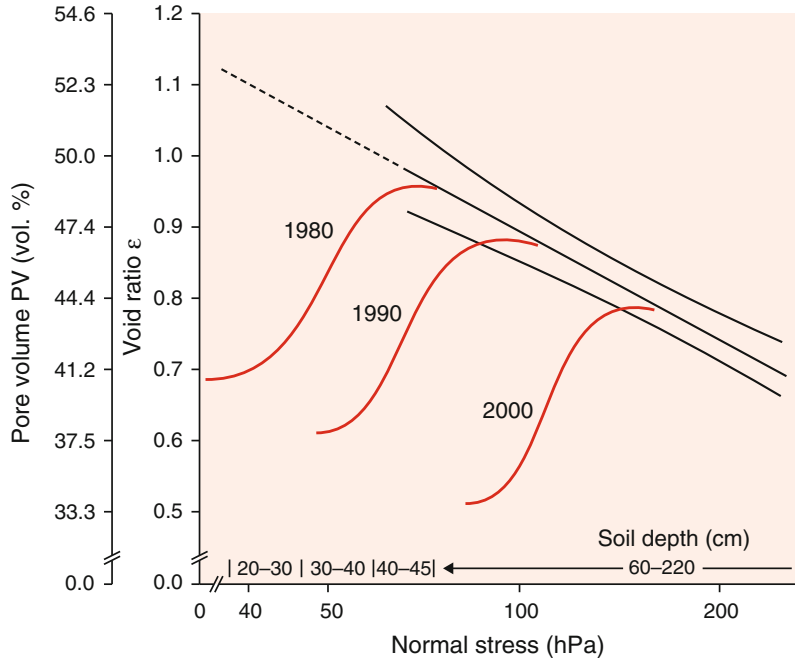

Fig. 6.25 Packing curves for loess soils and their changes with time (1980–2000). All of the curves are characterized by an over-compacted topsoil zone and a virgin compaction branch with increasing soil depth over time (after Ehlers et al. 2002, modified)

the packing curve from the straight line shows the depth in the soil reached by the previous deepest compacting effect. It maintains the same sequence of the concurrence of the most unfavorable circumstances to date. In Fig. 6.25, this is shown using the example of increasing overcompaction with time in Luvisols consisting of loess in Lower Saxony (Göttingen region).

Until 1980, only the topmost 30–40 cm were overcompacted, but by the year 2000, already a depth of more than 50 cm is classified as being irreversibly overcompacted due to land use, despite soil tillage. However, the course of the packing curve does not show the respective horizon-specific inherent stability. This would require the determination of the depth distribution of the precompression stress for given drying intensities, in order to quantify the mechanical loads that can be tolerated by this packing state without additional change in the pore space.

6.3.4.2 Natural Soil Development

Natural soil development is characterized both by mechanical influences (shrinkage and swelling, pedoturbation, see Sect. 6.3.2.2) and by the formation or alluviation of substances, which help to maintain a structural state that was achieved mechanically or make it insupportable again due to their eluviation. In general, changes in structure during the course of soil development are a result of the following processes:

1. **Increase in the coarse pore fraction** or aggregation, displacement of the aggregates relative to each other, and rounding. The resulting pores are called secondary pores, in contrast to the particle size-related primary pores. In contrast to the latter, they can be destroyed by soil compression (Fig. 6.26).
2. **Increase in the finepore fraction** through the formation of finely distributed substances (weathering formations such as clays, oxides, organic decomposition products). These formations can be produced in situ, or transported in from neighboring horizons. If, in the latter case, the bulk density increases, it is referred to as **intercalation compaction**. Compared to **soil settling**, the stronger increase in volume of the fine pores with increasing bulk density (see Fig. 6.26, at the right) is characteristic.

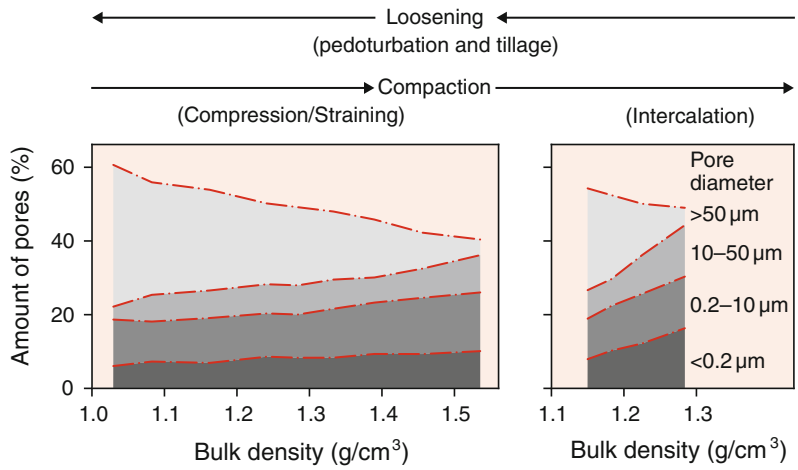

Fig. 6.26 Volume fractions of the coarse, medium-sized and fine pores as a function of bulk density for the 2 kinds of soil compaction

Intercalation compaction occurs mainly e.g. in Bt horizons of Luvisols (deposition of clay), in Bh and Bs horizons of Podzols (deposition of organic acids or Fe and Al oxides), in Cc horizons of Chernozems and Rendzic Leptosols ($CaCO_3$ deposition/calcrete), as well as in Bl horizons of Gleysols (deposition of Fe oxides through diffusive transport). Duripans or silcretes in "Durisols" are also a result of intercalation compaction (cf. Sects. 6.3.3.1b, 7.2.4.4).

3. The **mesopore range**, which mainly consists of primary pores, changes the least. Based on the volume fraction, it is generally reduced by mechanical loosening, and increased by subsidence or deposition. This leads to the formation of characteristic depth distributions, which are described using the example of a sandy soil and a clayey soil. The change in structure in soils consisting of loess and loam lies between these extremes (Fig. 6.27).

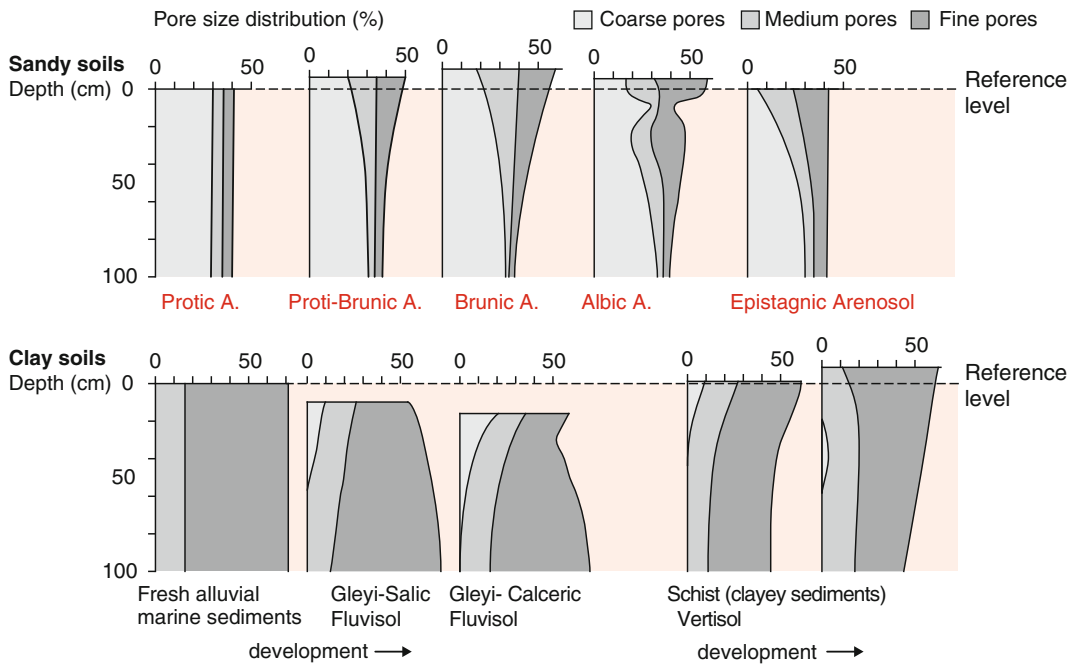

Fig. 6.27 Change in the pore volume, pore size distribution and location of the profile upper edge during the course of soil development in a sandy soil (*top*) and clayey soil (*bottom*) derived from marine sediments and from schist

(a) **Sandy soils**

In sandy soils with limited soil development (Regosols), the pore volumes in the surface soil, mainly consisting of coarse pores, hardly differ from those in the subsoil. During further soil development, organic substances and weathering products accumulate in the topsoil. Along with the associated bioturbation, this results in loosening along with an increase in the pore volume and lifting of the soil surface, which causes the soil matrix to break. The developed fragments are generally rounded and without sharp edges (subangular blocky, crumbs).

A portion of the coarse pores is often simultaneously filled with accumulated materials, leading to an increase in the medium and fine pore fractions. If the stability of such a loosened packing is reduced by leaching of the stabilizing substances, as is the case e.g. during podzolization, the soil subsides and is compacted again (cf. also Fig. 6.27). Just like with loosening, this subsidence begins near the surface. For this reason, although the hardpan horizons in Podzol are sometimes hard, they are often less dense and less percolation-inhibiting than the subsided bleached horizons above it. If a sandy soil that was strongly loosened during the course of soil development is compacted, the pores can be filled with the accumulated org. matter to such an extent that stagnant water after precipitation (e.g. sports fields, roadways) can be detected.

(b) **Clayey soils**

In clayey soils, there are two possible initial situations for soil development: (a) the freshly deposited sediment, where soil development begins with the first drainage and (b) sediments that were compressed and thus dewatered during the course of geological processes, where the input of rainwater plays an important role in their development.

In the former case, the soil initially has a coherent structure (Fig. 6.27) that gradually changes into an aggregate structure through drainage and shrinkage from the top downwards. In doing so, the aggregate size decreases with progressive shrinkage and fissuring, so that the sequence blocky—prismatic—coherent structure is established in the soil profile from top to bottom. The pore volume of the soil shrinks during this structure formation. Under the influence of plant growth and biological activity, a crumbly structure can finally develop in the surface soil.

However, this development process can also be reversed if, in the presence of abundant water, the newly formed secondary pores are destroyed by mechanical compression, soil tillage, livestock traffic or the impact of raindrops. Such strains promote the reswelling of the previously shrunken material. The pore volume in the soil therefore increases again. This means that there is no increase in bulk density here, but rather a coherent structure without secondary pores is formed that has a low bulk density and therefore a large pore volume.

In the case of pre-compressed, geologically older clays, changes in the pore system are characterized by water uptake and the associated swelling. Just like with young sediments, the pore volume increases. The secondary pores that were produced by pressure release and biological activity are closed. Near the soil surface, renewed shrinkage can lead to the new formation of aggregates. For this reason, the hydraulic conductivity of clayey soils varies over a large spectrum (see Table 6.7).

Table 6.7 Water vapor pressure p/p_o depending on the pore diameter (after L. PALLMANN) and pF value

Pore ø (μm)	0.0024	0.0096	0.024	0.125	0.22	0.56	5.6	12.5
p/p_o	0.4	0.8	0.9	0.98	0.987	0.995	0.9995	0.9998
pF	6.10	5.49	5.12	4.45	4.20	3.8	2.8	2.45

(c) **Bio- and cryoturbation**
The rummaging and digging activities of soil animals as well as the displacement of soil particles by root growth, particularly with trees, play an important role in the soil's structural development. Mixing caused by windthrow also contributes to structural change (**arboturbation**). Bioturbation and the resulting loosening and upheaval of the topsoil are usually more pronounced in forest soils than in grassland. The pore volume in forest soils is therefore greatest close to the soil surface. Bioturbation decreases with increasing aridity. It is hardly observed in semi-desert soils.

Influence of soil animals. Segmented worms (Annelida; see Sect. 4.1) are of special significance for the soil structure, especially earthworms. The fecal aggregates produced by earthworms demonstrate high stability towards precipitation and mechanical stress caused by soil tillage, which, in clay-rich soils, often exceeds the stability of artificial aggregates over a period of several years. However, the stability of fresh earthworm cast aggregates is not as high as that of older aggregates from indefinite biogenic origins, because a swelling capacity-reducing hydrophobicity is probably only achieved through the intermediate desiccation. Tensile strength measurements on fecal aggregates produced values that were twice as high as those on aggregates of the same size in neighboring soils at a comparable matric potential. The fecal aggregates produced by *Aporrectodea rosea* had a measured state of compaction corresponding to ca. 250 Pa. The strength must therefore be attributed to the high proportion of organic components in the feces, in addition to the fact that the high intestinal pressure and calcite secretions also have a stabilizing effect.

Worm species that build more or less vertical burrows like e.g. *Lumbricus terrestris* promote water infiltration by increasing the water-absorbing surface, provided that they are not dwelling in the burrows. This type of water infiltration is particularly favorable because there is no silting due to the impact of raindrops. Those species that search for food in the soil body (endogeic species) only mix the soil in the surface layers. They build numerous tunnels, but they are partly filled again with soil.

The individual earthworm genera can exhibit considerable differences in their soil stabilizing properties through axial and radial compression of the surrounding soil. Pressures of ca. 100 kPa were measured during the construction of tunnels through lateral pressing of the soil, whereby as an endogeic species, *Aporrectodea caliginosa* can develop maximum values of 295 kPa.

Despite their small size and their short life span, Enchytraeidae make a significant contribution to the porosity and aggregate stability in the topsoil. With a total abundance of several thousand individuals per square meter, they not only have an influence on the gas production, but also produce countless, usually spherical and very stable microaggregates in the size range from 100–500 μm. In doing so, they mainly process the excretions from endogeic earthworms. The produced microaggregates are found mainly in surface soils and decrease rapidly with increasing soil depth. In terms of their shape and size, these aggregates are classified as a pseudo-sand. However, because they are usually found in fine-grained substrates, they unite the soil chemical and biological advantages of fine-grained soils with the soil physical properties of sands. If these aggregates, which are important for the water and air regime, are destroyed by heavy harvesters, it often takes several decades for this natural structure to be reestablished.

Influence of plants. The various influences plants have on the soil structure are mainly based on the different types of root development and the density of the vegetation cover. It mainly affects the topsoil, because this is where there is the most rooting.

The stable crumbly structure under **grassland** without grazing is attributed to the high rooting intensity in the topsoil (usually 0–7 cm), the permanent vegetation cover (protection against the impact of raindrops), the continuous high production of root residues (intense microbial activity), and to the absence of soil tillage. Due to the more intense and more frequent shrinkage

and re-wetting associated with the dense rooting, the frequency and intensity of fissuring is increased so that smaller aggregates are produced. The roots mainly grow along the formed cracks or into areas with lower density.

On **intensively managed pastures**, the crumbly structure is easily transformed into a coherent structure with a low shear resistance during wet weather periods due to the influence of trampling by livestock.

Under arable field conditions, the soil stability depends particularly on the cropping intensity and the crop rotation.

Under **cereals**, a stable crumbly structure is less probable than under grassland due to the annual ploughing, even if the overall soil contains slightly more organic root residues due to the deeper rooting, and the desiccation intensity and frequency also increase slightly up to these depths.

The conditions under the cultivation of **root crops** and many **specialized crops** (hops, vegetables, maize, etc.) are even more unfavorable. The row spacing is wide and it takes a long time until the plant cover has closed over the rows and the soil is protected against the silting effect of raindrops. There are little root residues and they are often less uniformly distributed through the soil.

Influence of freezing. The term cryoturbation is used for soil movement processes that take place at temperatures below the freezing point of water. These include: (1) Contraction of the soil matrix through drops in temperature (negative expansion), (2) ice blasting as a result of an increase in volume when the soil water freezes, (3) growth of ice crystals (formation of ice lenses), in addition to fissuring and drainage, and (4) solifluidal movement of mudflows over ice and frozen, water-saturated subsoil.

The **increase in volume** by ca. 9 % during the transition from liquid water to ice seldom has an effect in soils, because pressure only arises on the surrounding soil particles when it is not possible for ice and water to move into air-filled pores, i.e. it only also occurs in water-saturated soils. However, the pressures that then arise are very high, 13 MPa at—1 °C, and ~ 200 MPa at—20 °C.

For this reason, the **crystallization pressure** occurring during ice crystal growth generally plays the decisive role in the effects of frost, because it can also have an effect in soils that are only partly saturated with water. It occurs when the regular development of the ice crystals is impeded. The crystallization pressure of ice under these conditions is relatively low. It is of about 0.13 MPa at—5 °C. Still, this is enough to lift a soil layer with a thickness of several meters. The extent of soil upheaval essentially depends on the size of the ice lenses, and increases with decreasing temperature. Such heaving can also lead to the lifting of stones to the surface and the tearing of roots in winter cereals.

Frost heaving does not occur in coarse-grained soils, because they only have a low hydraulic conductivity under unsaturated conditions and the water supply from the vapor phase takes place too slowly. In fine-grained soils, in contrast, needle-shaped ice crystals can form near the soil surface (needle ice), and massive ice lenses can form at greater depths. These are formed in rough layers parallel to the soil surface, i.e. perpendicular to the direction of heat loss. For this reason, they cause soil heaving as well strong desiccation in the surrounding soil horizons. Larger ice lenses do not form if cooling progresses so rapidly that the water freezes before it can be displaced to a greater extent. This can take place e.g. on surfaces without snow cover due to strong heat radiation.

An important effect of freezing on structural development is that the largest existing ice crystals also grow the fastest. Especially in fine-grained soils, the associated dewatering of the areas surrounding the ice crystals causes a temporary stabilization of the aggregates through shrinkage. This process, similar in principle to aggregate formation through desiccation, leads to the development of a **friable tilth**, and in clay-rich soils, it is often the only mechanism leading to the development of a fine-aggregated seedbed under arable land use. However, the frost tilth is only preserved after thawing if the ice crystals sublimate, or if their melt water can rapidly percolate between the produced aggregates. If neither is possible, the accumulation of

water in the frozen soil horizons results in waterlogging, and can therefore easily lead to the destruction of aggregates that are weak in this state. This can easily cause frost fractures on roads (pronounced e.g. in soils consisting of loess) and solifluction events on slopes (softening of the topmost soil layer as a result of the water surplus).

Finally, coarser particles are also sorted out both during bioturbation and during cryo- and peloturbations. Bioturbation leads to the burying of gravel and stones, so that *gravel layers* are often formed in deeper horizons, which was already discovered by Charles Darwin in 1837. With cryo- and peloturbation, in contrast, the coarser particles migrate upwards and sometimes form stone rings at the surface (see also Sect. 7.2.6.1).

6.3.4.3 Anthropogenic Effects

Human interference in the natural soil structure includes the temporary stresses caused by trampling and traffic. The effect of this process on structure depends on the one hand on its stability (shear parameter), and on the other, on the extent of the previous loosening through pedoturbation.

Until a few decades ago, compression of the soil occurring during agricultural practices could be rectified by ploughing before seeding each crop. Today, however, the load from the machines has an effect down to depths that are no longer reached through normal tillage by ploughing or harrowing. Depths of 50 cm and more are no longer unusual. For this reason, all cultivated soils are **over-compacted** (pre-compacted) compared to virgin compaction. This precompression is quantified by comparing the horizon-specific precompression stress (see Fig. 6.17b) with the depth-dependent increase in the pressures from the soil mass ($P_v / (\rho_B \cdot z \cdot g)$.

The period of time required for such over-compaction to be loosened again depends on the intensity of the pedoturbation. It can take many decades under arid condition, while under humid climate conditions, natural reloosening of the soil below the plough sole is negligibly low, due to the decreasing desiccation with increasing depth, and reduced bio- and cryoturbation, among other factors (see also Fig. 6.26).

Initially, the **cultivation of previously fallow soils** with natural vegetation almost always leads to compaction of the surface-near zone, because both deforestation and also the ploughing-up of grassland is associated with additional loads through traffic and treading. The extent of the developing compaction depends on the extent of the previous existing loosening. It is greater in soils with high bioturbation (under forest) than in those with low bioturbation (dry steppe). Traffic and trampling cause these soils to change from a state similar to virgin compaction to an over-compacted state. In doing so, mainly coarse secondary pores are destroyed, because the mineral particles on their sides have less support, and they are more mobile under loads than particles in a closed structure (Fig. 6.24).

In fine-grained soils, wetness can lead to smearing (kneading), which also destroys the secondary pores. However, in contrast to the previous case, here there is homogenization with a largely identical bulk density, but no additional compaction.

Tillage during the course of routine crop cultivation (arable farming) consists of a regular alternation of compacting and loosening processes in the topsoil (Fig. 6.23), as well as breaking up crusts caused by the impact of raindrops and silting. The loosening measures (ploughing) are sometimes necessary because harrowing requires loose material, and sometimes because cropping and harvest practices create a state that impedes seeding and germination.

The strong formation of crusts as a result of the impact of raindrops on a prepared seedbed can be reduced when the soil surface is covered. Crop residues, additional spread plant substances, or films and even extraneous material such as sand layers can be used for this purpose. These measures are called mulching.

Grazing on grassland leads to **overcompaction** just like traffic with machinery, especially in the topsoil. Because these loads always only occur on small areas, the soil can deflect to the sides. As a result, the topsoil is often more strongly compacted than the zones below.

Land improvement involves measures aiming to improve the site for a specific use on the

long term. In the scope of physical measures, these include: infiltration ditches, ripping (≥1 m), subsoiling, and drainage especially in excessively wet and compacted sites. Soils that are trenched or ripped to depths of more than 4 or 5 dm are called Anthrosol. Today, land improvement measures are performed more than in the past, because the required machinery power and technology exists. However, the success of such measures depends on the extent to which the principles governing the correlation between the state of loosening as a function of the load, soil depth, water content as well as the consequences of additional loads, such as compression, water pressure increase, homogenization are known and observed.

Recultivation in the form of packed beds represents a special problem. Here also, the success of an intended utilization depends on the observation of the load and stability situation. The prepared site must provide a pore system that distributes the climate-related incoming water quantities rapidly enough into the soil volume that a reduction in stability caused by wetness does not lead to undesirable sagging. Furthermore, the water supply that must be stored in the rooted zone must be determined in order to avoid damage to plants during dry periods.

6.3.5 Assessment of the Soil Structure for Agricultural Purposes

The significance of the soil structure for crop production both in the rooting zone and in the subsoil has been known for a long time, and was already emphasized in the book 'Die Bodenkunde' (soil science) by C. Sprengel published in 1837.

In the rooting zone, structure affects the pore size distribution as well as the unsaturated hydraulic conductivity, and thus the water supply for the plants. A pore size distribution with the highest possible fraction of plant-available water (PAW) is all the more important for the plant's constant water requirements the less a uniform water supply is provided by regular precipitation or a high groundwater table.

The accessibility of water in the entire pore space depends on the extent to which the plant roots find pores filled with oxygen when they penetrate into the soil. For this reason, the assessment of a soil as a plant site depends on the mesopore fraction, and because of the aeration, also on the fraction and continuity of the coarse pores. The quantity of fine pores, which can account for a large fraction of the pore space in clayey soils, is generally of lesser importance for the water supply, because the water they contain is not available for plant roots. However, plants do not all have the same acquirement capacity for water, halophytes and xerophytes being important extremes. In young clayey soils with incomplete shrinkage (proportional shrinkage or virgin compaction branch in Figs. 6.18 and 6.11), the fraction of non plant-available water is difficult to define.

In terms of the structure, the significance of the subsoil, as opposed to the more strongly rooted topsoil, lies in the fact that the overall storage capacity results from the volume-specific, i.e. the texture and structure-related components, and from the depth available for the roots (see Sect. 6.4). Thin soils on water-impermeable subsoil (e.g. 30 cm loess or glacial loam over clay or hard rock) are therefore just as unfavorable sites as on a subsoil where the pore size distribution cannot provide an appreciable contribution to the water supply (e.g. 30 cm loess or glacial loam over gravel, coarse sand or coarse-grained rock fragments or building rubble).

While in the first-mentioned case, except for the low storage capacity in the humid central European climate, ponding also has an unfavorable effect, in the second case, primarily the low storage capacity is detrimental, where dry periods of just a few days already cause drought damage.

In view of this, it is obvious that there is no existing ideal soil structure for all forms of crop production. Every crop and existing water supply during the cultivation period each require a different ideal soil structure.

More generally, it can be said that a high fraction of coarse pores is all the more important for the crops to thrive the more frequently high water contents are expected. This is equally true

for soils under the influence of groundwater or stagnant water, for climatic zones with abundant precipitation, and for irrigation in arid regions or in intensively managed horticulture. A lack of coarse pores always goes hand in hand with a lack of air and non-availability of the water supply.

Under more arid conditions, if the coarse pores and a portion of the mesopores are always filled with air, aeration is more seldom the limiting factor. Here, the magnitude of the storage of plant-available water plays a decisive role. Soils with a high mesopore fraction are particularly well suited.

Crop cultivation methods can influence the soil structure to a limited extent. In humid climates and in humid topographical locations, normal tillage routines aim to maintain a coarse-pored and thus loose state. Because of the looseness, the greatest concerns are compaction and the associated lack of air. Soil surface sealing is also a problem for the same reason. Here, the preservation of the artificially produced aggregation of a seedbed is decisive.

Inversely, in arid climates and arid topographical locations, the preservation of a higher soil density is advantageous. Here, loosening not only reduces the water quantity stored per unit of volume, but also especially the subsequent supply to the roots (see Sect. 6.4.3.2). This is particularly true for large-scale crop production in arid regions, because the requirements for seeding and water supply are detrimental to the seedlings. However, it must also be considered that unproductive evaporation is considerably reduced by a loose structure due to the capillary interruption especially in the transition zone to the atmosphere, and thus more water is available to the plants.

Because of the uncertainty associated with weather conditions, and thus with the natural water supply during the crop season, cultivation methods used to obtain the desired soil structure must be oriented on the most probable water balance situation. The more reliable the water supply and drainage on a cultivated field, the more precisely the soil structure can be adjusted for the crop requirements. In this respect, greenhouses are an exceptional situation, where the soil can be adjusted for the conditions of the intended water supply through the selection of the substrate (mineral wool, expanded clay, gravel bed consisting of quartz or pumice).

In nature, a structure where both requirements are largely fulfilled, i.e. enough coarse pores for sufficient aeration in periods of excess water and enough mesopores to store and maintain a large water supply, is most commonly found in loess soils, if they contain enough stable secondary pores. This is especially the case in Chernozems consisting of loess, and is one of the important reasons for the high soil values in these soils (90 to more than 100 in the German state soils evaluation). For this reason, on a global basis, loess soils often count among the most fertile soils in any landscape.

6.4 Soil Water

Under natural conditions, soils always contain water. In an 'air dry' state, i.e. at equilibrium with low air humidity, this water quantity can be very small. Soil water is removed by drying at 105 °C for 16 h: by convention, this state means oven-dried. The **water content** (% mass or % vol) is defined as the percent fraction of water in the soil that can be removed up to this temperature. Water fractions that are only removed by higher temperatures are not included in the soil water. They belong to the constitutional or crystalline water of the solid soil particles. In mineralogy, the characterization of clay minerals using differential thermal analysis (DTA) is even based on the lowering of the temperature in characteristic temperature ranges, resulting from the vaporization of this crystalline water.

Soil water is replenished by precipitation, the groundwater, and to a small extent through condensation from the atmosphere. It always contains dissolved salts and gases in changing proportions and compositions.

If more water is supplied through precipitation than can be absorbed and transported by the soil, the surplus is discharged as **surface runoff**. This fraction is greater the more intense the precipitation, the greater the slope of the soil surface,

and the slower the precipitation can be absorbed by the soil. Therefore, it is generally higher in clay- and silt-rich soils than in sandy soils, and in compacted soils than in loose soils. This fraction is particularly high if the soil is already largely saturated with water. Surface water is one of the important causes for erosion (see Sect. 10.7.1). When water fills the entire pore space, this state is called **water saturation**.

6.4.1 Introduction—Binding Forms

Compared to water in an open watercourse, only part of the water in soil pores is able to move freely. The rest is bound by properties of the solid phase, the soil matrix. Because the type of binding influences the behavior of certain water fractions, it is often used to classify soil water.

A portion of the water added to the soil through precipitation is held in the pores against the effect of gravity (see field capacity, Sect. 6.4.5.1a), and another portion is transported to deeper layers as **seepage water**. In doing so, the water already existing in the soil is displaced by the seepage water, and therefore also becomes seepage water. The water remaining in the soil is called **adhesive water** or soil moisture.

6.4.1.1 Groundwater and Stagnant Water

Groundwater or stagnant water are defined as the fractions of the soil water that are not bound in the soil matrix and therefore flow freely into ditches or boreholes. For this reason, these water fractions are also called **free water**.

Bodies of groundwater and stagnant water are formed over layers with low hydraulic conductivity, e.g. clays. **Groundwater** is defined as water that exists throughout the year; and **stagnant water as water that** is only present for part of the year, often in the spring, or after strong precipitation over e.g. compacted layers.

Groundwater and stagnant water are delimited at the top by the **groundwater surface** (GWS) and the stagnant water surface. It is defined as the surface in the soil where the hydraulic pressure is equal to the average atmospheric pressure. This illustrates that not the same water content in the soil, but rather the tension state (0 hPa) must be used to define the GWS.

If the groundwater is in hydraulic equilibrium, the groundwater surface is indicated by the **groundwater level** that is established in a water level tube (=phreatic surface, from the Greek *phrear*: well). However, if there is continuous water replenishment from the top of the profile, the groundwater level is lower than the groundwater surface. In contrast, if the pressure below the groundwater surface is higher than at equilibrium, the groundwater level is higher than the groundwater surface (=artesian pressure, artesian water). The groundwater surface is only rarely horizontal, which demonstrates that the water is usually in motion, even if only very slowly.

6.4.1.2 Adhesive Water and Capillary Water

The binding of water remaining in the soil against gravity is based on the effects of different forces between the solid soil particles and the water molecules as well as between the water molecules themselves. According to the type of forces involved, the soil water can be divided into adhesive and capillary water.

(a) **Adhesive water**
This term comprises water held by the effects of adhesive (in a more specific sense) and osmotic forces. It surrounds the solid surface of the particles without forming a meniscus. Adhesive or adsorption forces between the solid matter and the water molecules include (a) Van der Waals forces, which only act over small distances, and the H bonding between the oxygen atoms of the solid surface and the water molecules, as well as (b) the forces arising under the effects of the electrostatic field, especially of the counterions, and to a lesser extent, also of the charged solid surfaces, which act over greater distances. The water dipoles are aligned and attracted into this field. The adsorbed water molecules are attached to each other through H-bonds.
Figure 6.28 shows how the quantity of

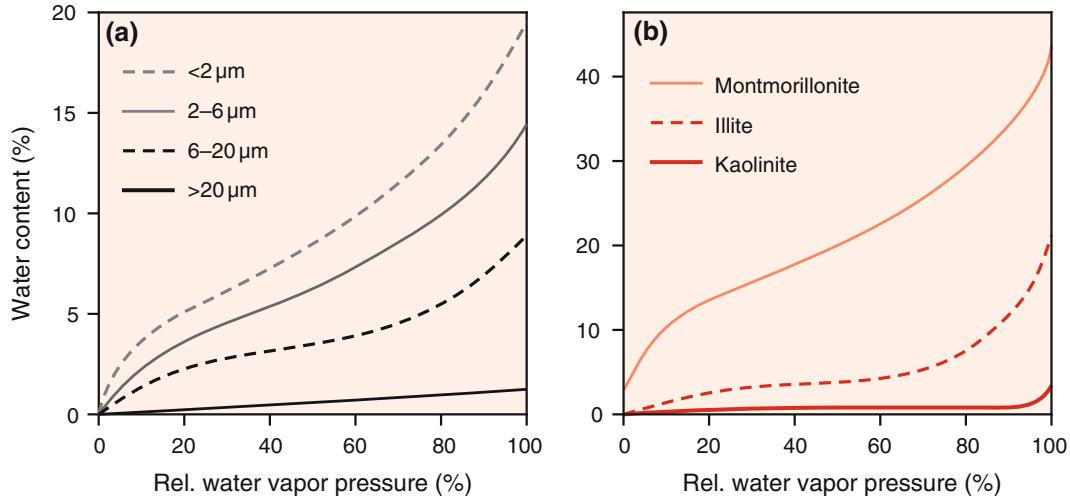

Fig. 6.28 Water content of **a** particle size fractions of a soil (Kuron 1930) and **b** clay minerals (Orchistron 1953) as a function of the relative vapor pressure in the air

adhesive water in soils increases with increasing relative water vapor pressure in the air. Furthermore, the figure shows that 'air-dry' soils also always still contain water, in fact, the more water the higher the relative water vapor pressure in the ambient air. When soils contain less water than the amount corresponding to this equilibrium, they absorb water from the air. Therefore, they are hygroscopic in this range, and the absorbed adhesive water is called **hygroscopic water**.

The water content also increases with decreasing grain size and therefore with increasing specific surface area of the solid particles. The sequence of water contents for several clay minerals at the same water vapor pressure is also attributed to their different specific surface areas (see Sect. 2.2.4 and Fig. 6.28).

The innermost molecular layers of adhesive water are very firmly bound to the mineral surface. For example, there is a binding force of ca. 600 MPa for the first unimolecular layer. The binding force decreases rapidly moving out towards the outer layers. The thickness of this layer is about 1 nm. The high binding energy is demonstrated by the fact that the temperature of oven-dried fine-grained soil samples increases when they are wetted. This is due to the kinetic energy of water molecules that is released during adsorption. Such rises in temperature are also measured in dry clayey soils ahead of the wetting front.

Adsorbed water has different properties than free water, which are attributed to the mobility of the water molecules and their arrangement. For example, a reduction in the soil water content leads to a rise in density (up to 1.5-fold) and viscosity, while the heat capacity and freezing point decrease. Adhesive water is sometimes also called 'osmotic water' because the adsorption process is similar to the return diffusion inhibition, which forces the accumulation of water in the area of higher salt concentration during osmosis.

(b) **Capillary water**

If an oven-dried soil is allowed to equilibrate with water vapor, not only is adhesive water attached, but also strongly curved **menisci** are formed already with the adsorption of several water layers at the contact points of the solid particles. They surround the contact point as a ring and are enlarged with increasing water attachment This formation of capillary water is caused by the tendency

of the boundary surface between water and air to minimize itself, because this achieves a lower energy state because of the high surface tension of water towards air (=capillary condensation, see Sect. 6.2.3). The formation of menisci is based on the interaction of adhesive forces between the solid surface and also on cohesion forces between the water molecules with the formation of hydrogen bonds.

Compared to free water, water that is bound in this way has a higher surface tension and therefore lower vapor pressure, like the water in circular capillaries. This is why it is also called **capillary water**, even though the voids in soils are only seldom circular in shape (Sect. 6.1.6). The smaller the diameter of these capillary voids (see also Table 6.7), the stronger the binding of water, and the more energy must be expended to liberate these water fractions, and therefore the lower the water vapor pressure. At every water content, equilibrium is established between the thickness of the adhesive water film and the curvature of the menisci that are subject to the same relative water vapor pressures.

Most of the soil water is subject to both adsorption and capillary forces. The higher the water content in the soil, the more the capillary binding outweighs the adsorptive binding, and vice versa.

The same mechanism that leads to capillary condensation also causes the rising of menisci in capillaries. Here also, this is caused by the tendency of water to minimize its surface against water. Because this effect is strongest when pores with a relatively large surface area and a small volume are filled with water, the water rises highest in the narrowest pores, and higher in pores with irregular shapes than in ideal circular pores.

6.4.1.3 Determination of the Water Content

The most important method for determining the water content involves weighing the soil sample before and after desiccation at 105 °C. The selection of this drying temperature is convention. Thus, all retention curves end at pF 7 (=105 °C). It is assumed that the loss of mass achieved at this temperature is produced by the expulsion of water that does not belong to the structures of readily degradable minerals or organic compounds (constitutional water). For special cases, lower temperatures are suggested (e.g. 65 °C for organic soils). This gravimetric water content determination requires sampling, and is therefore not without disturbance. For this reason, and because the determination must be performed in the laboratory, this working method is not suitable for continuous recording of changes in water contents of soils in the field. Indirect methods are often used for this purpose, where the installation of sensors in the soil enables continuous measurements.

These methods take advantage of the fact that the propagation of various impulses (e.g. electrical voltage, heat, neutron diffusion) in the soil essentially depends on the water content. These principles can be used to calibrate the transmission or subsiding of a signal against the water content. The gravimetric water content (g of water per g of soil) is used here, and if necessary, it is converted to a volume basis (cm^3 of water per cm^3 of soil) by multiplying with the bulk density ρ_B. Many of these methods are restricted to specific water content ranges, or their use is associated with high safety-related requirements. For this reason, time domain reflectometry (TDR method) became very popular in the last few decades, since it does not have many of these disadvantages under "normal soil conditions". If the iron content is too high, or the soils contain specific organic acids or minerals like allophane, a more detailed site specific calibration is needed. The TDR method is based on the reflection of an electrical pulse (voltage surge) from the end of a metal probe by the surrounding medium, where the pulse is delayed more strongly the higher the medium's dielectric constant (DEC). Water has a much higher DEC (≈80) than other soil components (<5). The advantage is the linear relationship between absolutely dry soil (DEC = 3) and pure water. Differences and changes in the volumetric water content can therefore be directly measured by changing the reflection speed/velocity of the electrical pulse in the sensor.

Like for precipitation, the volumetric water content at a given depth range in the soil can be expressed independently of the area as a water column or water head (WC/WH). At a water content of 0.26 $cm^3 \cdot cm^{-3}$, this is equal to 260 mm of water for a soil unit with a thickness of 1 m.

6.4.2 Water Binding Intensity

The described forces exerted by the solid phase in the soil, together with other external forces, cause the movement of water and affect its uptake by plants. Therefore, they are of great significance both in pedological and in ecological terms. However, because of the causes described in the section above, they have not yet been sufficiently characterized; in fact, data is lacking on their magnitude, direction and starting points. In a system as heterogeneous as soils, they vary and also alternate greatly, so that they are difficult to define and can therefore hardly be added up. For this reason, instead of the forces themselves, it is common practice in soil science to consider the work they can do, or even more commonly, the working capacity, the **potential**.

6.4.2.1 Potentials

In soil science, Buckingham (1907) was the first to apply the concept of **potential** in his research on the binding of water in the soil. Here, the potential is defined as the work required to transport a unit quantity (volume, mass or weight) of water from a given point in a force field to a reference point. This work corresponds to the work required to lift the unit quantity of water from a free water surface to a specific height in a pore (capillary) or to remove it from the soil matrix.

If the concept of potential is applied to soil water, all movement processes such as infiltration, drainage, and capillary rise (= water rise in the pores against gravity) can be reduced to a common denominator. Water always moves from areas of higher potential (= higher potential energy) to those with lower potential, because this process releases energy. This movement continues until all areas have reached the same total potential. The potential of soil water (ψ) is described by the following formula:

$$\psi = m \cdot g \cdot h \tag{6.18}$$

Here, m is the mass of water, g is the acceleration (always the acceleration of gravity in the field), and h is the height above a free water surface as a reference level (the groundwater surface in the field).

The potential can be related to the mass units of water, and the following is obtained:

$$\psi = g \cdot h \tag{6.19}$$

If volume is selected as the reference unit, ψ has the dimensions of a pressure (ρ = density):

$$\psi = \rho \cdot g \cdot h \tag{6.20}$$

However, the weight of water is most often selected (in the gravitational field = $m \cdot g$) as a reference unit, so that ψ has the dimensions of a length (cm water column, hPa):

$$\psi = h. \tag{6.21}$$

(a) **Total potential (ψ)**
By definition, the total potential is the sum of all specific potentials that are caused by the various forces acting in the soil. In terms of the definition given in the previous section, the reference point is a free water surface that is under atmospheric pressure, where the water has the same temperature and the same dissolved substances with the same concentration as the soil water.
In many cases, it is difficult to directly measure the total potential, because the available measuring devices only show changing groups of specific potentials. For this reason, it is important to recognize which components of the total potential are being recorded by the respective measurement, in order to assess how close the approximation is to the total potential. The following subdivisions are most commonly used:

$$\psi = \psi_z + \psi_m + \psi_g + \psi_o \tag{6.22}$$

The following sections will describe the specific potentials given here as well as other commonly used groupings.

(b) **Gravitational potential (ψ_z)**
Soil water is always under the influence of the Earth's gravitational field. Therefore, a gravitational potential can be defined. It corresponds to the work that must be performed to lift a specific quantity of water (expressed in units of mass, volume or weight) from a reference level to a given height. If weight is used as a reference unit, the gravitational potential is equal to the local altitude (z). Therefore, it is sometimes also referred to as a geodetic potential.
The reference level for the total potential is always selected such that the gravitational potential has a **positive** prefix. At the water surface, $\Psi_z = 0$ and exhibits more positive values with increasing upwards distance.

(c) **Matric potential (ψ_m)**
The matric potential defines the influence of the matrix. It comprises the effects caused by the matrix on water. The less water the soil contains, the stronger the matrix forces hold onto it, and the harder it is to extract it from the soil. In a state of energetic equilibrium, i.e. when the water in the soil is at rest and there is no movement, the greater the distance from the groundwater surface used as a reference level, the more strongly the water is bound to the matrix. Because the effects of this potential on water are opposite to those of the gravitational potential, it has a **negative** prefix. It is often also defined as a negative hydrostatic pressure (=negative pore water pressure, see Sect. 6.3.2.3).
As a result, the potential decreases with decreasing water content, and the value of the matric potential becomes more negative. Like for the total potential, different reference units can also be selected for the matric potential, the volume or weight of water being the most common.

(d) **Other components of total potential**
Because the water in the soil is never in a pure state, the total potential is always also affected by the **osmotic potential** (ψ_o). The fraction of this potential in the total potential depends on the amount of dissolved salts, and is therefore often of considerable significance in soils of arid regions, but also in salic tidalic Fluvisols at the coasts under humid conditions. Salt concentrations in saline soils (Solonchaks) can lead to water accumulation in the salt zone at the expense of the adjacent zones. This potential corresponds to the work that must be performed to extract one unit quantity of water out of the soil solution through a semi-permeable membrane.
A **gas potential** (ψ_g) must be considered if the air pressure in the soil does not correspond to the pressure at the selected reference level.
If the free water that is not subject to the matric potential is to be included in the potential concept, it is assigned with a **pressure potential** or **piezometric potential** (ψ_h or ψ_p). The subscripts h and p indicate that the energetic status is measured as a height **under the groundwater surface** or as free water pressure (e.g. with a piezometer).
Depending on the measuring conditions and on the conditions in the soil, several other component potentials can be recorded with the measurement, in addition to those described here.

(e) **Combination of the specific potentials**
Determination of the total potential over the entire range occurring in soils is only possible since a few years, and is also laborious. For this reason, the **hydraulic potential** (ψ_H) is often given as an approximation, which is defined as the sum of the most easily determined component potentials:

$$\psi_H = \psi_m(\text{or } \psi_h) + \psi_z \ldots (+\psi_g) \qquad (6.23)$$

Here, ψ_m is used for points above, and ψ_h for points below the GWS. ψ_g is usually not considered. To quantify the direction of flow and the pressure head, the hydraulic potential (ψ_H) is calculated using measured values for the matric potential at different depths over time.

Other combinations of specific potentials result e.g. from the properties of the measuring or recording instrument, or from the purpose of the investigation.

The availability of water for plants is given by the combination of the osmotic and the matric potential and is called **water potential** (ψ_w):

$$\psi_w = \psi_m + \psi_o(+\psi_g) \qquad (6.24)$$

Like with the hydraulic potential, ψ_g is generally not considered.

(f) **Determination of the potentials**

The total potential of the soil water can be determined through the relative water vapor pressure. Because the differences in vapor pressure compared to a free water surface at slightly negative matric potentials initially only amount to a few tenths of a percent, the measurement time-consuming. Psychometric methods are used for this purpose (cf. hygroscopicity, Sect. 6.4.5.1c).

It is easier to determine the matric potential using a **tensiometer** (Fig. 6.29).

These consist of a ceramic (porous) cell that is connected to a manometer either in the form of a simple hanging water column, or a much shorter mercury column or an electronic stress sensor. The cell and the free space around the sensor (manometer or water column) are filled with water. By convention, the reference point for the reading device is where the bottom half of the tensiometer is submersed under the water surface, and the top half is in the air. The drier the soil, the more the water in the tensiometer is subject to a vacuum, which can be read as a negative pressure. Tensiometers record the matric potential, and depending on the type of the manometer, sometimes also an existing pneumatic potential. The measurement is displayed in cm water column (WC) or in hPa, in which case the measuring range only reaches ca. −800 hPa.

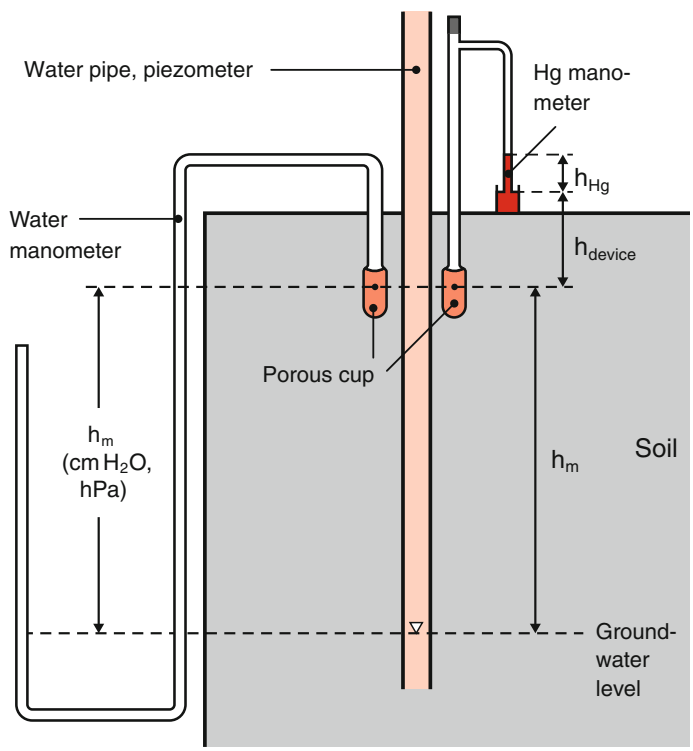

Fig. 6.29 Tensiometer (*left* water manometer, *right* Hg manometer) and water standpipe (piezometer). All values are in hydrostatic equilibrium ($\psi_H = 0$)

At equilibrium, the matric potential ψ_m expressed in cm WC or hPa, corresponds to the distance from the free water surface, or the distance from the GWS that can be seen in the piezometric tube. In the case of surface reading with an Hg column, the following applies:

$$h_m(\text{cm WS} = h\text{Pa}) = h_{Hg}[(\rho_{Hg}/\rho_w)-1]-h_{device} \quad (6.25)$$

Here, all heights (h) are measured in cm (see Fig. 6.29 for symbols).

Gypsum block electrodes are used for measurements in the range <−1000 hPa. They measure the water potential (ψ_w), however, a soil-specific calibration curve must be prepared. More recent tensiometers based on osmotic processes work in the same way, as well as ceramic cups filled with corresponding polymers, which can be used in extreme cases up to pF 4.

6.4.2.2 Potential Equilibrium

If a cylinder filled with dry soil, covered at the top with an evaporation cap, is placed in water, the water flows into the soil. After a while, equilibrium is established, characterized by a reduction in the water content towards the top (Fig. 6.30).

At equilibrium, the hydraulic potential ($\psi_H = \psi_m + \psi_z$) is equal at all points of the soil column. If the height of the water surface is selected as the reference point for ψ_H and is set here to be $\psi_H = 0$, the state $\psi_H = 0$ is also obtained throughout the entire soil column at equilibrium.

In order to reach equilibrium at all points in the soil column, the matric potential (ψ_m) and gravitational potential (ψ_z) must be equal in magnitude.

This is shown in Fig. 6.30 by the two oblique straight lines, the slope of which depends on the selection of the coordinate scale. At a state of equilibrium, the course of the potential lines (ψ_m and ψ_z) is linear. At the same time, a water content distribution is established (Fig. 6.30, to the right), the course of which is soil-typical and is generally not linear, depending on the distance from the GWS.

If the equilibrium is disturbed, e.g. through evaporation of water at the surface, the matric potential decreases here and reaches more negative values. However, because the gravitational

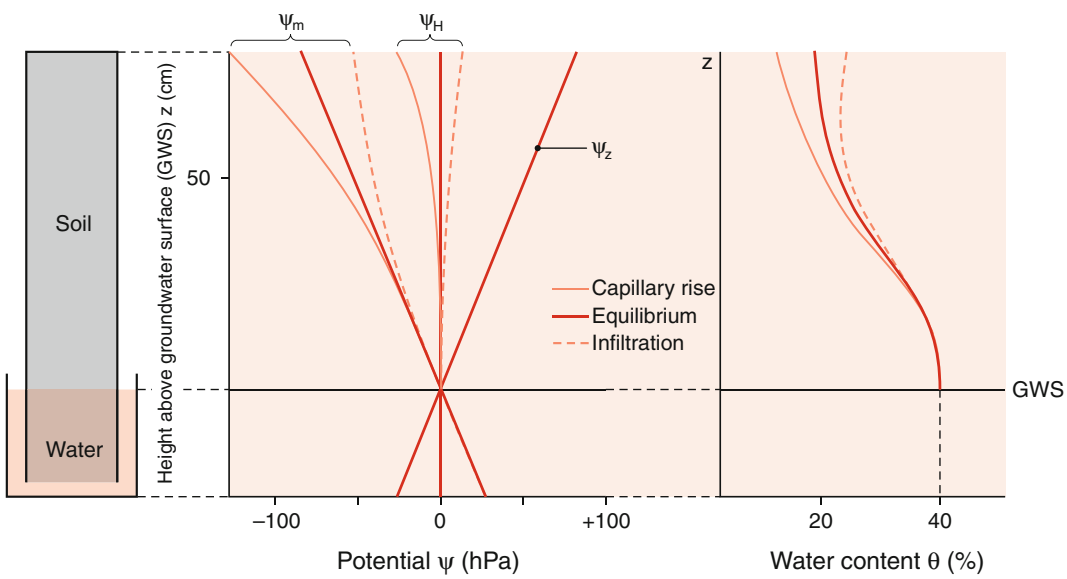

Fig. 6.30 Hydraulic potential, matric potential, gravitational potential and water content in a homogenous soil column at equilibrium (*solid line*), with infiltration (*dashed line*), and with capillary rise (*thin line*)

potential does not change, the hydraulic potential also decreases with a constant groundwater level and becomes $\psi_H < 0$ down to the GWS. This results in water movement towards the lower hydraulic potential, i.e. from bottom to top.

In contrast, if water is added at the top, e.g. through rain in the field, the inverse water movement takes place. Here also, the gravitational potential remains unchanged, and the matric potential in the soil layer above the groundwater becomes less negative. In doing so, it increases more the further the corresponding soil layer is away from the unconfined groundwater surface. This results in overall $\psi_H > 0$, forcing a compensating downward movement of the water.

6.4.2.3 Relationship Between the Matric Potential and Water Content

The water quantity that is present at a given matric potential at a site in the soil depends on the pore volume and on the pore size distribution. Therefore, the relationship between the water content and matric potential is characteristic for each horizon and each layer. It is called **water content/matric potential curve** (or matric potential curve for short, **pF curve** or soil water characteristics), and is a basic parameter for any calculation of water movement and other water balance parameters. The pF value corresponds to the logarithm of the magnitude of the matric potential (pF = log cm WC, log hPa).

The water content/matric potential curves for three soils with different textures are shown in Fig. 6.31. The abscissa is divided into a logarithmic scale, mainly in order to make differences visible in the low pF value range.

The different slopes of the curves are caused by the different pore size distributions of the soils. In these examples, the water contents at a matric potential of 0 hPa or 0 cm WC (pF = −∞) vary from 42 to 53 % vol., i.e. 42–53 % of the soil volume is filled with water at saturation. In the absence of trapped air, this volume corresponds to the respective total pore volume of the soil.

The matric potential curves represent idealized correlations between the water content and the matric potential. Because different mechanisms, described in the next sections, affect the

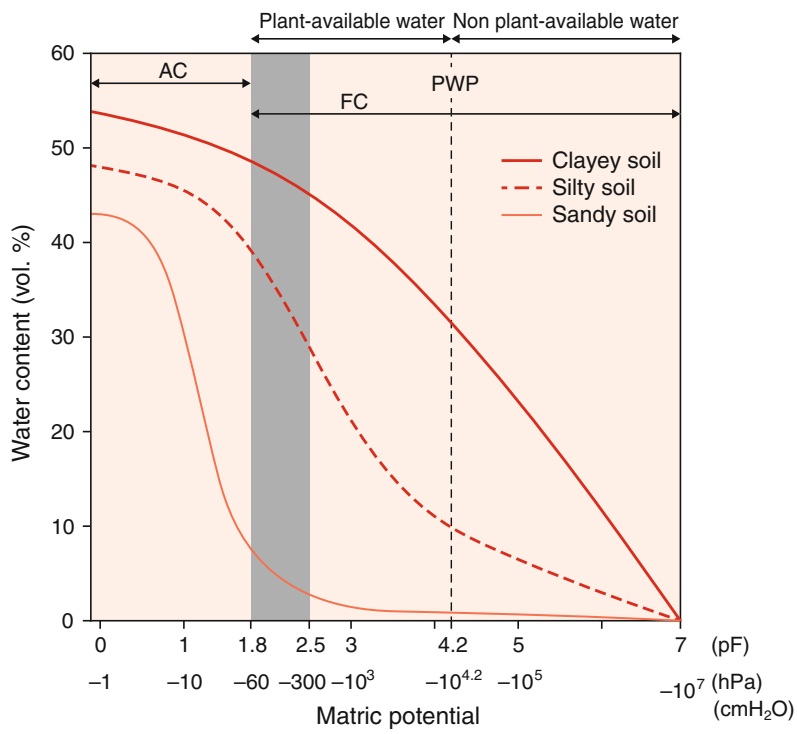

Fig. 6.31 Relationship between the matric potential and water content (pF curve) in a sandy soil, a clayey silt soil (loess soil), and a clayey soil (A horizons). *FC* field capacity, *PWP* permanent wilting point, *AC* air capacity

course of the curves, the accuracy of the determination strongly depends on strict compliance with constant methodical conditions when sampling and preparing the samples as well as with the preliminary wetting.

(a) **Influence of texture**

When water is extracted from soils, the course of the pF curve in sandy soils is initially steep up to about pF 1.8 (ψ_m − 60 hPa). This steep course indicates that the relatively weakly bound water (~30 %) released in this range has a relatively homogeneous binding strength, or expressed in the capillary model, it belongs to pores with a relatively homogeneous equivalent diameter (cf. wide coarse pores, diameter > 50 µm, see Table 6.4). In the field, sandy soils exhibit an abrupt capillary fringe above the GWS. The remaining 5 % water is fixed with increasing binding strength, and the last fractions are in the form of thin films of adhesive water and as rings around the contact points between the grains.

The different course of the pF curves in the two other soils compared to sandy soils is attributed to their different pore size distribution. In the silty soil (developed from loess), the medium-sized pores are strongly involved with ~20 % (pF range 2.5–4.2; (ψ_m −300 to −15,000 hPa), and in the clayey soil, the fine pores with about 30 % (pF > 4.2; (ψ_m < −15,000 hPa) (see Fig. 6.31).

Figure 6.31 also shows that at the same water content, the binding strength (i.e. also the matric potential) of the soil water increases in the sequence: sandy soil < silty soil < clayey soil, i.e. with increasing clay content. This also explains why e.g. at a water content of 20 %, the sandy soil feels wet, the silty soil feels moist, and the clayey soil feels dry. These different binding strengths of water depending on the texture are attributed to an increase in the adsorbing surface area and a reduction in the pore diameter.

(b) **Influence of soil structure**

In addition to the texture, the course of the pF curve is affected by soil structure and therefore also by the hydraulic stress state in the solid matrix. Because changes affect the secondary coarse pores most strongly, changes in the water content in the low pF value range are also particularly large, as can be seen in Fig. 6.32 (fluctuation range of the H_2O content or of the pore volume at pF = 0 between 36 and 61 %). The changes in the range pF > ~1.5 are opposite to those at low pF values, and they are also smaller (see also Sect. 6.4.2.3d).

The influence of the soil structure is of special significance in soils that swell and shrink. Apart from the fact that the total pore volume increases or decreases in the process, the pore size distribution also changes. When swelling, the fraction of coarse secondary pores decreases, and in contrast, the medium-sized pore fraction and especially the fine pore fraction both strongly increase. As shown in Fig. 6.32, the curves are then flatter. The inverse process takes place with shrinkage, which is particularly significant with the initial shrinkage or proportional shrinkage following sedimentation, because

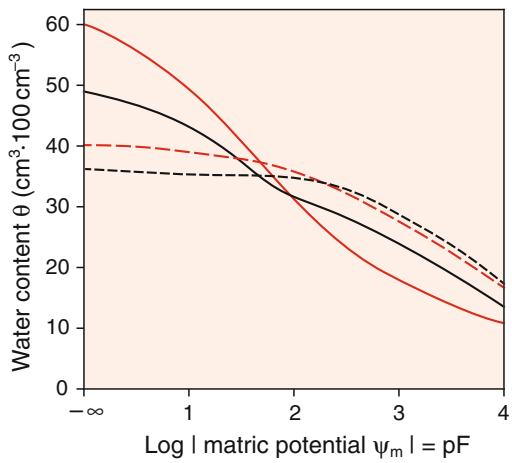

Fig. 6.32 Effect of soil structure on the relationship between matric potential and water content. The four curves characterize loess soils with the same texture but different pore volumes (see water content at pF = −∞) resulting from different structural states

complete reswelling is rare. The matric potential curves of clayey soils are therefore not such unchanging characteristics compared to those of sandy soils.

(c) **Hysteresis of the matric potential/water content curve**

The water content/matric potential curve not only depends on the texture and soil structure or the hydraulic stress state, but rather also on the direction of change in the water content.

Figure 6.33a shows different curves resulting from the course of wetting and drainage. This phenomenon is called **hysteresis**. The Figure shows the extreme cases.

There are a large number of looping transitions between the extremes, depending on how far the previous wetting or drainage progressed before the investigated reversal in drainage or wetting took place. Causes for hysteresis mainly include opposite effects of pore bottlenecks during wetting and drainage, different air inclusions, changes in the wettability, and also changes in structure induced by shrinkage and swelling in the range of proportional or standard shrinkage, which are only partly reversible (Fig. 6.33b).

(d) **Determination of the water content/matric potential curve**

Determination of the matric potential curve in the range pF < 4.2 ($\psi_m > -1.5$ MPa) is performed according to the pressure method by L.A. Richards using a water-saturated soil sample, letting it establish an equilibrium on a ceramic plate or a membrane with air pressures corresponding to specific matric potentials, and measuring the quantity of water drained off the soil or remaining in the soil. The pF curve is obtained when the applied pressures are plotted against the specific water contents (see Fig. 6.31). To determine the matric potential curve for pF > 4.2, the soil is equilibrated with different water vapor pressures, and then the respective soil water contents are measured. The water vapor pressures are generally produced in closed systems using sulfuric acid with different concentrations.

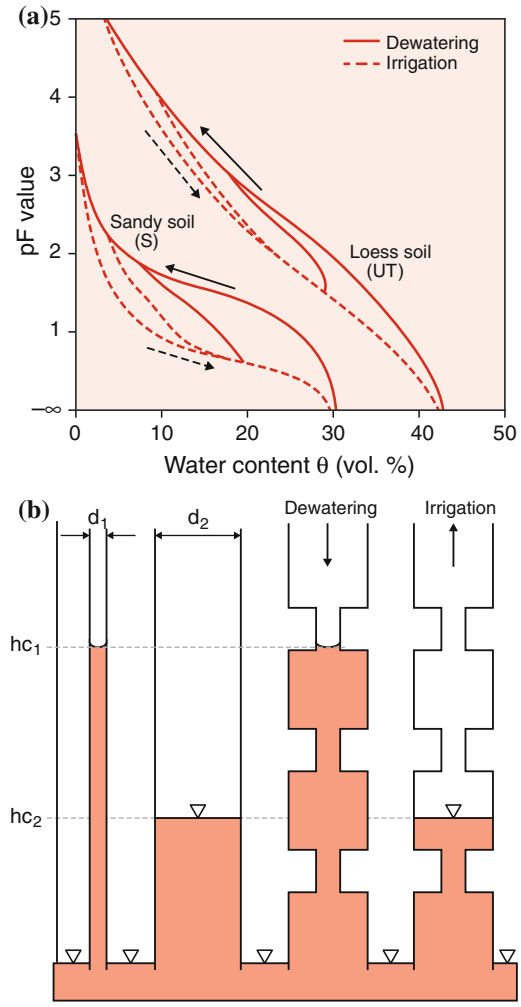

Fig. 6.33 **a** pF curves in a sandy soil (S) and a loess soil (Ut) with irrigation and drainage (hysteresis effect), with a loop for drainage after partial irrigation or irrigation after partial drainage. **b** Effect of pore bottlenecks and their consequence on the degree of pore filling with irrigation and drainage (from Bohne 1998)

The determination of the matric potential curve is time-consuming and requires suitable equipment. This is why various methods have been developed that enable the calculation of these curves using easily determined or routinely available data such

as texture, bulk density etc. These methods are based both on individual data and on functions such as textural curves, which are called pedotransfer functions.

6.4.3 Water Movement in the Liquid Phase

The water in soils is rarely in a static equilibrium, because precipitation and evapotranspiration are continuously interrupting the establishment of a potential equilibrium. It is rather usually in motion, always moving towards the lowest potential. This is true both for the water-saturated state in the area of influence of groundwater and stagnant water, and for the non-saturated range above a groundwater surface (GWS).

The extent of water movement depends on the potential gradient and the **permeability** or **hydraulic conductivity** of the soil. This is represented in its most simple form by the **Darcy Equation**, named after the French engineer Henry Darcy (1803–1858):

$$q = k \cdot \frac{\mathrm{d}\psi}{\mathrm{d}l} \tag{6.26}$$

Here, q is the water quantity flowing through an area, the flow cross-section, per unit of time. It is given in $\mathrm{cm}^3\ \mathrm{cm}^{-2}\ \mathrm{s}^{-1}$ or $\mathrm{m}^3\ \mathrm{m}^{-2}\ \mathrm{s}^{-1}$. ψ is the driving potential, l is the flow section, k is the substrate- or rock-specific proportionality coefficient, called the **hydraulic conductivity** or **permeability coefficient** or **hydraulic conductivity**.

The term $\mathrm{d}\psi\ /\ \mathrm{d}l$ (=the potential gradient) represents the change in the potential over the length of the soil volume. This is sometimes written as grad ψ'. It corresponds to the slope in a free flowing watercourse.

When the dimension for the water quantity flowing through a body per unit of area and time is reduced, it corresponds to the dimension of a velocity ($\mathrm{cm\ s}^{-1}$). It is therefore also called **flow velocity** (v), which corresponds to the Darcy velocity in hydrogeology. The term flux is also occasionally used ([Latin] *fluvius*).

$$v = q = \frac{Q}{A} \tag{6.27}$$

Here, Q is the total quantity of water per unit of time ($\mathrm{cm}^3\ \mathrm{s}^{-1}$), and A is the area (cm^2) through which the water flows.

When investigating water movement, the hydraulic potential gradient is generally used as the driving potential gradient:

$$\text{grad}\ \psi_\mathrm{H} = \frac{\partial\psi_\mathrm{m}(\text{or}\ \psi_\mathrm{h}) + \partial\psi_\mathrm{z}}{\partial z} \tag{6.28}$$

$$= \frac{\partial\psi_\mathrm{m}(\text{or}\ \psi_\mathrm{h})}{\partial z} + 1 \tag{6.29}$$

The prefix between the two component gradients is selected depending on whether the two run in parallel (+) or opposite (−) directions, when ψ_z has increasingly positive numerical values above the GWS (cf. Sect. 6.4.2.1; Fig. 6.30).

The weight is usually used as a reference unit, so that the potential has the dimension of a length and the hydraulic conductivity coefficient k has the dimension $\mathrm{L\ t}^{-1}$ (usually $\mathrm{cm\ s}^{-1}$ or $\mathrm{cm\ d}^{-1}$). In the described form, k is bound to water as a flow medium (k_f). If the behavior of other flow media (air, oil) is to be compared to that of water, the changed viscosity (η) must be taken into account and the reference unit for the potential must be converted to mass or volume. In this case, the conductivity coefficient has the dimension of an area (l^2) and is called **permeability coefficient** k_o:

$$k_\mathrm{o} = k_\mathrm{f} \cdot \eta \cdot (\rho \cdot g)^{-1} \tag{6.30}$$

The density of the manometer liquid (ρ) and gravitation (g) must be added to supplement the potential specification from the length to the pressure (see Sect. 6.4.2.1).

The validity of the Darcy equation depends on 5 assumptions:

1. the water flow is **laminar** (i.e. parallel-running flow lines), which is always found in soils under field conditions when they do not contain very coarse material (gravels, stones etc.). In hydrogeology, the Reynolds

number <1 is used as the threshold value between laminar and turbulent flow (where the flow lines are irregular). It is independent of the size of the pore within a flow cross-section that is involved in percolation. It applies for large and small pore volumes, and also for complete or also only partial water saturation of the soil. The latter case is particularly important, because partial water saturation (so-called **unsaturated state**) is much more common in terrestrial soils than complete saturation. However, at the same time, laminar flow includes always the highest flow velocity in the middle of the pores (Taylor flow), while slower flow velocities are observed towards the pore walls.

2. The Darcy equation in the form given here describes a flow process where the movement of all water particles in an **inert pore system** (i.e. without interaction between the liquid and solid phase)
3. the liquid flows in one direction (vertical or horizontal) (=**one-dimensional flow**).
4. the gradient during the measuring and observation time remains unchanged (=**steady state flow**).
5. The **pore walls** themselves must be rigid, i.e. there may not be changes in stability during the flow, neither through mechanical loads, swelling and shrinking, nor through chemical precipitation or dispersion processes (Fig. 6.34).

In a flow field with homogenous hydraulic conductivity, the Darcy equation can therefore be used to determine the potential and the quantity of flowing water in each part of the system. However, one-dimensional flow only occurs in soils if sufficiently small sections and especially short flow sections are observed, or if theoretically same-sized spheres were arranged in the densest packing, i.e. the smallest pore volume in the space with the same pore shape. Larger areas, like inflow in ditches, in other watercourses, to roots or also the water flow in aggregated soils (e.g. with prismatic structure, platy structure with horizontally aligned pores between the plates/sheets, and in stratified substrates or soils developed from e.g. glacial sediments), are always multi-dimensional. They can only be considered as being two-dimensional if a plane taken out of the flow area is considered. In these cases, however, the flow cross-sections are no longer constant, just as the velocity distributions vary not only in the pore, but also between the individual pores. In principle, the situation corresponds to the representation of the stream lines around a drainage pipe (Fig. 6.35).

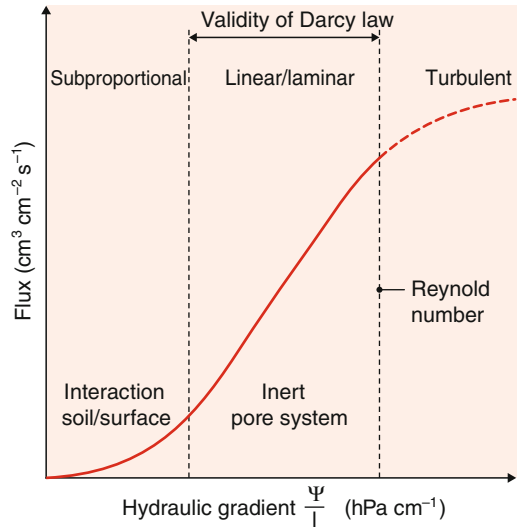

Fig. 6.34 Flow behavior of water in soils as a function of the hydraulic gradients—boundary conditions for the validity of Darcy's Law

In this situation, the Darcy equation is no longer suitable to describe the flow field, because changing flow cross-sections (A_1, A_2) with a constant total discharge (Q) require changing velocities (v):

$$Q = v_1 \cdot A_1 = v_2 \cdot A_2 \qquad (6.31)$$

This equation fulfils the requirement for the conservation of mass. It is the simplest form of the so-called **continuity equation**; here it is formulated for the case where two different flow cross-sections, each with one-dimensional flow, are compared to each other.

In a two-dimensional flow field where the direction of flow differs from place to place, the conservation of mass in the flowing medium

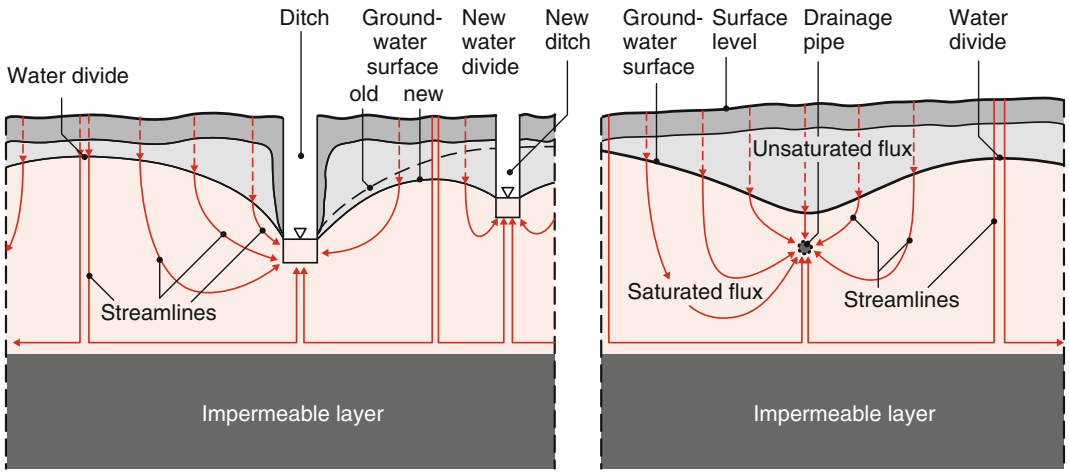

Fig. 6.35 Course of the groundwater surface (GWS), of the flow lines near a drainage trench, and the change in both with a reduction in the trench spacing (*left*) as well as near a drainage pipe (*right*) (based on KIRKHAM)

requires that an increase in flow (v) in direction x (=horizontal in Fig. 6.35) results in a simultaneous reduction in direction z (=vertical in Figs. 6.30 and 6.35, cf. ψ_z). The continuity equation is then:

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_z}{\partial z} = 0 \qquad (6.32)$$

If the corresponding term from the Darcy equation is inserted for the velocity v (=Q/A) in this differential equation:

$$\frac{\partial(k_x \partial\psi/\partial_x)}{\partial x} + \frac{\partial(k_y \partial\psi/\partial_z)}{\partial z} = 0 \qquad (6.33)$$

This equation is known as **Laplace's equation**. It describes two-dimensional flow of water, whereby the differences in the hydraulic conductivity both under saturated and unsaturated conditions of the pores must be considered in both the observed directions of flow x and z/y in the soil. The three-dimensional flow of water can be also quantified accordingly by extending the equation in the third direction. Mathematically, it is a **tensor function** describing the spatial dependence in connection with the shape and distribution of the pores. Therefore, for the prediction of water fluxes e.g. in aggregated soils and/or on slopes, the determination of the hydraulic conductivity, which differs in each spatial direction (i.e. the flow of water is then anisotropic), plays a decisive role both under saturated and under unsaturated conditions. One can only divide by k in Laplace's equation if the hydraulic conductivity is the same in all spatial directions, and the differential equation is then obtained as the second derivative

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} = 0 \qquad (6.34)$$

Solving Laplace's equation can therefore generally describe the potential distribution in the entire flow field. Depending on the type of formulation of the driving gradients, a length (h) can be used instead of ψ.

With the described conversion process, the hydraulic conductivity k was eliminated by canceling in Eq. 6.33. This emphasizes the important fact that in homogenous soils with isotropic flow behavior, the flow pattern is independent of the hydraulic conductivity. This soil property therefore only affects the absolute flow volume per unit of time and area, but not the spatial distribution of the flow. In contrast, if the pore system is anisotropic because of layered sedimentation or due to the formation of secondary pores, the distribution and anisotropy of the hydraulic conductivity is of considerable significance for the flow processes. At the transition to zones with lower hydraulic conductivity, the individual flow lines in the field

are then diverted towards the boundary surface, while the opposite direction dominates at the transition to zones with higher hydraulic conductivity. The phenomenon is similar to the refraction of light beams at the transition to optically denser or less dense media.

6.4.3.1 Effect of Texture and Soil Structure

The number, size, and shape of the pores through which the water flows significantly affect the hydraulic conductivity. This correlation is described by the **Hagen-Poiseuille equation**:

$$Q = \frac{\pi r^4 \cdot \Delta\psi}{8\eta l} \tag{6.35}$$

Here, Q = the water quantity percolating through a pore per unit of time, r = pore radius, $\partial\psi$ = hydraulic potential difference, η = viscosity and l = flow section.

The equation shows that Q and therefore also the hydraulic conductivity k depend on r to a particular extent, because

$$K = r^2/8\eta \tag{6.36}$$

This is the case when Q is transformed into the area and the Hagen-Poiseuille equation is converted into the Darcy equation. Because coarse-grained soils have a higher proportion of coarse pores, there is always a direct relationship between the texture and their hydraulic conductivity.

Therefore, the hydraulic conductivity of sands can be calculated from the texture. Using the example of a simply composed **Hazen approximation**:

$$K \sim 100 \cdot (\mathrm{D}_{10})^2 \tag{6.37}$$

Here, D_{10} is the particle diameter (cm), which corresponds to the ordinate value 10 % on the abscissa of the cumulative particle size analysis curve.

As shown in Fig. 6.36, the correlation between hydraulic conductivity and texture can be observed in the subsoil (80–120 cm) over a wide range of textures, even if the correlation is not very close (r = −0.47). However, the closer

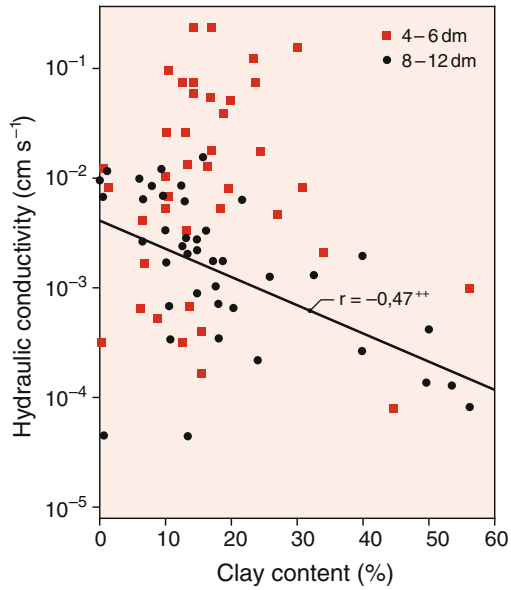

Fig. 6.36 Hydraulic conductivity of soils depending on the clay content. Sampling depth 40–60 cm and 80–120 cm; undisturbed samples

the samples were taken to the surface to determine their hydraulic conductivity, the less pronounced the correlation, because the influence of texture is overshadowed by that of the structural (secondary) coarse pores in the layers closer to the surface. This also leads to the conclusion that the hydraulic conductivity coefficients can be used to analyze the structural development. While the particle size-related primary pores usually exhibit a fairly uniform saturated hydraulic conductivity, the effect of the secondary pores can be very diverse.

As shown in Fig. 6.37, the hydraulic conductivity can be characterized by different pore systems with different k values and different occurrences. The figure illustrates that the frequency distribution of the measured values at depths of 5–10 cm exhibits one single maximum at 5.6×10^{-2} cm s^{-1}. At a depth of 25–30 cm, the distribution has two peaks and therefore demonstrates that in addition to the pore system affecting the upper layer, there is another layer with a hydraulic conductivity that is smaller by ca. one power of ten. Finally, at a depth of 40–50 cm, this narrower pore system dominates and determines the hydraulic conductivity.

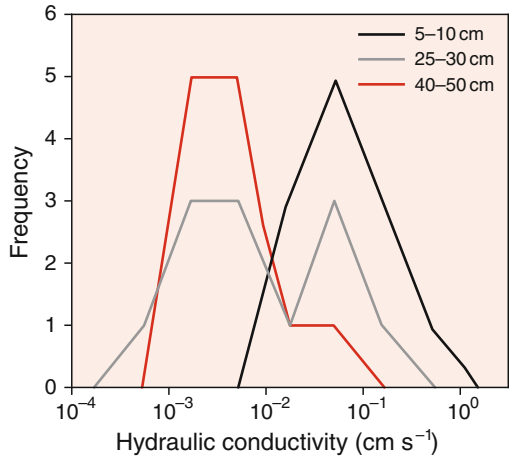

Fig. 6.37 Frequency curve for *k* values (hydraulic conductivity) in 12 parallel samples from a clayey Stagnosol (clay content 35 %) at three depths

The high hydraulic conductivity in the secondary pore range leads to a deformation of the water fronts for water bodies successively entering the soil. With short precipitation events or floods, a portion of the added water flows into crack-shaped and tubular pores and past the water that is already present in narrower pores. Because of this **macropore flow** (also called **preferential flow**), the water fractions only mix very slowly if laminar flow dominates in the adjacent primary pore areas. This is of great significance for translocation and transport processes (see Sect. 6.7).

The saturated hydraulic conductivity values for sandy, silty and clayey soils are highly variable (Table 6.8). In silty and clayey soils, the larger number corresponds respectively to soils rich in secondary pores, and the smaller number to soils without secondary pores or with higher bulk densities.

The hydraulic conductivity of swelling clay and clay-rich loamy soils also strongly depends on the type of adsorbed ions and on the salt content of the percolating water. It decreases with the percolation of low-salt water, if it is associated with a desalinization process. If the salt content of the percolating water increases again, the hydraulic conductivity increases, however, it does not reach the initial value because of the occurred soil surface sealing. These changes are most pronounced with Na ions in the water and on clay minerals. They are much lower with Ca ions in the percolating water and on the exchange medium.

6.4.3.2 Effect of the Water Content

As described in the previous section, the hydraulic conductivity is highly dependent on the diameter of the conducting pores. This is also true when the conducting cross-section in soils is reduced by the presence of air in the pores, so that they can only partially participate in water transport. The drainage of a portion of the pores therefore reduces the hydraulic conductivity. Because the largest pores, which transport the most water at saturation, are drained first, the hydraulic conductivity drops strongly at the onset of drainage. In the different soils, the course of the reduction depends on the pore size distribution (Fig. 6.38).

The conductivity therefore not only depends on the matric potential, but also on the water content. With progressing drainage, the more pores are drained, the more the hydraulic conductivity decreases, because in addition to higher meniscus forces in pores that are still filled with water, the water-transporting pore surface area becomes smaller. For this reason, it already decreases at slightly negative matric potentials in

Table 6.8 Common values for the hydraulic conductivity of water-saturated soils with different textures

Soil texture	Hydraulic conductivity	
	(cm s^{-1})	(cm d^{-1})
Sands	$\sim 4 \times 10^{-1}$ to $\sim 4 \times 10^{-3}$	$\sim 3 \times 10^{4}$ to $\sim 3 \times 10^{2}$
Silts	$\sim 4 \times 10^{-1}$ to $\sim 5 \times 10^{-5}$	$\sim 3 \times 10^{4}$ to ~ 4
Loams	$\sim 4 \times 10^{-1}$ to $\sim 1 \times 10^{-5}$	$\sim 3 \times 10^{4}$ to ~ 1
Clays	$\sim 4 \times 10^{-1}$ to $\sim 1 \times 10^{-7}$	$\sim 3 \times 10^{4}$ to $\sim 1 \times 10^{-2}$

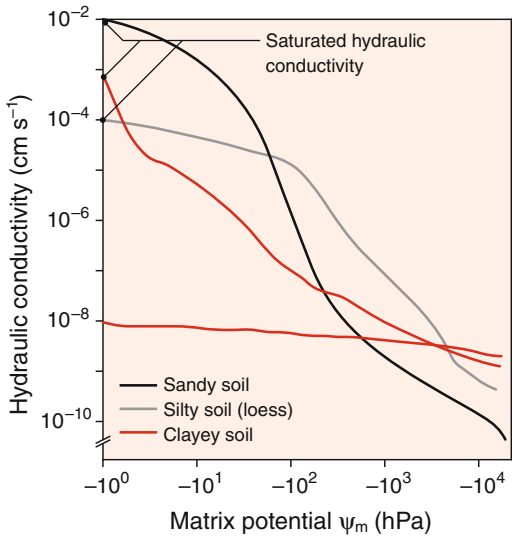

Fig. 6.38 Hydraulic conductivity (saturated and unsaturated) as a function of the matric potential for sandy, silty and clayey soils (after Becher 1970, supplemented)

soils with a high coarse pore fraction, only at somewhat lower matric potential values in soils with a high medium-sized pore fraction, and often hardly at all in soils with a high fine pore fraction. Therefore, although clays without secondary pores have a very low saturated hydraulic conductivity; it remains virtually constant up to very negative matric potentials. It only becomes greater than that of all other soils below a matric potential of ca. -10^{3-4} hPa.

Figure 6.38 also shows that the high hydraulic conductivity at water saturation in the sandy soil drops below the values for loess soils at $\psi_m < -10^2$ hPa (pF 2) due to drainage of the coarse pores. As a result, in the range from -10^2 to -10^4 hPa (pF 2–4), which is particularly common under field conditions in terrestrial soils, the loess soil has the highest hydraulic conductivity. This is an important reason for the preference of these soils for agriculture.

If clayey soils in a saturated state exhibit a relatively high hydraulic conductivity, this is due to the existence of secondary pores that are very coarse and are already drained at $>-10^1$ hPa (pF 1). With stronger desiccation ($\psi_m < -10^4$ hPa or pF > 4), the hydraulic conductivity of the clayey soil is greater than that of all other soils, because in this state, which mainly depends on the texture, it has the most flow cross-sections because of the still relatively high water content. Of course, this is only true as long as the flow section is not interrupted by drained shrinkage cracks, because these prevent flow due to the capillary blockage effect.

In terms of their unsaturated hydraulic conductivity in the range from $\psi_m < -10^2$ to -10^3 hPa (pF 2–3), the behavior of peat soils is similar to the sandy soil shown in Fig. 6.38.

The shape of the flow paths, characterized by bottlenecks and curves (tortuosity), strongly affects the hydraulic conductivity. It is therefore possible to draw generalized conclusions on the hydraulic conductivity from the morphological description of the soil structure. This is significant for soil mapping. At the same time, however, this property leads to high scattering of the data. The saturated hydraulic conductivity is by far the physical soil property with the highest variation, which can also clearly be seen in Figs. 6.36 and 6.37.

6.4.3.3 Determination of the Hydraulic Conductivity

The hydraulic conductivity coefficient k is determined by experimentally measuring the parameters of the Darcy equation, i.e. the flow cross-section, flow section, potential gradient, percolation time and percolated water quantity.

In the field, the **saturated** hydraulic conductivity is most easily determined in a borehole, if there is groundwater or stagnant water within its depth. A portion of the water is removed from the borehole, and the rerise rate of the water level is measured. There are a large number of formulas to calculate the hydraulic conductivity, the most well-known being that from Hooghoudt-Ernst. All of these formulas are based on the Darcy equation. Water can be added if there is no groundwater or stagnant water; however, special measures must be performed in this case to ensure that the measurement takes place in a water-saturated state (double ring method by Bouwer).

The **unsaturated hydraulic conductivity** k_ψ can also be determined directly in the field. Here,

the potential gradient is measured with tensiometers, and the change in the water contents is determined with TDR-sensors installed parallel to the tensiometers.

In the **laboratory**, the **saturated** hydraulic conductivity is determined on samples taken with sampling rings in a defined direction. The results strongly depend on the shape and size of the pores, provided that their volume is smaller than about 30 aggregates from the respective horizon. Parallel determinations then often result in the multi-peaked distributions shown in Fig. 6.37.

In the laboratory, the unsaturated hydraulic conductivity is also determined using core samples. To do so, one usually starts with a saturated sample that is placed on a porous plate, and the water discharge from the sample is measured as a function of time. The matric potential in the sample is measured using tensiometers. The potential gradient is determined according to the Darcy equation. The non-stationary character of the drainage process is accounted for by performing the calculation for a very short period of time. Regardless of the determination method, however, it must be ensured that there is no further shrinkage during the drainage process itself. This would cause the pore cross-sections in the sample itself to become finer due to the formation of new and denser aggregates, while the inter-aggregate area itself would exhibit coarser pores. It is then no longer possible to transfer such 'measuring' results to in situ conditions. Calculation of water fluxes using the Darcy equation then also only delivers approximate results, because one of the significant requirements, the rigidity of the pore system, is not ensured.

For the modeling of water flows, the matric potential/hydraulic conductivity relationship is often derived from the course of the pore size distribution curve and from the value for the saturated hydraulic conductivity using the **van Genuchten-Mualem** approach. Here, however, the significance of pore continuity in the different pore ranges is not taken into account for the water flow. For this reason, especially in soils with high secondary pore fractions, only approximate values can be obtained. Still, this method is very commonly used, because the determination of the unsaturated hydraulic conductivity is very time-consuming and requires expensive instruments. A good alternative is the determination of the parameters required for water balance modeling by means of field measurements (tensiometer and TDR).

6.4.3.4 Water Uptake—Water Discharge

The water movements described in Sect. 6.4.3.1c are based on the assumption that the water content does not change during the course of movement. This state is one of the properties of stationary flow, however, this only exists for longer periods of time in groundwater and stagnant water zones.

Above this zone, the water balance is characterized by the effects of evaporation, water uptake by plant roots, precipitation, infiltration and capillary rise, which alternate in their intensity. They cause constant changes in water content in each different part of the profile, and lead to equalizing water movements due to the associated changes in the soil water potentials. These movements, which seek to reestablish the potential equilibrium, are called **instationary flow**. In contrast to steady state flow, the driving gradient changes with time.

For the mathematical description of unsteady flow processes, just like for two- and three-dimensional steady state flow, the flow equation must be combined with the continuity equation. However, unlike with steady state conditions, the sum of the velocity changes is not equal to zero, but rather equal to the change in the water content (θ) over a time (t). The continuity equation is then:

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_z}{\partial z} = \frac{\partial \theta}{\partial t} \tag{6.38}$$

After combining with the Darcy equation, the following is obtained for two-dimensional water movement in the directions x (horizontal) and z (vertical):

$$\frac{\partial (k_x \partial \psi_m / \partial x)}{\partial x} + \frac{\partial (k_z \partial \psi_m / \partial z)}{\partial z} + \frac{\partial k_z}{\partial z} = \frac{\partial \theta}{\partial t} \tag{6.39}$$

The summand $\partial k_z / \partial z$ must be added to the left-hand side to take account of the effect of gravity in the vertical (z direction), because the hydraulic potential (ψ_H) in this direction also contains the term ψ_z in addition to the term ψ_m: $\psi_H = \psi_m + \psi_z$. Here, $\partial\psi_z / \partial_z = 1$ and

$$\frac{\partial(k_z \partial\psi_z/\partial z)}{\partial z} \text{ turns into } \frac{\partial k_z}{\partial z} \tag{6.40}$$

The two-dimensional form shown here, which applies to a x–z plane that is virtually cut out of the three-dimensional space, can be supplemented by inserting the y component for the three-dimensional case.

Because instationary, one-dimensional water movement in a vertical direction dominates in terms of the area in the unsaturated zone of terrestrial soils, it is given special attention. Because of the simple flow conditions, modeling methods for this case are particularly advanced. The **Richards equation** represents the basis for such models. Here, the change in water content of one unit of volume of soil is represented as the sum of the flows that are caused by the hydraulic gradients:

$$\frac{\partial\theta}{\partial t} = \partial\{k[(\partial\psi_m/\partial z) + 1]\} \tag{6.41}$$

The equation requires that the soil matrix be rigid, inert, homogenous and uniform, and that the moving air in the pores does not affect the flow of water.

In principle, these approaches correspond to the equation for instationary diffusion (Fick's 2nd Law), if the diffusion coefficient used there is replaced by the product of the hydraulic conductivity with the slope of the matric potential curve, the **diffusivity** (D):

$$D = k\frac{\partial\psi_m}{\partial\theta} \tag{6.42}$$

The diffusivity describes the propagation rate of differences in matric potential.

(a) **Infiltration**

The term **infiltration** is defined as the movement of seepage water from the surface into the soil, if the matric potential is higher than that corresponding to the equilibrium with the free groundwater or stagnant water level (see Fig. 6.30):

$$\psi_H = \psi_z + \psi_m > 0 \tag{6.43}$$

Infiltration is therefore a result of precipitation, sprinkler irrigation or flood irrigation. The course of infiltration is characterized by the **infiltration rate**. This indicates the water quantity that infiltrates per unit of time. The total infiltrated quantity is also sometimes given (=**cumulative infiltration**).

For the main part, the hydraulic conductivity of the soil surface is decisive for the course of infiltration. The infiltration decreases strongly as soon as it is reduced by destruction of the aggregates, soil surface sealing, and crust formation. Surface water is then formed when there are high water inputs, and the risk of erosion on slopes increases. For this reason, the correlations between aggregate size and microrelief after aggregate degradation are important influencing parameters.

The principle of infiltration processes is clearly visible in a homogenous soil that is not sealed at the surface, e.g. sand. Figure 6.39 shows the characteristic course of the water content distribution as a function of time for a constant water input and constant flooding by an infinitely thin water layer.

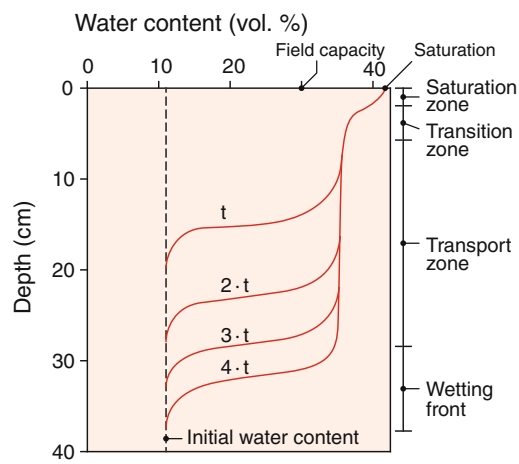

Fig. 6.39 Course of water infiltration in a homogenously flooded soil at equal time intervals (after Bodman and Coleman 1944)

Four zones are formed. While the **saturation** and **transition zone** only stretch over a few cm, the length of the **transport zone** increases strongly, and the wetting zone penetrates deeper and deeper into the soil. At first, the advancing velocity of the **wetting front** is fairly high, and due to the large differences in water content between the saturated zone and the initial soil water content, the hydraulic gradient is initially mainly determined by its matrix-related fraction. With increasing length of the transport zone, however, this effect becomes smaller and finally the hydraulic gradient

$$\frac{\partial \psi_{\mathrm{H}}}{\partial z} \approx \frac{\partial \psi_{\mathrm{z}}}{\partial z} \tag{6.44}$$

approaches a value of 1, whereby the advancing velocity of the wetting front is then constant. When water saturation is reached, the velocity depends on the respective hydraulic conductivity in the transport zone. Under field conditions, a water saturation of 70–80 % of the pore volume is hardly ever exceeded (the water content usually lies between saturation and field capacity).

When the soil is not flooded, but rather only a constant but small water replenishment through rain is taking place, a saturated zone is not formed, and the transition zone is also only weakly developed. Like with the case of flooding, here the downward movement of water takes place in the transport zone under the sole influence of gravity. The degree of saturation established in the process is such that the added water quantity can just be discharged at the respective unsaturated hydraulic conductivity.

This correlation with the water saturation has a strong effect on the course of infiltration when there are changes in the pore system in the profile. If the wetting front meets a layer of low hydraulic conductivity, its advancement slows down. If this **water retention** is strong enough that the matric potential above this layer becomes $\psi_{\mathrm{m}} = 0$, it results in the formation of **stagnant water**.

In the range of unsaturated water movement, water retention in the soil profile can occur not only due to fine-pored layers, but also due to particularly coarse-pored layers (e.g. sand, gravel), because the hydraulic conductivity at higher pF values in coarse-pored substrates is often very small (see Fig. 6.38). Furthermore, the participation of coarser pores is only possible if the matric potential in the fine-pored substrate has risen enough (i.e. is less negative) to allow the coarser pores to be filled. For this reason, water retention not only occurs on plow pans, in Bt horizons, in Luvisols etc., but rather also in Ah over E horizons of sandy soils, where a finer texture, i.e. a finer porosity lies over a coarser one. This phenomenon occurs particularly often in substrates that were transported and deposited through glacial, fluvial or eolian processes. The degree of water saturation during infiltration implies that coarse pores, e.g. root and worm tunnels as well as shrinkage cracks, are not filled with water below the saturation zone. These pores are only involved in water movement to a greater extent when the soil is completely flooded.

In addition to the infiltration rates (cm s^{-1}) described until now, the total amount of water absorbed by a soil within a specific time is also often of interest. There are empirical approaches for this **cumulative infiltration** i = Q / A (cm^3 cm^{-2}), e.g. by Kostiakov (1932):

$$i = c\,t^{\mathrm{a}} \tag{6.45}$$

Here, t is the time of infiltration and c and a are empirical parameters. They are determined by the soil properties, where c is mainly determined by the soil structure at the beginning of infiltration, and a by the water stability.

The equation by Philip (1957) includes the diffusivity:

$$I = s\,t^{1/2} + k_{\theta} t \tag{6.46}$$

Here, s is the initially predominant effective water uptake rate (**sorptivity**) and k_{θ} is the

increasingly strong influence of the hydraulic conductivity during the course of the infiltration time t at the saturation state of the transport zone characterized by the water content q. With longer infiltration times, the member $k_\theta\ t$ practically solely determines further water uptake. Thus,

$$\frac{k_\theta t}{t} \approx \frac{i}{t} \approx I \tag{6.47}$$

Here, I is the infiltration rate (cm s^{-1}). In the stationary end state of movement, i.e. when the infiltration rate is constant and the vertical gradient has become = 1, this corresponds to

$$I = k_\theta \tag{6.48}$$

k_θ is the unsaturated hydraulic conductivity belonging to the respective water content.

The described equations all assume a piston-shaped uniform advancement of the wetting front. In soil with high proportions of secondary pores, however, the water rushes ahead of the front in the pore-near zone. This also happens when a fine-grained layer lies on a coarser, not quite homogeneous layer. This causes the uniformly advancing wetting front to be dispersed and the water flows faster into the finer water-filled pores (fingering of the wetting front), where the gravitational movement is essentially limited to these 'finger zones', while lateral movement is caused by differences in matric potential.

Rapid flows at the edges of macropores also lead to a distortion of the infiltration process. The water rushing ahead, and therefore the preferential flow (macropore flow) on these flow paths is greater the more completely the surrounding matrix is saturated with water. It therefore plays an important role for mass transport in many soils, because the transmission of soil water contents is strongly accelerated. This strongly reduces the soil's filtering properties (Sect. 6.7.1).

(b) **Capillary rise**

Capillary rise is the opposite process of infiltration, and principally takes place both under unsaturated and saturated conditions. The water originates from groundwater, stagnant water or also adhesive water, and moves upwards. This movement occurs when the matric potential above the groundwater surface or any other water-conducting soil layer is lower than that corresponding to the hydraulic potential equilibrium:

$$\psi_H = \psi_m + \psi_z < 0$$

This is the case in the open field when water evaporates at the soil surface or is extracted from the soil by plants. Here, like with any water movement, water replenishment is strongly determined by the potential gradient in addition to the hydraulic conductivity at the respective degree of saturation. For the unsteady case, i.e. refilling, there is also the slope of the matric potential curve ($\partial\psi_m/\partial\theta$), and therefore, like with infiltration, also the diffusivity.

For this reason, the water initially rises rapidly in a sandy soil because of the high coarse pore fraction, but only up to a small height above the groundwater table. In a silty soil with the same potential gradients, although the quantity of water rising per unit of time is smaller, it decreases less rapidly on its way up.

This effect of the unsaturated hydraulic conductivity and pore size distribution causes the varying effects of the groundwater level, measured from the soil surface, on plant growth and therefore on crop yields in the different soil textures. In sandy soils, maximum yields are generally achieved at groundwater levels ≤50 cm below the ground surface. In loamy and silty soils, which have deeper rooting and a higher amount of plant-available water than sandy soils, the ideal groundwater level is at 1.4–1.8 m.

Here, groundwater levels down to 3.3 m below the soil surface still have an effect on

yields, because the degrees of saturation existing under central European climate conditions still allow for high replenishment by capillary rise (see Fig. 6.37, k is still very high between $\psi_m = -10^2$ and $-10^{2.5}$ hPa).
On clayey soils, the highest plant yields are achieved with groundwater levels between 0.9 and 1.3 m below the soil surface. Here, the capillary replenishment has an effect on yields up to groundwater levels 2.5 m below the ground surface (cf. k/ψ in Fig. 6.38).

(c) **Drainage**
Drainage is defined as the loss of water in a soil under the effect of gravity. To drain a soil, the GWS must be lowered as a reference basis for the matric potential in the profile. This is achieved with open ditches or covered subsurface pipes. Because a ditch and pipe system must maintain a slope to ensure that the drainage water runs off, the GWS may not be arbitrarily lowered and therefore the absolute potential difference can only be raised within a narrow range. Improvement of the soil drainage is achieved by shortening the flow sections in the soil matrix within the groundwater and stagnant water zone (Fig. 6.35, left). This increases the potential gradient, and the local flow velocity increases.
In humid climates, drainage can be required to improve soil **aeration**. In this case, the functional capacity of the drainage system depends on whether the GWS can be lowered far enough so that the coarse pores are emptied again within a few hours after precipitation, enabling the soil to be aerated again. A soil is considered not to be **worthy of draining** if the drainage pipes or ditches have to be laid very close to each other to achieve sufficient shortening of the flow times in a soil with low hydraulic conductivity, or be laid very deep to achieve a sufficiently negative matric potential in the soil layer to be drained. Figure 6.35 (right) shows an example for pipe drainage.
Formerly, the artificial drainage of agricultural land was achieved with open ditches, and today, mainly with drainage pipes. The spacing, depth, and diameter of the drainage pipes are decisive for the full efficacy of a drainage system. There are a number of equations for determining these three parameters, some of which are empirical and some theoretical. The formulation of the latter is based on knowledge of the one- and multi-dimensional steady state/stationary and unsteady/instationary flow processes, briefly described in Sect. 6.4.3.
Under arid climates, sufficient drainage, usually artificial, is a **crucial** prerequisite for the irrigation required by crop production. This is the only way to ensure that salts from the irrigation water accumulating near the surface with strong evaporation are leached out of the soil. The specialized literature listed at the end of the chapter provides more details on this extensive subject.

6.4.4 Water Movement in the Vapor Phase

In soils where the pore system is not completely filled with water, the soil air always contains abundant water vapor. Except for the topmost soil layer that is dried out by evaporation, the degree of saturation is always more than 90 %. With the development of potential gradients in the soil, this water vapor moves towards the lowest potential, i.e. the lowest vapor pressure. If water vapor is transported out of the soil, it is replaced by evaporation from the liquid phase. The high water saturation of the soil air is also the reason why small, highly specialized soil animals and fine roots (root hairs) dry out rapidly when they are taken out of the soil and exposed to the air.

6.4.4.1 Water Vapor Movement in the Soil

Different causes for the development of vapor pressure gradients in the profile can include: Differences (1) in the thickness of the adhesive water film, (2) in the curvature radii of the menisci, (3) in the temperature and (4) in the osmotic pressure of the soil solution. The

movement itself mainly takes place through diffusion; the effect of convective flow is generally restricted to the topmost cm of the profile. Because the water vapor pressures in the soil at matric potentials $>-10^4$ hPa (pF < 4.2) remain only insignificantly below the saturation vapor pressure (p/p_o > 95 %), temperature differences cause much greater vapor pressure gradients than the other factors.

Alternating heating and cooling of the soil surface in diurnal and seasonal rhythms leads to constant water movement going towards the colder zone. In terms of its extent, this movement is generally less than the movement in the liquid phase in humid climate areas. It is strongest in the fall with sunny weather and clear nights, when it can reach up to 1 mm of water per night for a layer with a thickness of 15 cm. In arid climates with greater temperature fluctuations, in contrast, vapor movement is much more significant, because there is little movement in the liquid phase due to the soils' generally low water content.

In proximity to soil heating pipes, as they are used e.g. in intensive crop production to warm the beds, this thermal water vapor transport in soils inevitably leads to considerable desiccation in the area surrounding the heating elements, and therefore not only reduces the heat transmission due to the reduced thermal conductivity at lower water saturation. Furthermore, in drier soil volumes, there is also an increase in the osmotic effect due to salt precipitation. This strongly restricts the applicability of such technical measures.

Lowering of the vapor pressures over water films and menisci causes water that condensed due to a decrease in temperature in the gaseous phase to be rapidly precipitated on these films and menisci. Table 6.7 gives an impression of the extent of the vapor pressure lowering over the curved menisci in narrow capillaries. It can be seen that the lowering of the vapor pressure only reaches an appreciable extent if the matric potential drops significantly below the permanent wilting point (pF = 4.2; $\psi_m = -1.5$ MPa, see also Fig. 6.31). However, because such strong drainage does not occur in soils, with the exception of the topmost layer that is exposed to direct solar radiation, the meniscus curvature factor plays a secondary role for vapor transport. The same is also true for the effect of the adhesive water films, which are at equilibrium with the menisci in terms of the binding strength and therefore also the vapor pressure above them.

In principle, the movement of water vapor in the soil is subject to the same laws as liquid water. Because the driving gradient, the **vapor pressure difference**, can be expressed through differences in the water vapor concentration, diffusion equations are used to describe the movement. For the case of **steady state diffusion flow**, the general transport equation for **steady state** diffusion in the form of the **1stFick's Law** applies:

$$q = D_s \frac{\partial c}{\partial x} \tag{6.49}$$

Here, q is the water volume that is transported per unit of time and area, D_S is the diffusion coefficient, c is the water vapor concentration, and x is the diffusion path. This equation has the same structure as the Darcy equation. It only has the concentration gradient instead of the driving pressure gradient.

Non-steady state diffusion flow can be described by the **2nd Fick's Law** if the diffusion coefficient D_S is independent of the flow path, i.e. it does not change along the path:

$$\frac{\partial c}{\partial t} = D_s \frac{\partial^2 c}{\partial x^2} \tag{6.50}$$

In both equations, similar to the hydraulic conductivity coefficient k, the diffusion coefficient D_S comprises all soil properties affecting the diffusion, e.g. the size of the air-filled pore volume, the distribution and shape of the pores. D_S values are therefore always smaller than values for water vapor diffusion through a gas-filled space.

6.4.4.2 Evaporation from the Soil

At the soil surface, the movement of water vapor plays a more important role than in the soil profile, because (a) it is exposed to solar radiation (energy required for the evaporation of water at 20 °C is 2.44 kJ g^{-1}), (b) the relative water vapor pressures in the adjacent air are usually lower than in the soil air, and (c) as a result of air

movement, the transportation is faster than solely through diffusion processes.

At the soil surface, water vapor transport is caused by the process of evaporation and the subsequent transportation by air movement. The motor for evaporation is the energy radiation (R_e) coming from the sun. It is counteracted by the energy transfer consisting of radiation (R_a), water evaporation (E), and the diversion of tangible heat into the atmosphere (H).

For the radiation the portion that acts on the soil surface, i.e. the total or global radiation minus the reflected fraction, must be inserted. The latter is given by the albedo (r). The albedo is the ratio of the amount of reflected to the amount of radiated energy. It depends on the reflective properties of the soil surface including the vegetation. It lies between 5 % for open water surfaces and about 50 % for pure white sand. Thus:

$$R_e(1-r) = R_a + E + H \tag{6.51}$$

The water evaporation (E) is described by the **Dalton equation**:

$$E = f(u)(e_s - e). \tag{6.52}$$

If related to evaporation, instead of the energy units J or kJ, it is converted to the water quantity (mm d^{-1}) that evaporates with an energy consumption of 2.44 kJ g^{-1} at 20 °C. In the equation, $f(u)$ is an empirical factor that takes account of the wind velocity (u; in m s^{-1}). ($e_s - e$) is the saturation deficit (in mbar or hPa), which takes account of the water vapor pressure gradients. This equation represents the basis for related equations, like e.g. those by Haude, Thornthwaite, Penman.

The evaporation losses at the soil surface are compensated by water movement in the liquid phase from deeper layers. As long as the replenishment is high enough, the soil surface does not dry out. The more the evaporation increases, the steeper is the required hydraulic potential gradient to compensate for the evaporation losses. However, as a result of this, the water content and the hydraulic conductivity of the surface-near layer decreases, and therefore also the evaporation often suddenly decreases, even if the dried layer is only very thin.

For this reason, a distinction is made in soils between the **potential evaporation** (E_p) and the **actual evaporation** (E_a). This distinction is mainly used for the joint calculation of the evaporation and transpiration of plants (evapotranspiration, Sect. 6.4.6.5). All of the mathematical methods mentioned here are based on the potential evaporation (E_p).

The sudden decrease in evaporation is particularly pronounced in soils whose hydraulic conductivity rapidly decreases with increasing drainage. This is mainly the case with coarse sand and medium sand soils, where a dry layer can be abruptly followed by moist soil. In fine sand soils as well as clay- and silt-rich soils, in contrast, the topmost layer remains moist for a longer time, because the evaporated water is supplemented by capillary water replenishment for a longer period of time. However, the total evaporated water volume is then also higher.

Because of the higher evapotranspiration resulting from faster water replenishment in wet soils, less groundwater recharge is possible in the annual hydrological cycle than on drier soils (Fig. 6.40).

The dry surface layer formed on sandy soils makes these soils particularly vulnerable to wind erosion. Water losses due to evaporation are low in soils where the pore system is coarse enough to ensure a low unsaturated hydraulic conductivity, but fine enough to inhibit air turbulence in

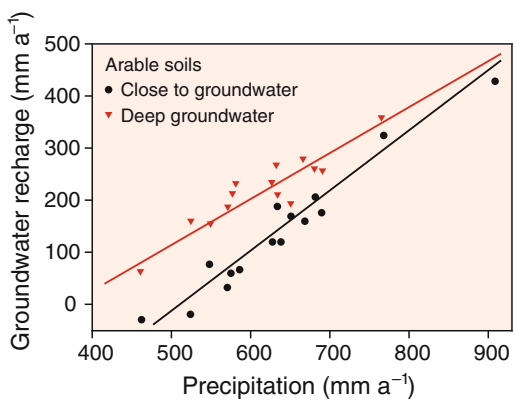

Fig. 6.40 Groundwater recharge in a sandy soil near Hannover depending on the precipitation and depth to groundwater (1968–1982). Near the groundwater: <1.75 m, far from the groundwater: >1.75 m (after Renger et al. 1986)

the pore system. This would be particularly favorably achieved with a layer of coarse sand at the soil surface.

Evaporation can be reduced e.g. by windbreaks and soil tillage methods. In the latter case, the focus is on producing topsoil resembling coarse sand in terms of the aggregate structure and pore system. For the same reasons, the evaporation under a dense plant cover (e.g. after crop closure, i.e. complete vegetative soil cover in arable farming and in forests) is lower than on unprotected areas.

In several cases, chemical treatments to reduce evaporation were tested, which (a) produce a crumbly surface structure, (b) reduce the water's surface tension, and (c) can form a unimolecular protective layer on the water (e.g. acetyl alcohol). The effect of the two first treatments comes from the fact that (a) the water infiltrates faster and (b) penetrates deeper into the soil.

6.4.4.3 Condensation in the Soil

Because the relative humidity in the soil is generally high, any decrease in temperature in a soil zone leads to condensation of water vapor out of the soil air. The same also occurs when a diffusive inflow of water vapor arises, because the vapor pressure in a neighboring zone increases due to heating of the soil. This correlation between temperature and saturation vapor pressure in soils causes water vapor from the heated topsoil to not only evaporate into the atmosphere during the course of the day, but also to penetrate into the subsoil and be condensed there. The inverse process takes place at night.

The extent of this water vapor movement depends on the temperature fluctuations in the surface-near soil. Under central European climate conditions, the effect is strongest late in the summer, in particular on uncovered, non-saturated soils.

Even in desert climates, nocturnal cooling of the soil surface with suitable cover can lead to an accumulation of small amounts of water out of the soil. In these areas, methods for collecting this water count among survival skills.

Ice lens formation in the winter is also promoted by the condensation of water vapor on particularly cold zones in the soil. This is especially true in arid soils, where the unsaturated hydraulic conductivity is too low to maintain heat replenishment with flowing water (cf. soil temperature, Sect. 6.6). This leads to water accumulation in the entire topsoil, particularly under the coldest spots, e.g. under rocks and pavement. Condensation from the vapor phase is therefore one of the causes for the formation of frost fractures and heaving in soils (cryoturbation).

6.4.5 Soil Water Balance

Changing weather conditions during the year and the resulting fluctuations in the metabolic intensity of plants lead to varying characteristic courses of water inputs into the soil and water losses out of the soil. The course of these changes, which are often grouped under the term **water balance**, also depends on the soil properties and the hydrological situation, in addition to the other mentioned factors. Here, especially the hydraulic conductivity of soils at different saturation states, and therefore the properties of the pore system, are significant. For this reason, the matric potential curves [ψ = f (θ)] and the hydraulic conductivity curves [k = f (ψ) or k = f (θ)] are important tools for the assessment of soil water balances.

6.4.5.1 Soil Parameters

Terms such as **field capacity** (FC) and **permanent wilting point** (PWP) are often used for the assessment of the water balance of soils. These values correspond to water contents that are characteristic for individual soil layers and horizons, and are always reestablished under defined conditions. It was often formerly assumed that these 'parameters' are soil constants, where the water content corresponds to a specific state of equilibrium. However, the occurring water contents are also affected by factors that have nothing to do with soil properties.

(a) **Field capacity** (FC)

When the water input is terminated, e.g. after long-lasting precipitation, the water content in the soil profile gradually moves towards a balanced hydraulic potential (ψ_H = 0 in Fig. 6.30). This distribution of water does not usually occur evenly; rather it slows down so much after 1–2 days that equilibrium can be assumed. The water content that is established in this state is called **field capacity** (FC). It is expressed in % vol. based on the volume of soil dried at 105 °C (see Sect. 6.4.1), and refers to a depth range or soil profile. The field capacity depends on the state of equilibrium of the soil water, on the profile depth, the texture, the organic matter content, the soil structure, and the horizon sequence. There are two situations for field capacity:

The first situation corresponds to the **hydraulic equilibrium** represented in Fig. 6.30. This can be established e.g. in the spring after a high-precipitation winter, if the GWS is not deeper than 3 m under the ground surface and the unsaturated hydraulic conductivity function (k_θ, see Sect. 6.4.3.2 and Fig. 6.38) in the soil profile does not exhibit any strong changes. The field capacity then has pF values <2.5. The range between pF 1.8 and 2.5 is most common. Close to the soil surface, these values correspond to a distance of 60 and 300 cm from the GWS. In a state of equilibrium, the water content at field capacity in a soil with uniform texture and uniform structure increases from top to bottom (see Fig. 6.30).

Contrary to the first situation, the second, much more common situation **does not represent an equilibrium**. It occurs when the GWS lies very deep (>3 m). In this case, the soil is so strongly drained before reaching equilibrium that the establishment of equilibrium is increasingly delayed due to low hydraulic conductivity. The extent of the delay is particularly high when there is an extreme change in texture and structure in the profile; moreover, it also depends on the shape of the pF curve. This is also why e.g. in sandy soils, the values for field capacity often already lie at a pF value of 1.5, which corresponds at equilibrium to a distance of 30 cm of the GWS below the ground surface.

The stronger the initial water discharge compared to the total water content, the stronger the reduction of the hydraulic conductivity and accordingly the delay in the establishment of equilibrium. For this reason, sandy soils exhibit a pronounced field capacity 1–2 days after the end of infiltration, while e.g. clayey soils often do not exhibit a field capacity at all. The dependence of the field capacity on the hydraulic conductivity is also the reason why values higher than pF 2.5 are rarely observed for the field capacity in soil layers far from groundwater. This is true even when e.g. the GWS lies at 10 m, so that theoretically, a pF value of 3.0 should be established in the topsoil. Furthermore, the water content at field capacity also depends on other parameters:

- influence of texture: The water contents that are established in different soils in the pF range of field capacity (pF 1.8–2.5) are higher the finer the texture of the respective soil (Fig. 6.41).
- influence of soil structure: Fig. 6.32 shows that the water content depends on the pF value occurring at the respective field capacity. The higher this pF value, the

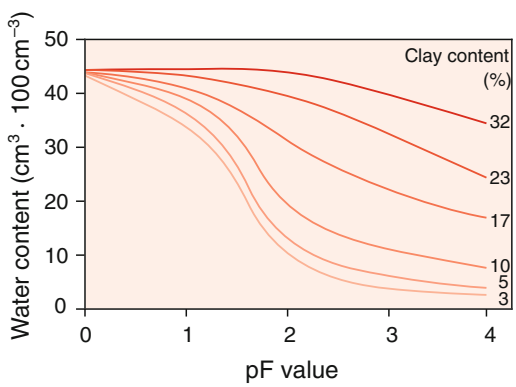

Fig. 6.41 Effect of the texture, represented by the clay content, on the course of the pF curve in soils with the same pore volume

stronger the water content is reduced when the pore volume increases due to the formation of coarse secondary pores (=reduction of the smaller pore fraction, see Fig. 6.32).

- influence of organic matter: The more evenly it is distributed in the soil, the greater the water content at field capacity. In this case, it corresponds to the water content that is measured with a fine distribution of the clay fraction in the soil.

In the field, the field capacity is determined by strongly wetting the soil and then covering it to protect it against evaporation. Field capacity is reached when further water loss becomes negligible after repeated determination of the water content. In humid climate regions, an approximation for the field capacity is often obtained in the spring after the melt water has run off, before evapotranspiration reaches greater extents.

(b) **Permanent wilting point** (PWP)

When a plant extracts water from the soil, it reaches a point, when no more water is replenished, where the water released by the plant through transpiration can no longer be replaced from the soil, and it wilts. The water fraction that is still present in the soil, when the swelling of the plant cells (the turgescence) does not return when water is added, is called the **permanent wilting point** (PWP). In this state, the matric potential corresponds to -1.5×10^4 hPa ($\psi_m = -1.5$ MPa or pF 4.2) in sunflower (*Helianthus annuus*) and pine (*Pinus silvestris*), if the rooting zone is restricted and is therefore not evenly rooted. This value applies to the majority of crops. For this reason, it is conventionally assumed to be universal and is used as a basis for the calculation of the plant-available water in the soil.

At pF 4.2, the water is only still bound in the fine pores and forms thin films on the walls of medium and coarse pores. The water content at the PWP is therefore closely correlated with the clay content, as shown in Fig. 6.41. In contrast, the influence of soil structure is reduced (see Fig. 6.32) and is mainly caused by the fact that the fine pore volume is greater the more fine-grained solid matter is contained in a soil volume, and the denser the packing of the soil.

The PWP is determined using a pressure membrane device, whereby 1.5 MPa is assumed as the pressure at equilibrium.

(c) **Hygroscopicity** (**Hy**)

Before the methods with porous plates and membranes were developed, the adsorbed water quantity at equilibrium with different relative water vapor pressures was used as a parameter for the water balance. The most well-known is the **hygroscopicity** according to E.A. Mitscherlich, which is determined at equilibrium with 10 % H_2SO_4 or a saturated Na_2SO_4 solution. The relative water vapor pressure is then 94.3 % and the pF value is 4.7 ($\psi_0 = -5$ MPa). This method records the total potential.

From the water content at hygroscopicity, a conversion factor of about 1.5 can be used to convert to the water content at the PWP. By changing the H_2SO_4 concentration, the hygroscopicity and therefore the total potential can also be measured at low relative water vapor pressures. However, the technical difficulties increase considerably at pF values >4.

6.4.5.2 Seasonal Pattern of the Water Balance

The course of the soil water balance is defined as the change in the water contents associated with the seasons and is regulated by the climate-related relationship between water loss and water input.

(a) **Water and air contents as well as the matric potentials**

Based on year-round matric potential and water content measurements, Fig. 6.42 shows both the changes in the available water quantities and the changes in the air contents for a podzolized Cambisol. The annual courses of the matric potentials are also shown for a period of almost 3 years for a Stagnosol developed from Saalian Stage

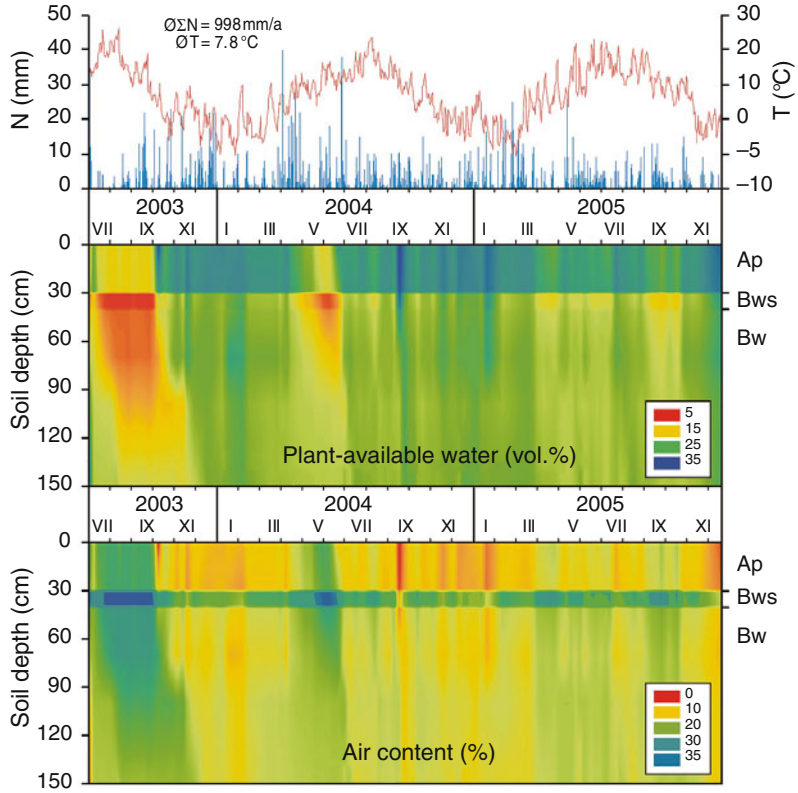

Fig. 6.42 Annual patterns of the plant-available water quantities and the air contents in a "podsolized" Brunic Arenosol under arable land use (from Gebhardt 2007)

calcareous glacial till (Fig. 6.43) in Schleswig-Holstein.

In the podzolized Cambisol under arable land use in Schleswig-Holstein, developed from Saalian Stage glacial sand, the amount of plant-available water decreases rapidly with the beginning of the vegetation period. In the year 2003, already in May, it only reached very low contents (ca. 5 %) down to greater depths. At the same time, the air content of the soil increased considerably. In the two subsequent years, due to the greater precipitation, the desiccation only reached a depth of 50 cm in 2004 for a short period of time, and in 2005, the fraction of plant-available water was never reduced below 15 % vol. Furthermore, it was observed that, with rare exceptions (in May of 2004 and more weakly pronounced also in the summer of 2005), most of the narrow coarse and medium-sized pores in the plowed Ap horizon were completely filled with plant-available water. Complete recharge takes place in the wintertime. It also becomes clear that, due to the incorporation in the Ap horizon, the humus layer also stores considerably more plant-available water, which then becomes available to shallow-rooting plants for a longer period during the year. The course of the isopleths of the air contents in the soil is complementary to the course of the plant-available water.

The Stagnosol exhibits short-term fluctuating changes in the matric potential over the entire soil profile (Fig. 6.43).

During the vegetation period of the drought year 2003, the coarse pores in the topsoil started to drain as of July because of the intense water uptake by plants and reached down to the lower boundary of the Sw horizon, while in the Sd horizon the large coarse pores up to a depth of max. 120 cm are drained to −60 hPa. In the two subsequent wetter years even the narrow coarse pore range is no longer drained, with very brief interruptions.

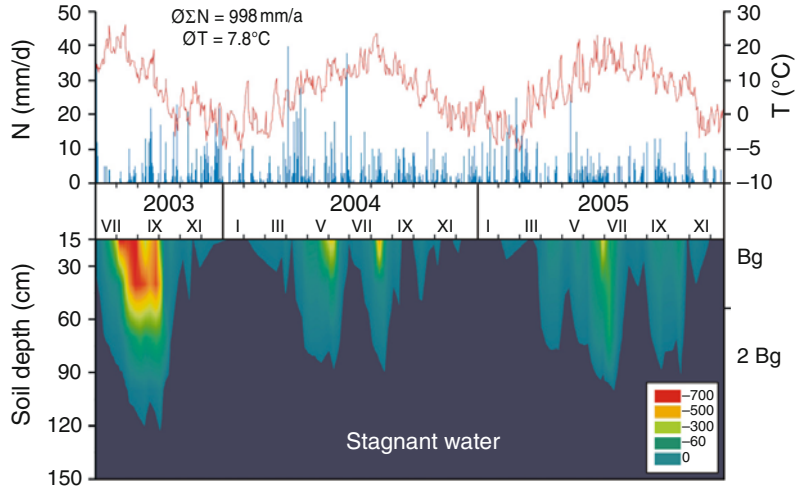

Fig. 6.43 Annual courses/patterns (2003–2005) of the matric potentials (hPa) in a Stagnosol developed from Saalian Stage over glacial clay under use as pasture (from Gebhardt 2007)

Stronger precipitation in the summer as well as higher precipitation in the winter half years result in a rapid resaturation and sometimes even complete recharge of the soil volume, and even lead to a short-term saturation of the soil up to the upper edge. Furthermore, it can be seen that despite the different precipitation and temperature conditions from one year to the next, there are soil type and site-dependent rules: In terrestrial soils, the field capacity generally represents the upper limit of the water content (see Fig. 6.31). Higher water contents only appear on the short term (Figs. 6.31 and 6.42). The drainage of soils beyond field capacity is primarily caused by plants, which, depending on the hydraulic conductivity and hydraulic gradients, could theoretically extract water up to the permanent wilting point (Fig. 6.31). However, the degree of water exploitation in the selected example is much lower and never reaches the value of the permanent wilting point, except maybe in the topmost soil layers that are exposed to evaporation. As a result, the extent of evapotranspiration and therefore of soil desiccation significantly depends on the unsaturated hydraulic conductivity and the hydraulic potential gradients during the course of soil desiccation. The more intense and the more evenly the soil is rooted, the more water is released into the atmosphere (cf. Fig. 6.38). However, the interpretation of long-term water balance measurements in Germany under different land uses have shown that there are only minor variations in the matric potentials under field and pasture use below a depth of 60–80 cm due to soil texture and structure, and values below −600 hPa were never observed in the evaluated ca. 300 experimental measurement years This also leads to the conclusion that especially in fine-grained soils, the theoretical quantity of stored plant-available water was never even close to being exhausted.

Because more water is added through precipitation during the course of the year than is evaporated under humid climate conditions, varying intensities of downward water movement ($\psi_H > 0$, in Fig. 6.30) can always be expected. This water movement, except for the topmost alternate wetting and drying zone, generally takes place in the form of a displacement, where the water fractions that are supplied later from the top push the earlier water fractions ahead of themselves. In the range of the soil profile in terrestrial soils, this downward movement happens almost solely in an unsaturated state. It can be interrupted during the vegetation period in the topmost parts of the soil, because upward transport due to evapotranspiration then dominates here ($\psi_H < 0$ in Fig. 6.30).

Between these two zones, which are characterized by upward or downward potential

gradients, a layer with the potential gradient $\psi_H = \pm 0$ can be observed. This layer, representing a **horizontal water divide** in the soil, moves downward in the profile during the course of the vegetation period. Under these conditions, water replenishment from the groundwater to the soil surface is only possible if the groundwater table is so high that the water divide drops below the GWS.

(b) **Groundwater recharge**

The quantity of seepage water, penetrating down to the groundwater through **deep percolation** and therefore providing groundwater recharge, is affected by two factor groups: (a) by the climate- and weather-related quantity and distribution of precipitation as well as evapotranspiration; (b) by the soil properties, such as the correlation between the matric potential on the one hand, and the hydraulic conductivity and water content on the other, as well as the infiltration capacity.

Groundwater recharge through the addition of seepage water varies considerably because it depends on the weather conditions. This is shown in Fig. 6.40 for a time period of 14 years respectively for a site with low groundwater and a site with high groundwater tables. Maximum infiltration generally lies in the period between December and May. In July to September, infiltration is lowest.

The effect of texture on the quantity of seepage water as a function of the depth to water table is shown in Fig. 6.44. It can be seen that with greater depths to the groundwater table, there are smaller amounts of seepage water in silty soils than in sandy and clayey soils. This is caused by the higher amount of plant-available water in the effective rooting zone. For this reason, with comparable precipitation during the vegetation period, silty and loamy soils have higher evapotranspiration than sandy and clayey soils. In the subsequent period (autumn and winter), silty soils need more water than sandy and clayey soils to reestablish field capacity and then a hydraulic gradient that is continuously going downward.

With small depths to the groundwater table, the varying water storage capacity of soils does not play a role, because the evapotranspiration and therefore also the infiltration are determined by the height of capillary rise. Figure 6.44 shows that for the same soils and climate, deep percolation (=groundwater recharge) very strongly depends on the land use. Thus, groundwater recharge decreases in the sequence field > grassland > coniferous forest.

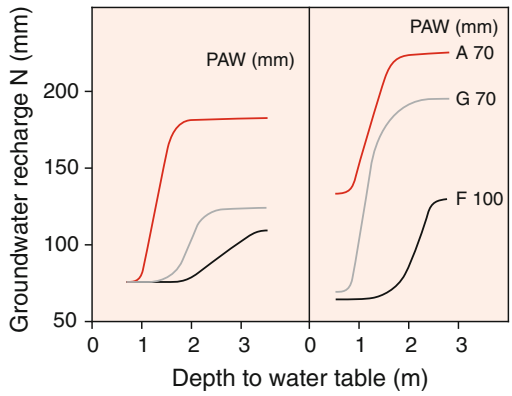

Fig. 6.44 Groundwater recharge *N* (mm) in the vegetation period (May–October) as a function of the depth to the groundwater table, plant-available water and soil texture (*left*), and the vegetation (*right*). *A* arable land, *G* grassland, *F* coniferous forest, *PAW* plant-available water in the effective rooting zone (after Renger et al. 1984)

6.4.6 Water Balance of Landscapes

The water balance of a soil at a given site is very significantly determined by its position within the close surroundings. Because this influences the entire soil development as well as the resulting soil properties, it is also necessary to consider the water balance of the surrounding landscape when analyzing the pedogenic properties of a site. Since water is always in movement in the soil, representation as a flow system is conducive. **Flow systems** are described by equipotentials, in the present case by contour lines of the terrain or of the free water body that is delimited by the GWS, by flow lines, and by the boundaries. The starting point of the flow lines for an arbitrary section in a

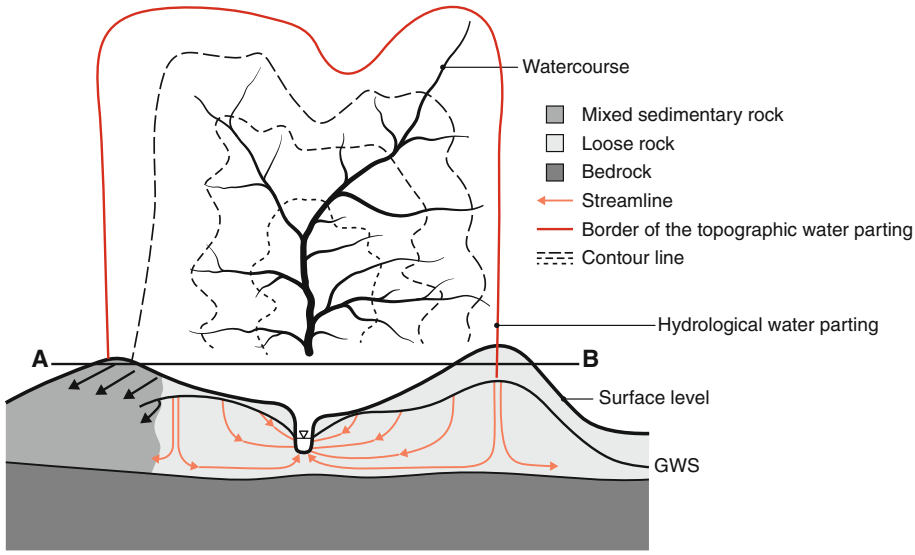

Fig. 6.45 Schema of a catchment area in a runoff situation. *Upper part* Top view, *lower part* terrain cross-section along the line *A–B*. The hydrological water divide defines the lateral boundaries of the water inflow

flow system is called the **source** (point, line or area source), and their end point is called **sink** (point, line or area sink). Using the example of a landscape, the open watercourses can be considered as **flow lines** in a first approximation. The water divide represents the boundary.

The water balance of a landscape is more difficult to record than that of a soil profile, because sources and sinks are not easily perceptible. Figure 6.45 shows a diagram with the correlation between the mentioned parameters and properties of the catchment basin.

6.4.6.1 Catchment Basins

The regional boundaries of an area, in whose water balance a soil is integrated, is determined by the catchment basin of the respective aboveground stream network. In hydrology, this is also called **receiving water system**. It is separated from adjacent catchment basins by water divides. **Water divides** are planes in the soil or bodies of rock through which there is no flow (cf. Fig. 6.35; cf. also the horizontal water divide, Sect. 6.4.5.2). Flow lines start from the water divides and run towards neighboring catchment basins. The hydrological water divides do not always concur with the course of the topographic contour lines. In general, however, the latter do provide initial indications of the hydrogeological conditions, and therefore also of the subsurface water divides (Fig. 6.45, bottom). Each catchment basin can be divided into a number of units of smaller order for which, in principle, the same conditions apply as for the superordinate basin.

6.4.6.2 Effect of Topography and Lithological Situation on the Water Balance

Figure 6.45 shows a schematic representation of a top view and vertical section of a landscape (top), consisting of jointed sedimentary rocks beside unconsolidated sediments over joint-free hard rock. The upper part of the Figure shows the course of the assumed contour lines and the surface waters (streams, rivers), which follow these contours. There is a correlation between the two, because water affects the geomorphological formations. In the example, the topographic divide on the right side of the figure concurs with the hydrological divide, because the unconsolidated rock exhibits identical, i.e. isotropic hydraulic conductivity in all spatial directions. This is not the case on the hill on the left side of the Figure, because the rock-related bedding planes on both

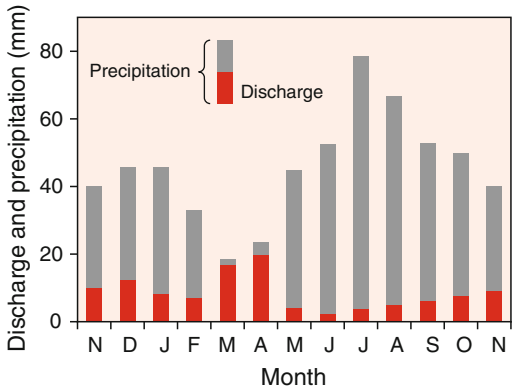

Fig. 6.46 Precipitation and monthly discharges from a catchment basin with an area of 88 ha near Uppsala (Sweden); mean values from 12 years (it starts and ends in November (N)). Clayey loam, annual precipitation 537 mm, mean annual discharge 98 mm, arable land use (after Hallgren and Tjernström 1966)

sides of the topographic divide conduct water out of the precipitation catchment basin.

6.4.6.3 Effect of Climate and Weather Conditions on the Water Balance

The diagram in Fig. 6.45 also shows a situation that can be observed under humid climate conditions in periods without a succession of flood events. The open channel here is fed by water that has traveled partly through the soil. The water leaves the catchment basin through this channel. The seasonal course of the quantity of effluent water depends on the weather and climate conditions.

As an example for the distribution within a year, Fig. 6.46 shows the measured discharge from an 88 ha catchment basin used as arable land, which is sealed towards the subsoil by clay layers. It can be seen that the average discharge in the 12-year measuring period does not correlate with the mean precipitation. Its maximum lies at the end of the winter half year and is intensified in March and April by snowmelt. The minimum in June results from the high evapotranspiration in this month.

Finally, it must be noted that there are certain points in the landscape where the free water comes particularly near the ground surface as groundwater (Fig. 6.47).

Here, its effect on soil development, caused by the topography, is different from the previously mentioned areas. Section 7.1, Factors of Soil Development, gives more details on this subject. Under arid climate conditions and under the influence of flooding, there is no inflow to the watercourse from the groundwater. In fact, the groundwater is fed by the high water levels in the watercourse. In deeper locations, far from the open channel, wet sites can develop with hydromorphic characteristics in the soils, such as gleying in humid climates and salt accumulation under arid conditions.

6.4.6.4 Effects of Water Movement on Soil Development

The water balance of a catchment basin affects soil development by influencing the intensity of infiltration or, under arid conditions, the rate of capillary rise.

The lower the soil water content, the more the dominating infiltration under humid conditions creates a gravitation-driven vertical translocation in the unsaturated soil profile. In the flowing

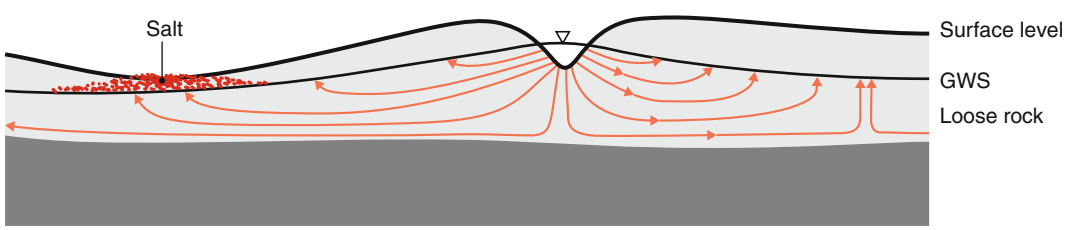

Fig. 6.47 Course of the groundwater surface (GWS) (groundwater dome) in an inflow situation, here for the case of an arid climate (natural river course, especially also channel irrigation). Under humid climate conditions, such patterns are observed under flood conditions

groundwater, in contrast, it essentially causes a lateral translocation of soluble substances. Another influencing factor is the non-infiltrated water fraction, which forms the surface water. This is the cause for water erosion (see Sect. 10.8.1).

Under forest vegetation, there is generally no formation of surface water, because loosening by bioturbation promotes infiltration. Instead, there can be landslides or earth flows on slopes when the combination of increase in weight, due to the infiltration of water, and pressure head (see Sects. 6.3.2.3 and 6.3.3.3) exceed the mobilizable shear resistance of the soil body.

Whether material transport by surface water within a hydrological catchment basin affects soil development as erosion or as accumulation depends on the location in the respective flow area and on the course of the discharge and therefore the flow, which are determined by the distribution of precipitation (cf. Sect. 7.2.7). In all cases, the landscape morphology then changes the water balance and therefore the soil development (Sect. 7.1)

Under arid conditions, evaporation due to the geomorphological proximity of the GWS leads to different accumulations of evaporation residues, i.e. salts. For this reason, salt accumulation can always be expected in such landscapes, in fact, the stronger the more the GWS approaches the ground surface (Fig. 6.47). This is caused by the high local evaporation, resulting from the constant high replenishment with existing high water contents and the associated high hydraulic conductivity (cf. Fig. 6.38). The direction of the flow lines when touching the GWS (cf. Fig. 6.45) and their relative concentration in the sink area (Fig. 6.47) also result from the change in the hydraulic conductivity occurring there. This, in turn, is caused by the different water saturations and flow cross-sections (Fig. 6.38).

6.4.6.5 Calculations

Depending on the type of available data and the goal of the interpretation, different approaches are used that are principally based on the general equation for a water balance, the water budget.

(a) **Water budget**

The water budget can be expressed in a general form as follows:

$$P + (I) = D + E + R \qquad (6.53)$$

The terms are defined as follows:

- P = Water input through precipitation. In the calculation for a catchment basin as shown in Fig. 6.45, it is the only source. This input is generally given in mm (L m^{-2}).
- (I) = Input from the soil body or through free-flowing channels. These include artesian situations (i.e. water standing under pressure) and water input from precipitation areas located upstream. Inputs of this type always represent a problem for the interpretation of discharge measurements under the conditions shown in Fig. 6.46.
- D = Discharge from the catchment basin attributed to P (mm or L m^{-2}). This includes the discharge volume that is measured in the main channel (Fig. 6.45) as well as groundwater flow that may be flowing beside and underneath the free flow cross-section.
- E = Evaporation from the attributed catchment basin. This parameter is either determined as a difference member/differentiating element or calculated from the sum of the evaporation at the soil surface (=evaporation) and transpiration of the vegetation (evapotranspiration, see Sect. 6.4.4.2) using meteorological data and empirical correction factors for the vegetation (mm, see Sect. 6.4.4.2). It then includes the potential evapotranspiration (ET_p) or approximations thereof using correction factors that are based on the vegetation. The simplest calculation method is the formula from Haude, which only requires the measurement of the water vapor saturation deficit of the air at 14:00 ($e_s - e$; see Sect. 6.4.4.2). b is a variable month factor that ranges between 0.27 and 0.54:

$$ET_p = b(e_s - e) \quad (6.54)$$

- R = Changes in water storage; this parameter is only relevant for the observation of short periods of time. It then has a positive prefix for predominant water input, and a negative prefix for predominant water loss. It can be neglected for longer periods of time, if the hydro(geo)logical situation has not changed. In the case of changes, e.g. through the construction of weirs, it is expressed by a change in the level of the GWS, and associated with changes in the water contents in the unsaturated range above the GWS as well as in the water level of the surface waters. In addition to hydraulic engineering measures, such changes can also occur through changes in land use (cf. Fig. 6.44), and on the long term, as a result of changes in the morphology through substance translocation.

(b) **Flow paths**

For landscape water balances, in addition to the budgets, the path taken by the individual quantity fractions of water from the source to the sink through the observed landscape is important. This is especially true for the path taken by water constituents according to the flow path. For such flow paths, the point of entry (contamination point) is the source. Any area that must be crossed by the respective water quantity during the course of its flow can be considered as a sink.

Schematic flow networks can be drawn to follow the paths of the individual quantity fractions by determining the sources and sinks, and then following the flow paths between them. The required equipotentials can be defined through measurement of the water pressures with piezometers or water pipes (Sect. 6.4.1.1; Fig. 6.29). An initial rough estimation can then be obtained using the course of the contour lines on topographic maps.

Marking technology with **tracers**, which is an extensive working field of its own, is used to follow the flow paths directly. For the interpretation of data obtained from measurements in conjunction with the landscape water balance, there is an extensive collection of evaluations methods, especially in the form of simulation models.

6.5 Soil Air

All parts of the soil's pore volume that are not filled with water contain air. Because water has a higher density than air, all of the water tends to collect in the deepest zones of the pore space due to the acceleration of gravity. In doing so, the air is more or less fully displaced and can only fill the pore fractions that could not be filled by the existing water volume. In principle, these are the pores that are located higher in the profile near the soil surface. Because water is more strongly adsorbed to the surfaces of solid soil particles than air, and also has a considerable boundary tension towards water, part of it is found above the groundwater in the unsaturated soil zone. This water fraction also reduces the volume remaining for soil air. Because water in an adsorbed state always fills the narrowest pore range first, the widest pores remain open for air.

The amount of air contained in a specific soil at a specific depth therefore depends on the water content and also on the water balance-determining soil properties and ambient conditions.

The pore volume and pore size distribution are therefore decisive soil properties for the air fraction in the soil. Since these are subject to strong fluctuations during the course of soil development and due to tillage measures in arable soils, the air content of soils is a parameter that varies within a broad range.

In general, the air fraction in the total volume of mineral soils fluctuates between 0 and 40 %. The **field capacity** gives an indication of the lower limit of the air contents that are commonly observed in terrestrial soils, because it indicates the most probable maximum degree of filling of the pores with water. At field capacity, the average air volume is about 30–40 % in sandy soils, 10–25 % in silty and loamy soils, and

5–l0 % or less in clayey soils, depending on the degree of compaction (see Sect. 6.4; Fig. 6.31).

However, the actual air content is generally higher, because soils only rarely exhibit a water content corresponding to field capacity during the vegetation period.

6.5.1 Composition and Origin of the Constituents

The composition of the soil air is influenced by biological processes taking place in the pores, and depending on the type and extent of these processes, it therefore deviates more or less strongly from that of the atmospheric air. The deviations in the composition consist of a reduction in the O_2 fraction, an increase in the CO_2 fraction, and a water vapor content that is generally close to saturation.

In connection with microbial activities, other gases are also formed, among which methane (CH_4) and nitrous oxide (*laughing gas*, N_2O) have special significance due to their contribution to global atmospheric warming (*greenhouse effect*) (Sect. 6.5.3.1). In addition, other trace gases are also found, including nitrogen oxides (NO_x), carbon monoxide (CO), ammonia (NH_3) and more. In the presence of any metabolic processes, the **oxygen content** in the soil air is lower than in the atmosphere, because the consumed fractions are only slowly replaced from the atmospheric air. It is therefore lower the more intense the root growth and the metabolic activity of the edaphon (see Sect. 4.1). For the same reason, it decreases with increasing depth in the soil, and is lower in fine-grained soils than in coarse-grained, and lower in wetter than in drier soils. In seasons with low biological activity, the oxygen content is therefore also lower than in periods with slow metabolic activity (Fig. 6.48).

The **CO_2 content** in the soil air is generally higher than in the atmosphere, because CO_2 is produced by the respiration of the roots and the edaphon. It is therefore higher in deeper soil layers than near the soil surface, higher in fine-grained soils than in coarse-grained, higher in wet than in dry soils, and higher in seasons with high biological activity in the soil than in seasons with minor metabolic activity (Fig. 6.48).

The CO_2 development in soils under aerobic conditions is equimolar with the O_2 consumption, and therefore does not result in a change in gas pressure. This is characterized by a **respiration quotient** (*d*) of 1:

$$RQ = \frac{\text{mol } CO_2}{\text{mol } O_2} \tag{6.55}$$

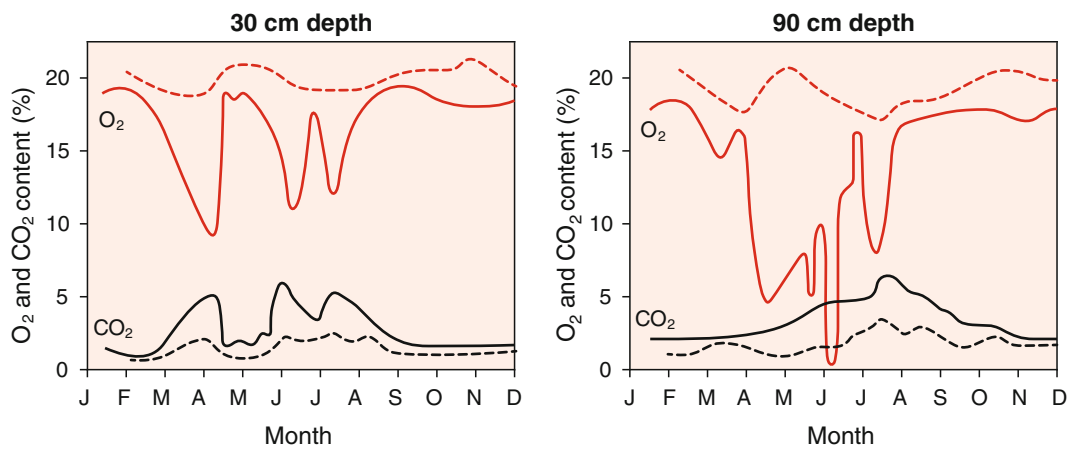

Fig. 6.48 Oxygen and carbon dioxide contents in the soil air at depths of 30 and 90 cm throughout the year from January (J) to December (D) in a sandy loam (*dashed curve*) and a silty clay (*solid curve*) under apple trees (Boynton and Compton 1944)

Because CO_2 has a higher solubility in water than oxygen, the overall observation of the individual gas volumes must also take account of the dissolved fractions in the soil water. Under these conditions, the quantity of gases that is transformed in the soil, i.e. newly formed and locally consumed is subject to strong fluctuations. On average, about 4000 m^3 (8000 kg) of CO_2 ha^{-1} a^{-1} are released into the atmosphere from forest and arable land, of which about 2/3 comes from the activity of soil organisms and 1/3 from root respiration. However, these quantities vary with the type of vegetation, the amount of organic matter, the fertilization, the season, etc. CO_2 production increases with the addition of organic matter to the soil and with the mineralization of vegetation residues. Furthermore, it is strongly affected by the temperature and humidity of the soil, so that it is subject to daily and seasonal fluctuations.

The maximum production usually lies relatively near the soil surface. Immediately below the surface, however, the production is often low because of the relatively high desiccation (Fig. 6.49).

The **water vapor content** in the soil air is higher than that in the atmosphere. It strongly depends on the soil temperature, because the water uptake capacity of the air increases with increasing temperature. For this reason, changes in temperature lead to considerable water movement in soils, which are described in more detail in the section on soil temperature (Sect. 6.6).

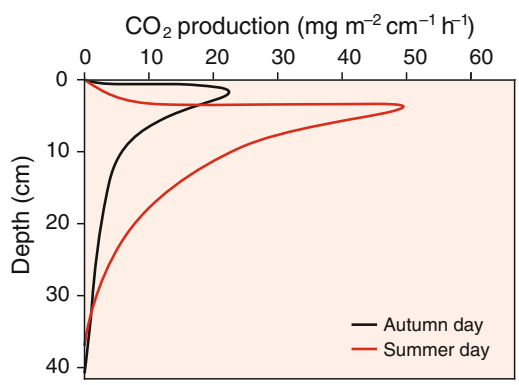

Fig. 6.49 CO_2 production as a function of depth in a loess Luvisol under arable land use (from Richter and Großgebauer 1978)

The relative humidity of the soil air is higher than that of the atmosphere, and is greater than 95 % at all matric potentials <pF 4.2. Because pF values higher than 4.2 are hardly ever observed in subsoils outside of deserts, the relative air humidity seldom falls below 95 %. However, in the topsoil, especially in the topmost 2 cm, the air humidity can drop lower because the soil here often dries out more strongly (pF > 4.2), even in humid climate regions.

In addition to carbon dioxide, the decomposition and transformation of org. matter also leads to the formation of other gaseous carbon and nitrogen compounds. Methane is produced simultaneously with carbon dioxide through the metabolic activity of anaerobic microorganisms. For this reason, more methane is found the wetter the soils containing decomposable org. matter, i.e. mainly in subhydric, semi-terrestrial soils and moors. Wetlands and paddy rice soils are the most important sources of soil-borne methane. **Methane production** takes place extensively as *marsh gas* in moors, sapropels Thioni-Limni-Subaquatic Fluvisol (Sect. 7.5.19.1) and mudflats. It increases with temperature, and under otherwise identical conditions, it increases from swamp cane brakes through to fens, and depending on the pH etc., up to bogs. In paddy rice cultivation, it can reach particularly high intensities because of the high temperatures. On a more local scale, methane is produced under livestock compounds, especially of ruminants, as well as in waste, sewage and harbor sludge landfills (biogas, landfill gas). Apart from these sites with high production, methane is also produced in all soils directly near the GWS. Here, the respiration coefficient can reach a value of 10.

While there are no changes in the number of gas molecules and therefore in the gas pressure (respiration quotient = 1) in the aerobic zone, because oxygen consumption and carbon dioxide formation are equimolar according to the molecular formula (example: glucose degradation),

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + 2800\,\text{KJ}\,\text{mol}^{-1} \quad (6.56)$$

in the anoxic zone, there is a new formation of gas molecules according to the molecular formula:

$$C_6H_{12}O_6 \rightarrow 3CO_2 + 3CH_4 + 188\,\mathrm{KJ\,mol^{-1}} \tag{6.57}$$

This leads to an increase in the gas pressure when the pressure equalization is impeded.

Nitrous oxide (N_2O, laughing gas) is produced in soils as a gaseous byproduct with all nitrification and denitrification processes. Its formation is strongest in the topmost soil zones. In a beech forest, there was an annual production between 0.6 and 2.2 kg N_2O–N a^{-1} ha^{-1} at a depth of 7 cm and in the range of pH 4.3–7.2, regardless of the extent of denitrification. Increasing use of N fertilizers makes agricultural soils one of the most intensive sources. In global terms, wet forest soils are the most significant producers.

Ammonia is released in alkaline and therefore also calcareous soils. Due to the predominantly low pH-values, the liberation from the large areas of tundra and boreal coniferous forest regions (taiga) is low. It is usually negligible because of the short turnover time of ammonia in the atmosphere. In these regions, the low levels of biological activity resulting from low temperatures impede oxidation to form nitrate.

6.5.2 Transport Mechanisms

The uneven distribution of various gas components within the soil air, resulting from the location, geometric development and intensity of the sources and sinks, seeks to reach a state of equilibrium. The equalizing movement takes place through convection and diffusion.

Convective gas transport can result from barometric or temperature-related changes in volume. Furthermore, the effect of wind over vegetation-free soils can also cause convective gas transport due to turbulence, and flowing groundwater can also cause inputs or outputs of dissolved gases. Convective movement occurs when the rainwater initially penetrates into the coarse pores and displaces air out of the respective narrowest pores, so that it collects in the wider pores. Flood irrigation can also sometimes lead to local increases in pressure in the gaseous phase, and therefore to convective translocation of air bubbles/pockets.

The new formation of gases in the soil also leads to convective flow. This is always the case when methane and carbon dioxide are formed under anoxic conditions. N_2O formation must also lead to convective gas movement, because the number of gas molecules increases and therefore the pressure gradient becomes greater. This is negligible for N_2O because of the small quantities involved, however, for methane, a reduction in pressure leads to the formation of gas bubbles/pockets and to active leakage from landfill bodies and moors.

Finally, convection can be caused by rising and lowering of the groundwater surface in the soil. This process leads to strong convective gas exchange especially under the water balance conditions found in the flooding zones of riparian floodplain soils.

However, **diffusion** as an equalizing movement is generally more significant, because it does not require a pressure gradient within the entire gas phase; partial pressure gradients and therefore concentration gradients are the sole cause. Here, in turn, diffusion within the soil air plays the most important role for the overall concentration balance, because diffusion within the soil water is about 10^4 times lower than in the air. As a result of this, the entire process of diffusive gas transport is strongly affected by the quantity and even more by the distribution of water in the pore space (Fig. 6.50). In contrast to convection, however, diffusion is not totally interrupted by the exclusion of gas volumes, e.g. by water.

The lower diffusion through water is significant because of the influx of oxygen and the transportation of carbon dioxide towards or away from the roots, since these are always surrounded by a thin water film.

For the steady state, i.e. unchanging state over the course of time, diffusive movement of gas molecules in the soil can be described by the 1st Fick' Law:

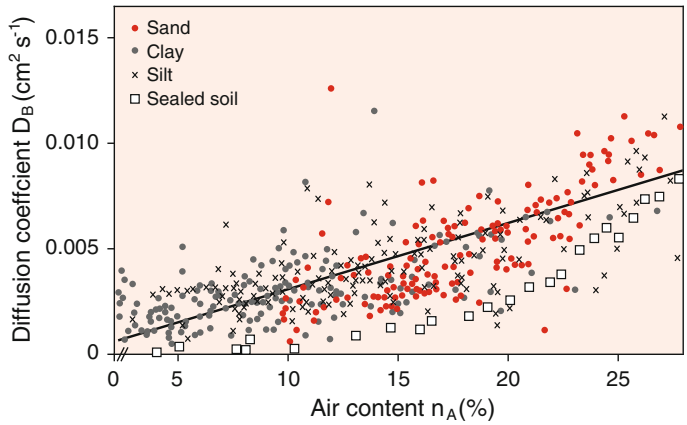

Fig. 6.50 Diffusion coefficient for CO_2 (D_S) in soils depending on the air content (n_A) (Richter and Großgebauer 1978)

$$I = -D_s \frac{dc}{dx} \tag{6.58}$$

Here, I is the gas flow in mol per unit of time and area, c is the concentration (mol cm^{-3}), x is the diffusion path (cm), and D_S is the diffusion coefficient (cm^2 s^{-1}).

The diffusing molecules collide with the molecules of all the substances in their surroundings. For this reason, the diffusion coefficient for any gas, in addition to the size of the diffusing molecules themselves, depends on the type of medium where the diffusion is taking place. This means that both the composition of the gas phase and its spatial distribution, and in the range of the aqueous phase of the soil, also the salt content of the water influence the diffusion coefficient.

This fact is taken into account by relating the diffusion coefficient to the air-filled pore fraction n_A (Fig. 6.50) and introducing a correction factor τ, which describes the difference between the diffusion coefficient in the air (D_A) and in the soil (D_S):

$$D_S = -1/\tau \cdot n_A \cdot D_A \tag{6.59}$$

The more tortuous the pores in the soil, the more strongly the gas flow is delayed. For a given gas, e.g. CO_2, the relationship between D_S and n_A can also be used to characterize a soil structure. The diffusion coefficient in the soil (D_S) is often also called 'apparent'. The effects of the various inherent diffusions of the gas components caused by the molecule size are overshadowed by those caused by the shape and size of the air volume.

Because all gases are more or less strongly water soluble, their contents in the soil water vary. These quantities depend on the pressure and temperature. For this reason, there are more gases dissolved in the water below the GWS than in the unsaturated zone. This is true for all gases, especially for CO_2, but is particularly noticeable with H_2S when subhydric soils e.g. Thioni-Limni-Subaquatic Fluvisol (Sect. 7.5.19.1) and horizons in the groundwater zone are dug up, because in doing so, the 'overburden' pressure on the gas and water is suddenly reduced.

Oxygen enters the soil air through the soil surface. Therefore, in terms of a potential distribution, it is an area source. The potential sink is the diffuse zone of O_2 consumption, which is greatest near the soil surface (see also Fig. 6.49). Diffusion in underlying soil layers therefore always depends on the remaining partial pressure gradient.

For CO_2, the production maximum of the potential source generally lies at a soil depth between about 10 and 50 cm. Their intensity as a function of soil depth is shown in Fig. 6.49. The soil surface in contact with the atmospheric air is the potential sink for CO_2.

The fact that high CO_2 concentrations can be found (Fig. 6.48) at greater soil depths, despite the intensity distribution of the CO_2 source shown in Fig. 6.49, is a result of the position of the potential source and sink relative to each other. In periods of increasing CO_2 production, the concentration maximum lies in the area of maximum production. The liberated CO_2 is transported to the soil surface through diffusion,

and to a lesser extent also to the subsoil. When the CO_2 production decreases in midsummer and winter in the range of the early summer or autumn maximum, the diffusion flows upwards in the entire soil profile, because there are still high concentrations in the subsoil.

6.5.3 Gas Balance

As a result of convection and diffusion, the quantity and composition of the soil air are in constant exchange with atmospheric air. Here, the atmosphere is the source of oxygen, the soil is the sink, and their respective potentials determine the **diffusion rate**. The sources and sinks, between which the translocation of the other gases takes place, are not always be clearly established.

6.5.3.1 Gas Balance and the Environment

As already described at the beginning of Sect. 6.5.1, mainly carbon dioxide, methane and nitrous oxide (*laughing gas*) are formed in the soil pore space. Compared to these, the quantities of all other soil-borne components are so small that they can be neglected here. Gases from the soil enter the air space. This takes place through the described processes of diffusion and convection (Sect. 6.5.2). From there, a portion is returned to the soil, and a portion can escape all the way to the stratosphere. This latter portion is given increasing attention, because it is considered to be one of the causes for the currently observed trend towards global warming (**greenhouse effect**).

The **return** into the soil requires consumption, i.e. fixation. On global terms, the soil is an important sink for **carbon dioxide** if there is organic matter accumulation. Inversely, it adopts a source function when the organic matter content decreases. Triggering factors can be weather conditions, changes in land use, and especially the changing accessibility of the adsorption surface associated with aggregate formation in the soil (e.g. due to denser pore walls), but also changes in the composition of the vegetation.

Changes in the water balance with an increase in wetness can lead not only to an accumulation of org. matter due to reduced decomposition, i.e. give the soil a sink function, but also can also inversely cause very significant liberation. For example, a liberation of ca. 1 Mt of C (≈3.5 Mt of CO_2) per year was calculated as a result of draining 1000–2000 ha of forest in Sweden. Very different cycles can be observed in individual cases.

In terms of quantity, the fixation of CO_2 mainly takes place through the production of org. matter by higher plants and their subsequent conversion. Ultimately, it leads to the filling of the CO_2 pool in the form of org. matter in the soil.

Beside carbon dioxide, **methane** is the most strongly involved soil-borne gas in the overall gas balance. The pressure gradient, which forces free convection, plays an important role here because of its conditions of formation (Sect. 6.5.1). It leads to greater translocations than diffusion alone. This is demonstrated when gas bubbles rise out of wet organic substrates (e.g. subhydric soils like dy (Humi-Limni-Subaquatic Fluvisol), Calci-Limni-Subaquatic Fluvisol, Thioni-Limni-Subaquatic Fluvisol (Sect. 7.5.19.1)). Because methane is decomposed by bacteria in the presence of oxygen, it only enters the atmosphere when no oxygen can enter the soil because of the mass flow of CO_2–CH_4 mixture. The drainage of moors therefore leads to the oxidation of CH_4 in the topsoil that was produced in deeper zones. On the other hand, e.g. as a result of soil deformation, a corresponding accumulation of methane must always be expected, especially in silty, loamy and also clayey soils, when impeded oxygen supply allows obligate anaerobic organisms (see Sect. 4.1) to continue reducing the still existing CO_2 for their own energy balance. This leads to the formation of CH_4 at low (negative) redox potentials. Sources of methane in soils are therefore always surrounded by a zone with high CO_2 concentration.

In addition to this source characteristic, the soil can also represent a sink for methane. This is the case when methane-decomposing bacteria, which are always present in the soil, lower the CH_4 concentration in the soil air under strongly aerobic conditions such that diffusive transport

takes place into the soil from the atmosphere. This process, observed both in forests and in arable agriculture, is inhibited by the input of nitrogen through fertilization. In terms of its influence on the greenhouse effect, methane is 32 times more harmful than CO_2.

Every nitrification and denitrification is associated with the liberation of **nitrous oxide** (laughing gas, N_2O). Increasing nitrogen inputs in soils also stimulate the production of soil-borne N_2O. It is assumed that up to almost 10 % of the nitrogen gas escaping from soils into the atmosphere is in the form of N_2O. In contrast to carbon dioxide and methane, there is no known constellation where the soil acts as a sink for a flow of N_2O. In terms of the greenhouse effect, nitrous oxide is ca. 300 times more harmful than carbon dioxide.

6.6 Soil Temperature

The thermal properties and thermal energy balance of soils can be most easily investigated using the **thermal state**, measured with the temperature. In contrast, the thermal capacity characteristics of soils, e.g. the heat content or the specific heat capacity, is much more difficult to determine and is of lesser importance in pedogenic investigations than the temperature measurement. Especially when working in the field, almost only temperatures are measured when statements are required on the thermal energy balance of soils.

As a result of these measuring circumstances, it is difficult to recognize a series of principal parallelisms between the heat/thermal balance and the water balance in the soil. This is because contrary to the thermal properties, the hydrological properties have always been measured through their capacity. The energetic approach, i.e. based on the potentials, has only been gradually adopted here in the last few decades. For this reason, investigations on the heat in soils are designed differently than for water. In principle, however, the capacities, potentials and transports are also decisive here for the observed processes and states.

6.6.1 Significance of Thermal Phenomena

For the assessment of the thermal properties of soils, in addition to their effects on chemical and physical processes of soil development, the effect on biological processes in the soil and on the growth of higher plants was the focus of interest for a long time.

In the last few decades, new points of view have appeared, e.g. the utilization of heat stored in the soil or the possibility of expanding cropland in cold climates or the influence of the surface temperature on the climate. There are also interactions in connection with the observed global warming.

6.6.2 Energy Gains and Losses

The thermal energy of soils, the magnitude of which is recorded through temperature measurements due to technical reasons, comes from several sources. The most important by far is the sun. In comparison, geothermal energy or microbial conversion during the decomposition of org. matter is of lesser importance. However, both can supply such considerable local and temporary amounts of heat that they can even be used for technical purposes. This is true e.g. for org. matter, which was formerly often used in horticulture for substrate heating (hotbeds), as well as for regions with volcanic activity. Here, water that was heated by geothermal energy can be used to generate electricity, but also to heat greenhouses.

The effects of advective energy input with flowing water are similar to the warming in cities. This plays a role in the spring in temperate latitudes (*warm spring rain*). At higher latitudes (tundra), heat input with summer rain is a decisive factor for the soil heat balance. On the large scale, heat input with fluvial water in Siberia e.g. enables the cultivation of soils further north near rivers flowing from the south than in areas that are far from the rivers.

There are basically two independent primary thermal sources of energy, the sun and the Earth

body, both of which can act over extensive areas, and there are secondary sources of energy, the effect of which is limited, still, it can sometimes be temporarily decisive on a regional scale.

The **energy input** from solar radiation consists of three parts: (1) the direct radiation, (2) the indirect radiation after reflection and scattering through the atmosphere, and (3) the thermal radiation of energy that was previously adsorbed by the atmosphere.

This energy input is opposed by an **energy loss**, which can be just as important over long periods of time, e.g. one or several years, and over large areas. This correlation is demonstrated by the fact that despite constant solar radiation, the surface temperature of the Earth does not change appreciably, so that it is sensible to provide mean soil temperatures for specific sites and periods of time.

The cause for energy losses out of the soil is mainly the radiation, which has longer waves than the radiation due to **Wien's displacement law**. This *dark earth radiation* or *terrestrial radiation* depends on the temperature of the soil surface, and lies for the most part in the range of heat radiation. It is the decisive component for heating of the air near the soil. A second process leading to energy losses is evaporation, during the course of which the soil looses vaporization heat. Only a small portion is temporarily returned to the soil on a small scale with frost and dew formation. The majority is only released with the condensation of water vapor in the atmosphere.

Apart from this large-scale phenomenon, there are several others that are significant on a small scale. This primarily includes the incidence angle of the sunbeams and therefore the **inclination**, i.e. the angle of the soil surface towards the horizontal plane. Furthermore, the **exposure**, i.e. the orientation of this angle with regards to the geographic direction, plays a decisive role.

Changes in the radiation due to the inclination and exposure depend on the season and time of day, and on the latitude of the site. Another factor of this type is the position in the energy input field of the Earth. This includes all restrictions of the amounts of radiation due to impurities in the atmosphere. For this reason, there is particularly strong direct radiation at high altitudes a.s.l., and particularly low direct radiation under the smog dome of low-lying highly industrialized and populated metropolitan areas.

Finally, the absorption capacity of the soil surface should be mentioned, which depends on the color of the soil and its properties, especially the roughness. Because dark soils reflect less radiation, they become about ≈3 °C warmer up to a depth of ca. 20 cm than light-colored soils with similar properties. For the surface roughness, mainly organic layers play a role, such as natural humus layers or mulch, and also cultivation methods and the produced structural forms.

6.6.3 Thermal Properties

Like the surface of any body, the soil surface also has a specific **absorption capacity**. Only the absorbed fraction of the radiation has an effect on the soil temperature. The fraction that is not absorbed is reflected. In meteorology, this is called **albedo**. The correlation between soil properties and the albedo is an important parameter for remote sensing. For soils (Fig. 6.51), it lies between about 5 and 60 %, which corresponds to an absorption of 40–95 %. The color of the soil surface is decisive here. Therefore, the org. matter content, its color, and the soil moisture are important factors. The vegetation cover also has an important influence. Black and white aerial photos provide a good impression, where water surfaces almost appear to be black (cf. Fig. 6.51).

In contrast to the previous property, the heat capacity is a purely intrapedogenic parameter, i.e. it is not affected by external influences. This term generally designates a **specific capacity**, and not the total capacity. It is the product of the specific heat (c) and the density (ρ), and indicates the amount of heat required to warm up 1 unit of volume of soil by 1 unit of heat ($c \cdot \rho = c^{w}$). The units here are J cm^{-3} K^{-1}. This value differs for the various soil components (Table 6.9) and is

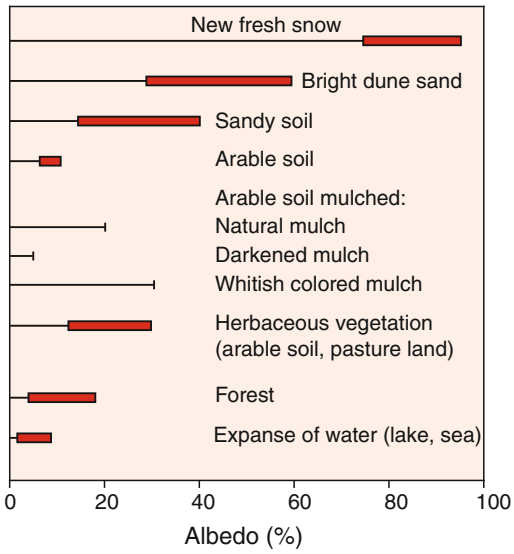

Fig. 6.51 Albedo of different soil surfaces and vegetation types, water surfaces and fresh snow (after Geiger 1961; Sharratt and Campbell 1994). The values for dune sand, sandy soil and arable land (Ap) in a dry state lie on the *right side of the bar*, and in a wet state on the *left side*

Table 6.9 Thermal conductivity (λ) and heat capacity (c) of soil constituents (after Bolt and Miller 1958, modified)

Soil constituents	(λ) (J cm^{-1} s^{-1} K^{-1})	(c) (J cm^{-3} K^{-1})
Quartz	8.8×10^{-2}	2.1
Clay minerals	2.9×10^{-2}	2.1
Humus	2.5×10^{-3}	2.5
Water	5.7×10^{-3}	4.2
Ice	2.2×10^{-2}	1.9
Air	2.5×10^{-4}	1.3×10^{-3}

also very strongly dependent on the water content (Fig. 6.52), because water has the highest specific heat capacity among all the soil constituents.

Another important parameter for thermal phenomena is the **thermal conductivity** (λ). It indicates the amount of heat (I) that flows in one second through a cross-section of 1 cm^2 under a gradient of 1 K cm^{-1}. This delivers a simple transport equation with a structure similar to that of the Darcy equation (Sect. 6.4.3):

$$I = \lambda \frac{\partial T}{\partial x} \tag{6.60}$$

The units for λ here also depend on the selection of the heat units. They are listed in Table 6.9. The values for the soil components in the Table apply for continuous pore-free substance.

However, because soils consist of individual particles, and are therefore discontinuous in terms of the solid substance, the thermal conductivity of the disturbed soil volume depends on the number of contact points. It is therefore affected by the bulk density and by the contribution of the water menisci in the magnitude of the conducting cross-section, i.e. by the water content. This correlation is shown in Fig. 6.52.

Because determination of the thermal conductivity (λ) is laborious, the **thermal diffusivity** ($\lambda\ c^{-1}\ \rho^{-1}$) is often measured instead, which is easier to determine. It is calculated from the change in temperature as a function of time (t) and distance (x), and can in turn be used to determine the thermal conductivity if the specific heat capacity of the soil is known. It is described by the following formula:

$$\frac{\partial T}{\partial t} = \frac{\lambda}{c \cdot \rho} \cdot \frac{\partial^2 T}{\partial x^2} \tag{6.61}$$

Like the two other properties, the themal diffusivity strongly depends on the water content of soils (see Fig. 6.52).

6.6.4 Heat Movement

Heat movement takes place in all soils when there are differences in temperature. This is the rule in soils, the isothermal state is the exception (Fig. 6.53).

Two mechanisms cause heat equalization movements in the soil: **heat transfer** and **convection**. While the former is always taking place, the latter is bound to the presence of a mobile carrier. This carrier is generally water. In the liquid phase, it is an effective carrier because of its high heat capacity. In the gaseous phase, although it has a low capacity, it is compensated

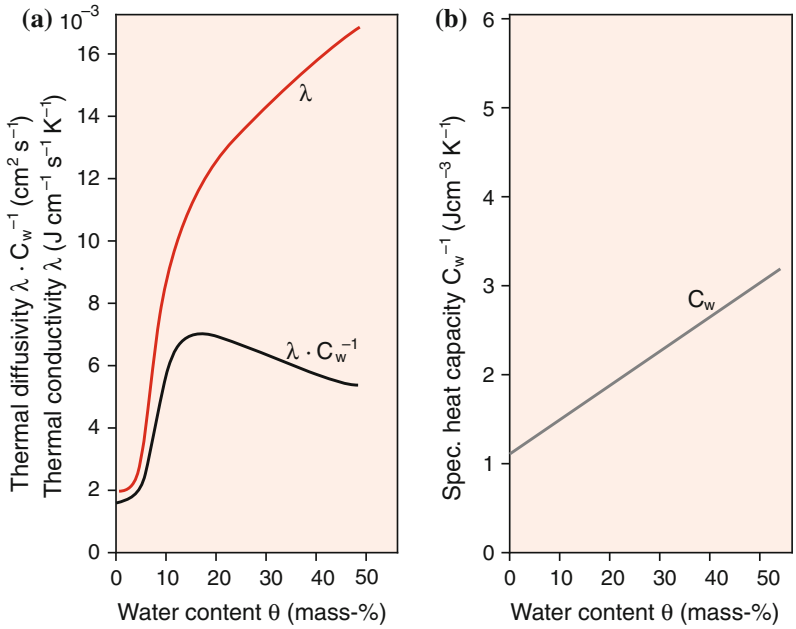

Fig. 6.52 Relationship between **a** the thermal conductivity λ, thermal diffusivity $\lambda \cdot C_W^{-1}$ as well as **b** specific heat capacity (C_W) of the soil depending on the water content

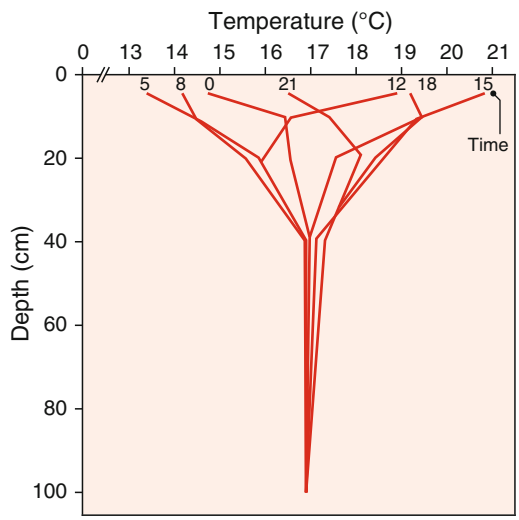

Fig. 6.53 Lines of simultaneous temperatures (isochrones) in a sandy Cambisol near Worpswede on a day in August. See also Fig. 6.54 (after Miess 1968)

by the high vaporization or condensation heat (ca. 2500 J g^{-1}). For this reason, in non-saturated soils, **water vapor transport** plays a considerable role as a heat transport mechanism. This is especially true when large temperature differences occur, i.e. under vegetation-free soil surfaces, and in connection with soil heating as it is used e.g. in horticulture. Therefore, in unsaturated soils, there is a coupling of heat and water transport.

Heat transfer is particularly effective when not only the heat of condensation, but also the heat of solidification of water (ca. 300 J g^{-1}) is released with the transition to the solid phase (=ice). In conjunction with largely unimpeded dissipation out of the soil into the atmosphere, this strong heat release at the phase transition is an important cause for the fact that even in uncovered soils, the soil temperature in the range below 0 °C only closely follows a further drop in air temperature in the topmost 2–3 cm. In the underlying soil zones, the more space there is for the inflow of additional water, the more slowly the temperatures follow the decrease of the air temperature. For this reason, they generally remain much higher.

The other mechanism, **heat transfer**, strongly depends on the extent of the conducting cross-section in the soil. Because of the low thermal conductivity of air, this cross-section strongly depends on the water content. Low water contents, because of their meniscus-shaped distribution in the soil, cause particularly strong increases in the flow cross-section and therefore

lead to greater transport quantities. This results in a more rapid rise in temperature in the entire soil body (Fig. 6.52). At the same time, however, because water requires high amounts of energy to be heated due to its high heat capacity, there is a point where the increase in transport, resulting from the increase in the flow cross-section and therefore the conductivity, is compensated by the increase in capacity. The latter inhibits the regional increase in temperature that would be required for continued transport, and therefore also the formation of strong temperature gradients. This eventually leads to the decrease in temperature conductivity shown in Fig. 6.52.

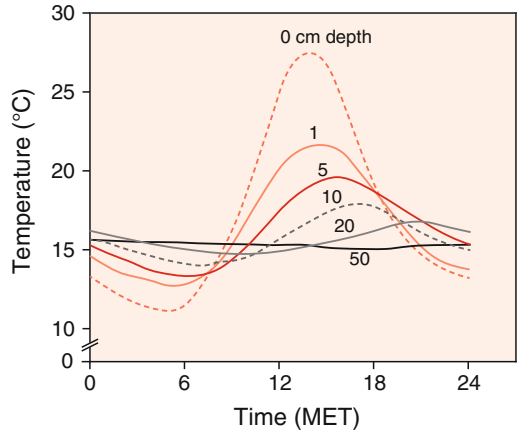

Fig. 6.54 Daily course of temperatures as a function of depth in a sandy Cambisol near Worpswede in August (high pressure weather conditions, same soil as in Fig. 6.55) (after Miess 1968)

6.6.5 Heat Balance

The strongest energy input, solar radiation, strikes the soil surface. The strongest removal, the emission out to space, also originates from this zone. For this reason, the soil surface is the zone with the strongest temperature fluctuations. From here, both the air and the inside of the soil are warmed up or cooled off.

In view of this, the interaction of the factors described in the previous section determines the magnitude and change of the soil's heat contents and thermal state, depending on the site, time and soil depth. This results in the heat balance.

6.6.5.1 Natural Heat Balance

Regular periodic alternation of the predominance of radiation and emission results in likewise regular temperature fluctuations in the soil. Because radiation and emission take place at the soil surface, this is where the amplitude of the temperature fluctuations is greatest.

This is true both for the diurnal (Fig. 6.54) and for the seasonal variations in temperature (Fig. 6.55). This general course is affected by the soil properties and ambient conditions.

The former includes the heat capacity, which usually has a damping effect on the temperature amplitudes, regardless of whether they are caused by a high bulk density or high water content. The second important soil property is the thermal conductivity. Here, high values have a

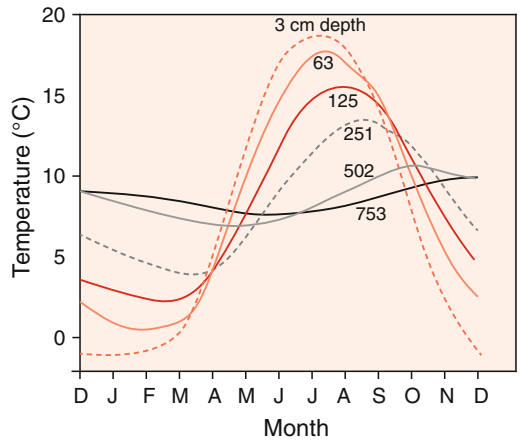

Fig. 6.55 Annual course of temperatures as a function of depth in a soil near Königsberg from December D onwards (after SCHMIDT and LEYST, in Geiger 1961)

damping effect on the temperature amplitudes at the soil surface, but promote the propagation of the temperature wave in the subsoil.

Inversely, low thermal conductivity increases the temperature amplitudes at the soil surface, but blocks the propagation of the wave into deeper layers. The effect of the interaction of both properties on the heat balance depends on the soil degree of water saturation (cf. Fig. 6.52). As a result, wet soils, such as groundwater-affected soils and Stagnosols, warm up less and more

slowly than drier soils. Their surfaces warm up less than in drier soils, but they also cool down less with nocturnal emission. In extreme cases, this leads to particularly frequent ground frost in drained moors, because they absorb a high fraction of the radiated heat due to their dark color, and hardly transmit it downwards in the drained profile, causing heat build-up and therefore high temperatures in a very thin topmost layer. At night, this entails corresponding strong emissions with cooling down into the freezing range. All soils behave similarly, although not as pronounced, depending on their color and the looseness of the soil surface. Looseness and dryness of the soil surface therefore promote heat build-up and simultaneously the danger of late frost.

On the other hand, water vapor in soils as a heat transport medium is more efficient the more the soil contains coarse pores. Its contribution to heat transport is therefore correlated with aggregation in clayey soils, and with the degree of peat humification in moors.

In addition to its water balance, the soil heat balance is also affected by increased evaporation, which causes additional heat losses in wet groundwater-affected soils and Stagnosols.

The influence of stones on the heat balance of a soil can be considerable. These are characterized by a higher thermal conductivity than their environment, and a lower heat capacity than water (Table 6.9). The 'heaving' of stones is a result of this difference, because they promote the formation of ice crystals under them as well as the associated lifting. The course of diurnal fluctuations in temperature, which are low compared to the annual fluctuations (Figs. 6.54 and 6.55), only affect stones in the subsoil in regions with permafrost. In general, plant cover has a damping effect on the temperature amplitudes.

Among the ambient conditions, the **exposure** should be mentioned first of all. In the northern hemisphere, there is less radiation on slopes facing north than on south-exposed slopes. Therefore, the soil temperatures as well as the evaporation are lower; the soils there are then wetter. This leads to damping of the temperature amplitudes. The exposure effect increases with increasing steepness of the slopes (inclination) as well as with increasing elevation above sea level.

In general, the mean annual temperature of soils at a depth of 50 cm follows the annual mean of the air temperature fairly precisely. As shown in Table 6.10, it always lies a certain amount above their measured values at a height of 2 m.

Taking account of the seasonal radiation, given by the date, it can even be calculated on a daily basis. This demonstrates that the maximum and minimum values for the soil temperature in the topmost 5–7 cm of soils without plant cover are almost always 7–10 degrees higher than the maximum or minimum values for the air temperature at the standardized meteorological stations (2 m above the ground). In general, neglecting local influences such as topography and vegetation, the soil surface plays the role of a heating plate for the adjacent air, as long as the radiation predominates. This is the cause for updrafts, the thermal lift for gliders, and the 'shimmering' of air on hot days. This state is only interrupted for shorter periods of time at the end of periods with longer extreme emission phases.

The correlation between air and soil temperature is disturbed by snow cover, which inhibits deep cooling of the soil even near the surface.

Table 6.10 Classification of the heat balance of soils using the mean annual temperatures and temperature fluctuations (USDA1999)

Difference of the mean values for the 3 summer and 3 winter months (°C)[a]		Annual mean temperature at a depth of 50 cm (°C)[b]			
	<0[c]	0–8[d]	8–15	15–22	>22
>6	Cryic	Frigid	Mesic	Thermic	Hyperthermic
<6	Cryic	Isofrigid	Isomesic	Isothermic	Isohyperthermic

[a]Northern hemisphere: summer months: June, July, August; winter months: December, January, February
[b]This temperature is 0.3 (at 6 °C) to 3° (at 30 °C) higher than the air temperature at a height of 2 m
[c]Summer mean <15 (<13 if wet, <8 under humus layer, <6 in moors), no permafrost
[d]Summer mean ≥15 (≥13 if wet, ≥8 under humus layer, ≥6 in moors)

Inversely, although vegetation fires cause heating of the soil surface, they hardly affect the soil temperature below a depth of 5 cm, as shown by investigations on controlled fires in Brazil.

The classification of the American soil taxonomy (USDA, see Sect. 7.4.3) provides a general overview of the heat balances of soils in very different climate regions. Here, the soils are classified in terms of their heat balances based on the mean annual temperature and the amplitude of the annual temperature fluctuations at a depth of 50 cm.

6.6.5.2 Anthropogenic Interference

The heat balance of soils is affected by every human activity that changes the radiation and emission situation and the heat capacity. In equal measure, the input or removal of heat energy or of substances releasing energy have the same effect.

The radiation and emission situation can be affected by the orientation of the exposure and inclination (e.g. building of ridges for crops), by coloration/(sand cover method on moors and dark seedbeds), by ground covers (mulching methods), and by loosening or compaction (rollers) of the soil surface. Sealing against infiltration and evaporation, as is observed mainly on roads, but also with other building projects, affect the heat balance not only through inhibition of the mentioned water transport processes, but also by changing the albedo.

In general, the albedo increases with the transition of forest to herbaceous vegetation (Fig. 6.51). It is highest on surfaces where the A horizons were removed (e.g. building sites, erosion surfaces) or have not yet developed (e.g. recultivation areas, alluvial areas). This is accompanied by reduced heating. At the same time, the heat loss that would occur through transpiration from a vegetation cover also ceases.

The heat capacity can be primarily affected by changes in the water content. Here, especially drainage plays a role in cool climates (Sect. 6.4), which accelerates the heating of the soil in the spring compared to undrained surfaces, and therefore lengthens the vegetation period.

In principle, heat input that affects the temperature profile in soils takes place with every addition of organic matter. However, the heat energy released during its decomposition is only effective with high accumulations of organic material. Formerly, this was used in horticulture with the creation of 'hotbeds'.

Soil covers over waste and sewage sludge landfills have constant heat input from below through the decomposition of organic compounds in the landfill body. Here, the mean annual temperatures measured at a depth of 50 cm were 3 °C higher than in a sandy mineral soil in the surrounding area, and 9 °C higher at a depth of 180 cm. Especially in the winter half year, the constant heat supply from the landfill body leads to strongly elevated temperatures in the subsoil compared to natural soils, and also reaches up into the topsoil.

Here also, water vapor transport, which leads to desiccation of the warmest and wetting of the colder parts similar to soil heating in greenhouses, is an effective convective heat transfer (Sects. 6.4.4 and 6.5.2). It inhibits the development of steep temperature gradients, but simultaneously leads to strong desiccation.

Heat extraction from soils (e.g. for heating purposes) is only profitable when the heat exchanger can be installed in the free-flowing groundwater. In this case, it can make use of the radiated energy from the total area. Removal from the more slowly flowing adhesive water would require the installation of exchangers in areas where the size enables sufficient energy storage under the local radiation intensity. In both cases, heat extraction leads to lower temperatures in the soil.

6.7 Transport Processes and Translocations

The transport of matter through the soil surface and within a soil body primarily takes place through **convection**. It is the most effective and most common transport mechanism. Water and air are the transport media, and more rarely, ice. Transport processes within the soil take place in the pore system and are therefore affected by its properties.

Transport by flow taking place over and essentially parallel to the soil surface produce erosion and accumulation (Sect. 10.7.1). Translocations without transporting medium that equalize potential gradients include e.g. gravitational mass movement (landslide, soil creep; see Sect. 6.3.3) and diffusion.

The course of convective transport is bound to the flow system of the flow medium. This system can be described in the respectively relevant section through **source**, **sink** and the **flow** along the flow lines (Sect. 6.4.6.5). It is only within this system that the transport events are affected by the behavior of the constituents in the flowing medium itself and in the conducting pore system.

Sources in soils are e.g. the soil surface or the groundwater surface (GWS). The corresponding sinks would be e.g. the bottom of a soil (=pedon), the GWS, and free water surfaces such as ditches or drainage pipes.

In the unsaturated zone of all soils, on a macroscopic scale and in flat locations, mainly vertical, and therefore **one-dimensional** processes going upwards or downwards take place, where the lateral edges of the flow system can be arbitrarily defined. Transport processes in landscapes must be based on **two-** or **three-dimensional** flow systems. The transport of constituents is affected by biological processes (decomposition, conversion, liberation, excretion and uptake by the soil biota and roots), which can act as the most important sources or sinks in this case. There are also chemical (e.g. adsorption and desorption, redox processes) and physical (diffusion, hydrodynamic dispersion) processes. In the following, the focus is mainly on transport in the liquid phase, which dominates in soils, while references to extensive specialized literature are provided for the corresponding transports in landscapes, including existing model approaches.

6.7.1 Transport in Soils in the Liquid Phase

Every water movement in the soil matrix involves the transport of constituents, i.e. **convective** translocation. In doing so, the soil solution can transport substances both in a dissolved and in a suspended or emulsified state. This process is one of the most significant factors of soil development. This is because the constant movement of soil water prevents the formation of equilibriums between the different components of the soil solution, and between these and the adjacent surfaces of the solid matrix. Convective transport is the basic requirement for the continuation of all reactions, and therefore also for weathering as well as exchange, leaching and accumulation processes.

The transporting flow of water corresponds to a **capillary flow**. The influence of the pore system causes a 'dispersion' of the flow process, compared to flow in a single large capillary where the flow cross-section corresponds to that of the capillary cluster (Fig. 6.56). This is caused

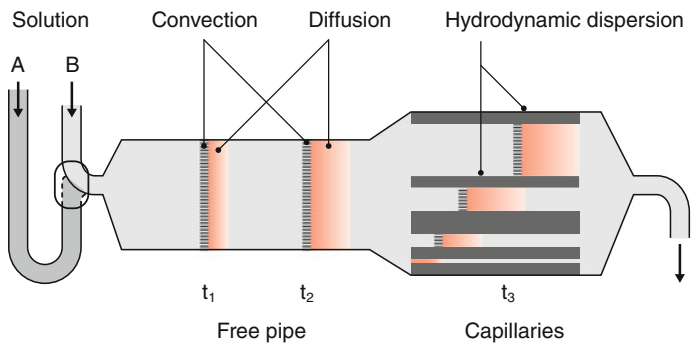

Fig. 6.56 Diagram of the effect of diffusion (in the free part of the pipe) and hydrodynamic dispersion together with diffusion (in a group of capillaries) when starting the input of a substance in a percolating medium (time frame = t_1 to t_3)

by the large influence of the capillary diameter on the velocity of the flow taking place within it (Sect. 6.4.3.1).

This dispersion of the constituents in the soil pores at the advancing front is called **hydrodynamic dispersion**. Its extent is affected by the soil structure, and is therefore soil- or even horizon-specific.

Their effect becomes particularly clear when the composition or concentrations of the constituents suddenly change, e.g. after fertilization, or when water with low constituent concentrations suddenly enters the soil after strong precipitation.

The interaction of hydrodynamic dispersion and **diffusion** is represented schematically in Fig. 6.56. In this case, laminar flow is assumed (Sect. 6.4.3). Neglecting the form of the hydraulic velocity profile, the piston-shaped advancement of the concentration front is represented for the free-flowing part (Fig. 6.56 on the left), after the input of the transport medium has been converted (from solution A to solution B in the figure). Here, the more slowly the front advances, the more effectively diffusion pulls the constituents apart ahead of the advancing piston-shaped concentration front. In the capillary range (Fig. 6.56 at the right), hydraulic dispersion causes an additional distribution of the constituents. The dispersion of the concentration front increases with increasing flow section and progressing time. This can be followed in trials by determining the changes in concentration in the collected percolate (Fig. 6.57).

The course of the **breakthrough curve** or **passage curve** strongly depends on the pore geometry. When elongated pores (cracks, channels) or aggregate packages are present, the first increase in concentration in the percolate appears particularly early, because the solution flows around zones of slow flow particularly effectively.

Due to the large diversity of shapes in the aggregate structure (Sect. 6.3.1) and the macropores, the **preferential flow (macropore flow**, see Sect. 6.4.3.1) varies in shape and form, and significantly affects the shape of the breakthrough/passage curve. This makes them

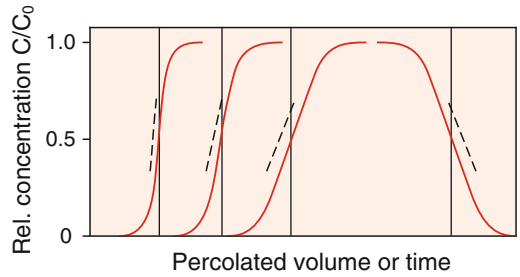

Fig. 6.57 Diagram of the course of the increase in concentration of a substance added to the flow medium (breakthrough curves) through hydraulic dispersion depending on the flow section (*left*) and the decrease in concentration after the end of the input (*right*). The pulling apart through hydrodynamic dispersion increases with the flow section and therefore the turnover time. The *dashed* parts of the curve show the effect of diffusion, which alters the hydraulic dispersion

difficult to describe. In addition, the effect of the macropores on the total flow and the transport of the volume that was recorded with the measurement depend on the continuity of the macropores. This fact must be accounted for either by selecting the size of the sample, e.g. the volume for a measurement, such that the fractions of blind ending cracks or channels of various shapes are representative for the sampled area (**representative elementary volume, REV**) or by performing a sufficiently large number of parallel measurements. One option to avoid these difficulties can be the use of special morphological classifications of the structure.

Furthermore, the longer the flow section, the more the supply of reaction partners, e.g. ion exchange media, redox systems, and decomposing organisms, influences the shape of the breakthrough. The correlation between the breakthrough curve and the flow section characterizes the filtering properties of a soil.

The laws governing the distribution of the constituents in the percolating water also apply in the case of a decrease in concentration. Their course is also distorted by hydrodynamic dispersion. An important difference compared to the seepage situation is that diffusion leads to a longer residence time of the constituents in the matrix (Fig. 6.57), and the **displacement curve** is shifted towards the right.

Mathematical representation of the transport of water constituents starts with the conservation of matter within a unit of volume and time interval. Here, the **continuity equation** serves as a basis, where the transport into and out of the soil, the storage as well as any sources or sinks are expressed. For the simplified case where the soil water constituents do not occur in gaseous form in the adjacent soil air, they can be described with a differential equation as follows:

$$\frac{\partial C_T}{\partial t} + \frac{\partial I_C}{\partial z} + r = 0 \qquad (6.62)$$

C_T = Total concentration, sum of the groups of constituents to be recorded in all existing states or forms, e.g. dissolved in the water fraction ($C_l \cdot \theta$) and adsorbed on the solid phase ($C_{ads} \cdot \rho_B$) of the observed volume.

I_C = Constituents translocated by convective transport. This factor consists of the flow described by the Darcy equation (Sect. 6.4.3), the hydrodynamic dispersion, and the diffusion. The two latter phenomena are determined using equations that correspond mathematically to the diffusion equation (Sect. 6.4.4.1). Diffusion only has a clear influence with extremely slow flow movement. In soils, the distribution of the constituents is generally more strongly affected by hydrodynamic dispersion.

r = Reaction rate for sources or sinks.

The following form of the continuity-dispersion equation is used as a starting point for computer modeling of the transport of water constituents:

$$\frac{\partial C_T}{\partial t} = \frac{\partial [D_{hd} \cdot (C_l/z)]}{\partial z} - \frac{\partial (I_{fl} \cdot C_l)}{\partial z} - r \qquad (6.63)$$

D_{hd} is the effective dispersion-diffusion coefficient, C_l is the concentration of the constituents in the solution, and I_{fl} is the water flow according to the Darcy equation. The other symbols correspond to those in the previously described equation.

A special case of convective transport is heat transfer with flowing water. Because water has a high heat capacity compared to the solid soil particles, warm spring rain promotes growth through the input of heat with the infiltrating water. The effect is so considerable that the 'warm rain' expression has become everyday speech. In cold regions, the inflow of groundwater from warmer areas can significantly improve the agricultural suitability of soils compared to areas further away from the river.

In principle, the mathematical formulation is the same as for the soluble constituents of water. The temperature T is used instead of the concentration C. The differences in temperature cause heat transfer, which formally corresponds to the diffusion of dissolved substances in water. Furthermore, they cause vapor pressure gradients in non-saturated soils, which in turn lead to convective heat transfer (Sect. 6.6.4).

6.7.2 Transport in Soils in the Gaseous Phase

While convection and dispersion have the greatest influence on translocation processes with transport in the liquid phase, diffusion dominates as the driving mechanism in the gaseous phase. On the one hand, this is caused by the 10^4 times greater diffusion of molecules in the gaseous phase compared to water, and on the other, by the fact that gravitation does cause any gas flow movement in the soil. Convection-producing gas flows are only observed in soils with gas production, e.g. with the production of methane (Sect. 6.5.2) or in connection with temperature gradients causing vaporous water movement (see Sect. 6.4.4).

The description of gas transport through a soil volume, like the transport of water constituents, must take account of the following sub-processes: entry, stockpiling, exit, and if required, new formation and decomposition. This is formulated in the mass conservation equation (=continuity equation) according to the same principle as for transport in a liquid medium.

6.8 Soil Color

The color is a soil property that is visible at first sight. The spectrum of colors found in soils is wide. Because the different shades can often be attributed to specific soil components or specific states, it is possible to draw conclusions from the classification of the color or color distribution on the composition of mineral and humus bodies, on redox conditions and soil moisture, including their respective distribution and intensity.

For this reason, the color description is an important component of every pedological field survey (Sect. 7.3). This not only applies to the description of soil horizons on a profile wall (Sect. 8.3), but also for recording the properties of surfaces, therefore representing the basis for any remote sensing. However, this requires more elaborate methods of spectral analysis, which enable higher accuracy than visual classifications and can even go beyond the range of visible light. For the visual classification in the range of visible light, the color is characterized by the parameters: **hue**, **value** and **chroma**.

6.8.1 Color Classification

Color classification during field surveys records the parameters **hue**, **chroma** and **value**. In principle, the colors that are perceptible with the eye are produced by scattering and absorption of electromagnetic radiation between 400 and 780 nm. The sensory physiological color impression is created by the light absorption of the rhodopsin into three ranges of wavelength, which can be represented by color sensitivity curves.

The relationship of the three parameters to each other is represented in Fig. 6.58. It is based on the system developed by Munsell (1954), whereby the description of the hue is already based on **Newton's color theory**. Complementary colors are arranged opposite to each other on the chromatic circle. For representation in the direction of increasing frequency, it is divided into the color sections red (R), yellow (Y), green (G), blue (B) and purple (P). A transition zone is defined between each of these elementary colors, containing the corresponding mixtures, e.g.

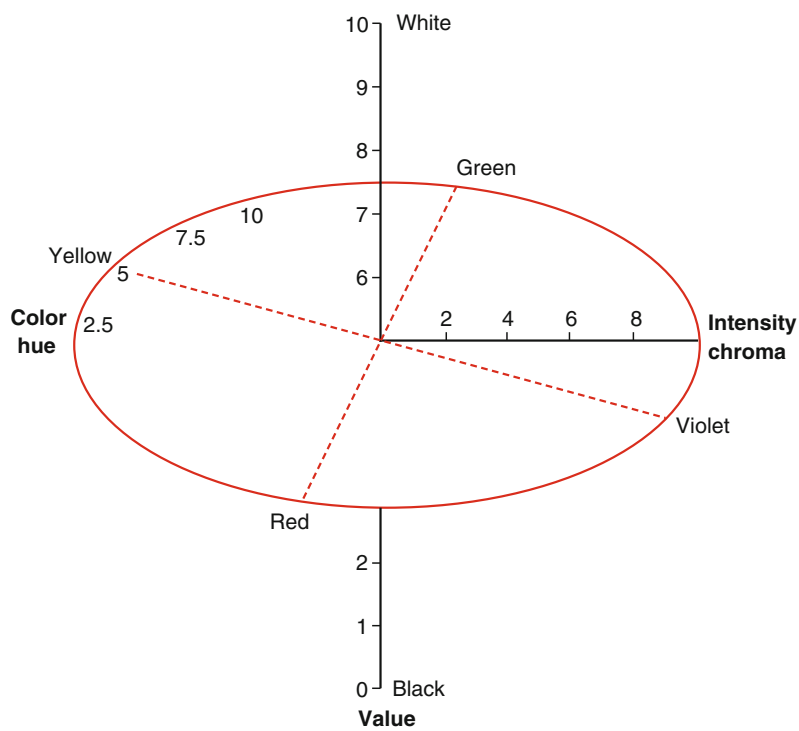

Fig. 6.58 Color description according to Munsell. The hue is on Newton's *color circle*, the intensity (chroma) of each hue is on the radius, and the value is on the axis

yellowish red or greenish yellow. Each zone is described using the numbers 2.5; 5; 7.5 or 10, which document the increasing frequency of the hue. The value is plotted on a straight line that is axial to the chromatic circle, whereby the maximum value (maximum reflection, white) is defined by the scale value 10. Complete absorption of visible light (black) is characterized by the value 0.

As a result, in conjunction with profile descriptions, the color of the soil or a surface can be classified in a clear and comprehensible manner using a combination of these 3 parameters. In the Munsell chart, e.g. a light reddish grey soil sample is defined with 7.5 R 7/3. An important feature of the Munsell color charts it that transitions can also be identified, e.g. 9 YR 6.5/3.5, because the color space can be considered as a continuum (Fig. 6.58).

6.8.2 Coloring Components

Black, grey and brown hues in the topsoil (A horizons) are essentially caused by humic substances. The color intensity within a range between 2 and 6 percent by mass of organic matter varies so considerably at the same carbon content that other factors, such as the soil moisture (darker when moister), the texture (clay-rich soils contain more humus with the same color because of the greater surface area), the degree of humification (black carbon fractions) or dissolved organic carbon (DOC), must be considered. With the humic substance fractions, in turn, the color becomes darker from the fulvic acids to the humic acids.

Yellow, brown, red, blue and green hues characterize different Fe minerals, whereby these colors are most common due to the dominance of iron in soils (minerals, rocks). As a result, they are decisive especially for the soil horizons below the A horizon. In temperate climates, soils are usually yellowish brown, brown or reddish brown in color (Munsell hue: 7.5 Y–10 YR), because goethite dominates here. Ferrihydrite, which is found e.g. in acidic Cambisols, Bs horizons of Podzols, and in Bg horizons of Gleysols, shifts the hue into the red tones (7.5–5 YR). The strong red color of many soils in warmer climates is caused by hematite (10 R), where the red alters the yellow of goethite. The more hematite such soils contain, the more intense the red color. In doing so, the reddening intensity/degree of redness (according to Torrent) increases linearly with the hematite content up to ca. 5–10 % hematite, depending on the soil group; beyond this point, the chroma no longer increases (saturation).

Grey, green and blue hues are observed when the iron is found in the mobile divalent form at low redox potential values, and is then either transported/translocated or converted into corresponding hydroxy compounds. The translocation of iron then reveals the inherent color of the other minerals, whereby e.g. quartz appears to be pale white, and silicates and clays also appear to be grey. If, in turn, the clay minerals contain Fe, green hues can also be observed when a portion of the Fe is present in a reduced form in the crystal lattice.

Strong blue-green hues can be an indication of Fe(II, III)-hydroxy compounds (so-called 'green rust'), which lose their color with the input of oxygen. Similar is true for vivianite, where the bright blue color changes to rusty brown in the presence of oxygen.

Dark black colors in strongly reduced environments, e.g. in marsh sediments, are caused by finely distributed FeS or FeS_2. The presence of black concretions under oxidative conditions is an indication for the presence of 4-valent manganese oxides or coal residues (black carbon).

White colors are often caused by local accumulations of calcite, gypsum or soluble salts as precipitates on the surface of aggregates or also on profile walls, especially in soils of arid climates. The chemical composition of these precipitates depends on the direction of flow and the composition of the capillary water rising in the profile. Kaolinites also have a similar white color, like e.g. pure kaolinitic saprolite in the tropics. Finally, in addition to the type of coloring components, the hue of soils also depends on the particle size. Therefore, when the crystals become larger and the surface area decreases accordingly, the hue of finely distributed goethite

changes from reddish brown to yellow, that of lepidocrocite from brownish red to orange, and that of hematite from bright red to purple. In contrast, the **chroma** and the **value** depend more on the amount of the coloring components.

6.8.3 Correlations Between Color and Soil Properties and Processes

The advantage with the easy accessibility of the color specifications, which can be described even without touching the corresponding material, is used the draw conclusions on other soil properties and states. Due to the close correlations with other properties, it can provide both generalized and very specific information. The distribution of hues, chroma and values in the soil profile provide information on the intensity of soil pedogenic processes such as brunification, gleying, pseudogleying, podzolization or lateritization, which can be defined by typical color patterns or distributions (Sect. 8.3).

Apart from the fact that moist soils, with otherwise identical composition, are always darker and often more intensely colored than in dry sites (because water in the soil absorbs the radiated energy to a greater extent than the solid constituents: see also albedo 6.6.3. and Fig. 6.51), yellow, brown and red hues generally indicate aerobic conditions, i.e. a high redox potential and also a higher rH value. These colors are therefore synonymous with high oxygen inputs and only very rarely occurring water saturation. However, red hues are very persistent in soils, and in hematite-rich soils of central Europe, they are an indication of more humid and warm climates in the past. The same is also true for brown hues, which, e.g. in soils with a lowered groundwater level, document formerly higher transitions from the aerated Bg to a reduced Br horizon still after many years (decades).

Partially occurring stagnant water characteristics also observed at greater soil depths, e.g. under wheeltracks or hoof trampling, indicate changes in the degrees of pore saturation and functions, caused by plastic and elastic soil deformation.

In principle, the greater the proportion of quartz-rich sands, the less such horizons document the physical, chemical or physicochemical processes, while on the other hand, the strong inherent color of the minerals simulate corresponding soil processes. Therefore, with red parent materials, conclusions drawn on the degree of waterlogging and/or soil structure formation and therefore on the water balance are imprecise, while for yellowish red and brown hues, they are easier to identify (e.g. shrinkage states).

In these cases, in addition to complete color specifications for the matrix, it is particularly important that color specifications also be made for e.g. concretions, as well as the mottle size and cutane.

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7 Soil Development and Soil Classification

Soil genesis is the study of the development of soils. Soil is a natural body, developing from rock at the Earth's surface through **pedogenic processes** (weathering and mineral formation, decomposition and humification, structure formation and various substance translocations) under a specific climate, specific litter-delivering vegetation, and population of soil organisms.

This **soil development** generally begins at the surface of rocks and progresses in depth over the course of time, whereby layers are formed with different properties, called **soil horizons**. In contrast, layers were also formed through sedimentation, which are layers of rock formation.

The soil horizons are similar to litter at the top (especially the organic **layers**), and become increasingly similar to rock with depth as **mineral soil horizons**. All horizons together form the **solum**. A two-dimensional vertical cut through the soil body is called the **soil profile**. By definition, the litter (partly) covering the soil and the rock below the soil do not belong to the soil. However, they are often also called horizons.

Soil horizons are designated with letter symbols. The **O horizon** is defined as the organic layer consisting mainly of organic matter covering the mineral soil. The **A horizon** is the first mineral soil layer that is darkly colored by some organic matter, or bleached as a result of the removal of colored substances (like iron oxides). Below the A follows the **B horizon**, which often contains translocated substances from the A horizon. Finally, underneath the B horizon, there is a layer of soft rock that was not or hardly influenced by soil development, and is designated with the symbol **C** if it corresponds to the parent material of the solum (whereas hard rock is called **R** layer). See Sect. 7.3 for more information on the classification of soil horizons.

In contrast, in agricultural practice, the repeatedly (15–35 cm deep) cultivated **Ap** horizon of a field as well as the strongly rooted (7–10 cm) horizon of grassland is also called the **topsoil**. The **subsoil** follows below this, which leads over to the parent rock in most terrestrial soils.

The course of development of a (often strongly differentiated) soil from undifferentiated (parent) rock can vary greatly at different sites of a landscape or in different regions of the world: It depends on the constellation of pedogenic factors present at a site or in a region.

These **factors** also interact mutually, and their sum determines the extent and direction of their effects. They often also interact mutually with the soil itself, which is especially true for the flora and fauna (biota). Climate is the most independent factor, but also acts on the soil in a form modified by the terrain and vegetation.

Depending on the prevalent constellation of these factors and the duration of their effect, soils evolve with different levels of development and profile differentiation, and their properties undergo constant change. A change in the factors (e.g. climate change) can result in a new direction of soil development.

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Humans also influence soil formation by intentionally or unintentionally changing the soils themselves or the natural factors.

Modern soil classification is based on soil genesis and classifies soils according to the properties they have acquired during pedogenic processes. In doing so, soils with similar pedogenic characteristics that typically differ from soils of another development state are classified together in **soil types**.

Soils are parts of landscapes. **Soil geography** studies the distribution and the arrangement of different soil units in a landscape.

7.1 Factors of Soil Formation

Factors of soil formation are the climate, the parent rock, the gravity (caused by gravitational pull), the topography (position of the soil in a landscape), flora and fauna (biota), and often also groundwater or river, lake or sea water. All of these factors act over time (see Sect. 1.1). Since ca. 5000 years, humans have also influenced the development of many soils.

For the first time in 1897, the Russian soil scientist V.V. Dokuchaev summarized the pedogenic factors in an equation:

$$\text{Soil} = \text{f}(\text{climate, flora and fauna, parent rock}) \times \text{time}$$

In doing so, he emphasizes that all of these factors act over time, i.e. that soils undergo constant change and development.

The Swiss-American soil scientist Hans Jenny further developed the ideas of Dokuchaev in his book *Factors of Soil Formation* (1941) and *The Soil Resource* (1980). He added the factor *topography* and tried to quantify the efficiency of individual factors over time.

E. Schlichting (1986) offered a different view. He stated that

$$\text{Rock} + \text{Litter} \xrightarrow[\text{Flora, Fauna, Humans}]{\text{Climate, Topography}} \text{Soil}$$

In his view, the soil parent materials, i.e. rock and litter of vegetation, act as factors that are transformed into soils, while the other factors regulate the course of the processes, quasi like catalysts. Ultimately, different soils are formed depending on the constellation, and also with the effects of human activities.

7.1.1 Parent Rock

On the one hand, parent materials of soil formation are bedrocks or parent rocks, and on the other, the litter from plants, which grow on the soils. For the latter see Sect. 7.1.5. Parent rocks provided some of the soil minerals directly; and some were produced from its dissolution products. As a result, the mineral composition of young soils is very similar to the parent rock. In more strongly developed, older soils, this is only still true for the poorly weatherable minerals. For example, as typical soils of very old terrestrial surfaces in the humid tropics, *Ferralsols* hardly contain any weatherable minerals (Sect. 7.5.12.1).

The direction and intensity of soil development depend strongly on the soil structure (loose or hard rock, porosity, jointing), mineral composition, and the rock texture. The development of soils formed from unconsolidated sediment is usually much deeper than in neighboring soils from hard rock, even if these have been disintegrated through frost weathering in the Pleistocene, as shown in Fig. 7.1 for loess compared to limestone. In Central Europe, soil development on hard rock without periglacial layers seldom reached depths of more than 20–40 cm, so that usually only A/R soils are found.

Among **hard rocks**, intrusive rock with a coarse structure weathers more readily than chemically similar extrusive igneous rocks with a fine-grained structure (granite > rhyolite; gabbro > basalt), because a coarse rock structure provides better possibilities for an attack by physical weathering: The various minerals in a rock expand at different rates when heated. This results in tensions between the minerals, which are stronger the larger the minerals. For this

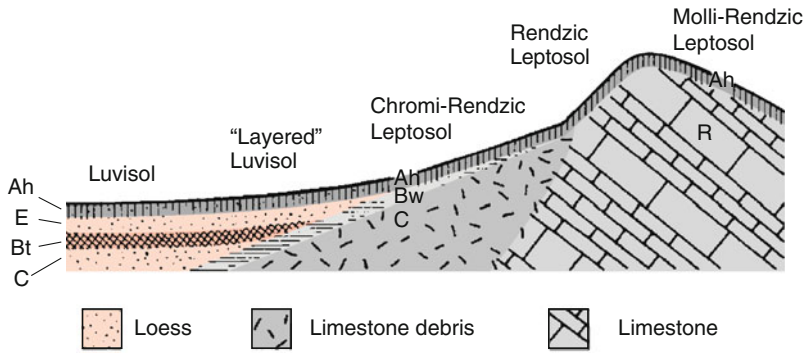

Fig. 7.1 Soil community on a limestone slope, partly covered with loess in Northern Germany (WRB classification)

reason, plutonites disintegrate more readily with temperature blasting (Sect. 2.4.1) than volcanites. First thin cracks develop, where water and roots can penetrate and frost or root blasting can take place. Because schist and sediment boundaries represent weak points in a rock, strongly foliated metamorphic rocks weather more rapidly than weakly foliated rocks for the same reason, and strongly layered sedimentary rocks more readily than bedded rocks, especially when the foliated or layered/stratified surfaces are slanted or steep, so that water and roots can easily penetrate into the thin cracks.

In **unconsolidated rock**s, the texture and bulk density are decisive for the permeability (Sect. 6.4). Coarse-grained sediments facilitate percolation and thus transport processes in the soil. Fine-grained sediments often reduce the permeability: This promotes water retention, the dissolution of Fe and Mn oxides through reduction, and thus the formation of redoximorphic characteristics (Sect. 7.2.5). On slopes, it also favors surface runoff. For example, in the "Odenwald" in the German uplands soils developed on sandstone mudflows containing loess, the high permeability and poorly weatherable silicates resulted in strong acidification and Fe and Al translocation in the profile (podzolization), while in multi-layered soils formed from loess over argillaceous rock, the poor permeability resulted in waterlogging.

If the rock's **mineral composition** contains high amounts of readily weatherable minerals, acidification and dealkalization and thus the depth of soil development is delayed. This is particularly true with higher **carbonate contents**, because silicates only weather more strongly if the carbonates are washed out and the pH drops. Soils consisting of loess (Fig. 7.1) are therefore decalcified to a great depth, and in contrast, those consisting of limestone are not, because here, in addition to the weathering resistance of a hard rock, higher carbonate contents prevent complete eluviation. On the other hand, in pure quartz sands and quartzites, it is also possible that there is no visible progression of soil development, because the lack of weatherable Fe and Mn minerals does not allow the formation of a visible profile differentiation.

Unconsolidated sediments with high bulk densities also promote waterlogging. For this reason, in the North German lowlands, under the same climatic conditions, soils formed from densely bedded (d_B 1.7–1.9 g cm^{-3}) calcareous glacial till (due to ice pressure) more often have redoximorphic characteristics than soils formed from loess (d_B 1.4–1.6). As a result of secondary translocation of the loess by water or solifluction (Sect. 7.2.7.1), densely bedded flooded loess or loess mudflows were formed, leading to the development of soils with pronounced hydromorphic characteristics.

Soils are not always formed from the same rock as is found below it. The parent material also often consists of primary layers (e.g. many water sediments), or the soil developed from a younger layer of sediments (e.g. loess or aeolian sand), which have completely different properties than the underlying soil. In soil science and geology, the bottom refers to underlying layer, and the roof refers to the overlying layer.

In Central Europe, the parent rock usually consists of multiple-layered **periglacial layers**, generally developed as solifluidal deposits. In

many solifluidal deposits of mountains, only the **bottom layer** is formed solely from the underbed, while the layers above it are often more fine-grained, because they contain loess or were more strongly degraded by frost weathering (**base, middle** and **cover layer**). In such soils, it is hard to differ between lithogenetic and pedogenetic properties.

7.1.2 Climate

Solar energy is the most powerful driving force for soil development. On the one hand, it acts directly on the soil as solar radiation and diffuse skylight radiation, and on the other, through various climatic factors (such as precipitation, air temperature, air humidity, wind), and especially through the fauna and flora. The effective energy for soil development essentially results from the intensity and seasonal distribution of the **radiation balance** (i.e. the difference between the input and output of solar energy). In comparison, the internal heat of the Earth is less significant (below 0.01; solar radiation on average 8.37 J × m^{-2} min^{-1}).

Dependent on the net total radiation, the **soil temperature** (Sect. 6.6) has a direct effect on decomposition, weathering, and mineral formation processes. Decomposition and chemical weathering are considerably intensified by rising temperatures, so that they are much stronger in the humid tropics than in temperate climates, or near the poles or in high-altitude mountains. However, more intense weathering of many soils in humid tropics is not only attributed to higher temperatures, but also to longer periods of soil development. Because temperature also has an effect on the vegetation, it influences the production of litter, the parent material for humus formation. In warmer soils, more organisms are involved in litter decomposition and structure formation. If soil temperatures sink below the freezing point, most chemical and biochemical processes come to a halt. Special physical processes then take place, especially with the alternation of freezing and thawing: frost weathering, frost-related mixing (cryoturbation), and soil creeping over frozen subsoils (solifluction).

Despite lower biomass production, more humus generally accumulates in soils in cooler climates than in the more humid tropics, under otherwise equal conditions (Fig. 7.2). Even at average annual temperatures of −9 °C, Antarctic soils can still contain 8–10 kg of humus per m^2 (in peat soils >20 kg), because even under these conditions, the layer of air just above the ground can sometimes reach temperatures of more than +10 °C, and therefore enable plant growth. In contrast, the soil temperatures rise much less, so that only very little organic matter is decomposed in the soil.

The soil water is supplemented by **precipitation**, enabling dissolution and translocation processes. The fraction of precipitation that passes through the solum as **seepage water**, carrying away weathering and decomposition dissolution products, has the most important effect on soil development.

Climate factors are often very dominant in relation to all other soil development factors. This becomes visible when comparing soils developed from the same rock and relief, but in different climates. At similar temperatures, loess soils exhibit higher clay contents the higher the precipitation and therefore soil wetting, while the pH value dropped (Table 7.1). This can be attributed to the fact that with increasing moisture penetration, the chemical weathering of primary silicates and their transformation into clay minerals is enhanced and there is increased leaching of Ca, Mg, K and Na ions. Stronger moisture penetration also leads to more rapid

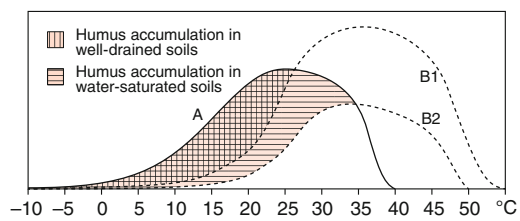

Fig. 7.2 Biomass production (*A*) and intensity of decomposition by soil organisms in aerated soils (*B1*) and wet soils (*B2*), in relation to the mean annual temperature (after Mohr et al. 1972, extended)

Table 7.1 Relation between the intensity of rain (N) and properties of loess soils (mean annual temp. +11.1 °C after Jenny and Leonhard 1934)

Rain (mm a^{-1})	Clay (%)	CEC ($cmol_c$ kg^{-1})	pH (KCl)	Soil unit
370	15	12	7.8	Kastanozem
500	19	16	7.0	Chernozem
750	23	24	5.2	Phaeozem
900	26	27	5.2	Phaeozem

decalcification, which in turn enables clay migration. In cool humid climates, nutrient depletion inhibits soil organisms and thus litter decomposition and structure formation, so that raw humus can be formed.

Storm rainfall and snowmelt cause soil erosion on slopes. **Wind** increases evaporation, and in case of dryness, particularly on surfaces without vegetation, it can also cause erosion. Other climate factors, such as cloud cover and air humidity, mainly affect soil development by modifying the radiation and evaporation.

The conditions are different in **arid climates**, where more water can evaporate than is added by precipitation. Here, there is only slight chemical weathering because the dissolved weathering products are not leached out, but rather accumulate. At the same time, salts added to the soil by dusts or rainfall remain in the profile. In doing so, the more arid the soil, the less the liberated and added ions are transported and accumulated lower in the profile. This involves a differentiation according to the solubility: water-soluble salts are accumulated further down in the profile than gypsum or even lime. However, even in extreme deserts, the salt maximum is not found at the surface, because the salts are transported several dm downwards by episodical storm rainfalls (Sect. 7.2.4.5). Soils can be acidified even under arid conditions. For example, in semiarid West Africa, especially sandy soils are strongly acidified and dealkalized, because strong leaching of substances took place during the rainy season.

With similar mean annual temperatures and similar land use, the humus contents of the topsoil increase with increasing precipitation: In India, for example, Ah horizons under natural vegetation and 24 °C mean annual temperature contain 0.4 % with 35 mm of annual precipitation, 2.0 % with 400 mm, and up to 4.5 % with 3200 mm (Jenny 1980). The significance of climate becomes particularly clear in the fact that the most important soil zones on Earth largely correspond to the climatic zones (cf. Sect. 8.4).

7.1.3 Gravity and Relief

All soils are formed under the influence of **gravity**, which e.g. causes the percolation of soil water with dissolved substances in coarse pores, puts a load on deeper soil layers, and can cause materials to move parallel to the surface on slopes.

The **relief**, i.e. the elevation, terrain and exposure, modifies soil development by influencing the effects of gravity, climate, rock, water, organisms, and finally also human activities.

The relief mainly determines the climate through elevation (m above sea level): increasing elevation in mountains is accompanied by decreasing temperatures and increasing moisture penetration in the soil. This results in an elevation zonal pattern of individual soil properties and entire soil types. In the Caucasus Mountains, for example, with elevations rising from 10 to 5000 m a.s.l., a sequence is observed from steppe soils (*Kastanozems* and *Chernozems*), over forest soils (*Phaeozems*, *Luvisols* and *Podzols*), to hardly weathered mountain soils (*Cryosols* and initial soils).

Different **macrorelief forms** include plains, culmination areas of elevations (crests, ridges, hills, mountains), hollows (depressions, valleys), and slopes with their different areas (upper, middle, and lower slopes) and profiles (convex, concave, straight). **Microrelief** includes other forms, described as rills, dents, humps, potholes, steps, broken, smooth and level. These also include special forms such as natural and artificial walls, protruding rocks, cliffs and dolina. The relief units can be described using the length, width and slope (inclination). The orientation of

a slope (**exposure**) is also significant; here, a distinction is mainly made between sunny slopes (SE–W in the northern hemisphere) and shady slopes (NW–E).

A local **microclimate** forms depending on the inclination and exposure, which can have stronger effects on soil development than the predominant macroclimate. Lower air and soil temperatures, as well as lower light intensity and evaporation values are generally observed on shady slopes than on sunny slopes. The alternation between soil freezing and thawing is also less frequent on shady slopes than on sunny ones. As a result, the soils on shady slopes exhibit stronger and deeper water penetration and are often more deeply developed than those on sunny slopes; at the same time, however, the weathering intensity is lower on the cooler shady slopes. This was demonstrated in e.g. the analysis (Table 7.2) of *Luvisols*, where despite the greater thickness of the horizons, soils on the shady slopes had lower clay contents and weaker clay migration than on the sunny slopes. On the other hand, sunny slopes often suffer from persistent dryness. In such cases, soil development on the wetter shady slopes can be more advanced than on the sunny slopes. According to PALLMANN, using the example of the Swiss Alps, *Rendzic Leptosols* developed from limestone on the sunny slopes with a thin Ah horizon and pH values between 6.8 and 7.5, while on the shady slopes, *Foli-Rendzic Leptosols* were formed with a thick humic organic layer and pH values between 4 and 6 (Sect. 7.5.1.2). However, this phenomenon can often also be additionally altered, e.g. in Europe where the rain-bearing low pressure systems mainly travel eastwards, so that west-facing slopes are more strongly wetted. Finally, depressions are particularly wet and cool, because water flows in from the slopes and also cold air on radiation nights.

On level sites, mass transport in the soil mainly takes place in a vertical direction. Slopes favor lateral or surface-parallel mass transport, which surpasses the boundaries of the pedon. The soil body can then move as a whole under the influence of gravity, e.g. in cold climates as mudflows.

In contrast, runoff surface water more often causes soil erosion, and/or the slope water transports dissolved substances from upper slope soils to the lower slope or valley soils (see Sect. 7.2.7.2). The development of low-lying landscapes is often affected by groundwater (see Fig. 7.3 and Sect. 7.1.4).

7.1.4 Water

In addition to rainwater, groundwater or flowing and standing waters also affect the development of certain soils. The boundaries between the groundwater and soil water, similar to the boundaries soil/parent rock, are gliding because parts of the groundwater body or water body generally belong to the soil. They completely fill the voids. Their influence is given such great importance that in German soil systematics, a distinction is made between terrestrial soils (groundwater-independent soils), groundwater affected soils (semi-terrestrial soils) and subhydric soils (semi-subhydric and subhydric soils).

Surface-near groundwater modifies the vegetation and affects the decomposability of litter. The soil solution is supplemented with water and dissolved substances from the groundwater through capillary rise. The latter are partly accumulated in the soil: in humid climates

Table 7.2 Influence of exposition upon clay content and thickness of Luvisol horizons from glacial sands under temperate-humid climate conditions of Southeast Michigan, USA (Cooper 1960)

Exposure	Mean clay content (%) of horizons				Thickness (cm) of horizons					
					upper slope			lower slope		
	Ah	E	Bt	C	Ah	E	A/E + B	Ah	E	A/E + B
S	3.8	5.7	12.6	2.6	6	34	64	8	56	85
N	2.8	4.6	7.7	2.7	8	57	91	14	52	103

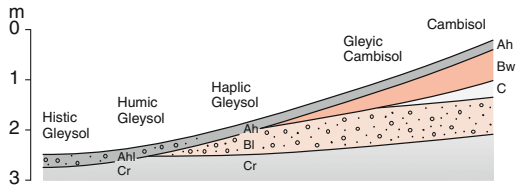

Fig. 7.3 Soil community in relation to the groundwater table (WRB classification)

mainly iron oxides or carbonates, and in arid climates also sulfates or chlorides.

High groundwater tables displace soil air and induce anoxic conditions, which inhibit microbial decomposition, so that **half-fens or *Histic Gleysols*** (Fig. 7.3) and **moors** (Fig. 7.34) can be formed. The groundwater also influences the percolating movement of water in the unsaturated soil zone and retards leaching processes.

The water from rivers, lakes or oceans is located between subhydric soils and the atmosphere, and thus largely protects the soil from atmospheric effects. It promotes a balanced heat budget, but inhibits gas exchange. This reduces the oxygen content, and therefore produces anoxic conditions and inhibits the decomposition of organic matter.

Watercourses often periodically flood the coastal marine environment, i.e. the floodplain soils. Their water adds dissolved substances to the soil, at the ocean coasts mainly NaCl and Mg salts. Depending on the regime, clastic sediments are either deposited or eroded. The addition of unweathered minerals and dissolved salts can delay or sometimes also reverse weathering and dealkalization, and therefore soil development.

7.1.5 Fauna and Flora

Together with the fauna and flora, the soil represents an **ecosystem**, the development of which is influenced as a whole by the previously mentioned factors (see Sect. 1.1). Soil organisms are therefore not an autonomous, independently functioning factor. For this reason, only the interactions between organisms and the soil will be discussed in the following.

The influence of the **edaphon**, i.e. of the fraction of the fauna and flora living in the soil, was already discussed in detail in Chap. 4 and is only briefly reviewed here in terms of its profile-forming effect.

For soil development, the first decisive factor is the **vegetation** that supplies litter for the organic parent material of soils, which is partly transformed by the soil fauna and microorganisms into humic substances. The litter quantity and composition differ depending on the plant community, and therefore also as a function of the climate and soil conditions. This results in great differences between the litter from tundra, desert and steppe vegetation, or from deciduous, mixed or coniferous forests, whereby different humus forms can develop. The vegetation takes up water from the soil and therefore retards translocation processes. At the same time, nutrients are relocated through root uptake and litter restitution from the subsoil into the topsoil (=base pump effect).

The **vegetation cover** acts as a protective shell for the soil. For example, the plants soften the impact of raindrops (Sect. 10.7.1) and store a portion of the precipitation in their foliage (=interception). This reduces or even prevents the removal of solid soil particles by water and wind erosion, as well as the degradation of aggregates and the sealing of the soil surface.

Roots and microorganisms excrete organic acids and complexing ligands, which play an important role in weathering and translocation processes. O_2 removal and reducing conditions in water-saturated soils result in dissolution and translocation, especially of Fe compounds, and thus concretions and/or mottles are formed (see gleying and stagnization, Sect. 7.2.5).

Soil fauna and microorganisms contribute to the formation of stable aggregates, which prevents translocation processes. Burrowing soil animals, such as earthworms and rodents, mix and rearrange the soil. In doing so, they counteract downwards translocation processes and horizon differentiation (see bioturbation, Sect. 7.2.6.1). At the surface of desert soils, crusts can sometimes form under the influence of microorganisms (Büdel and Veste 2008), which

can inhibit soil moisture penetration, especially on slopes.

7.1.6 Human Activities

Humans have a direct effect on soils through land use: (a) through crop cultivation methods, whereby soil development is inhibited or accelerated, or even steered in a new direction; (b) through building measures, whereby soil development is generally aborted, e.g. with surface sealing (Sect. 8.3.2). Indirect effects on soils include changes in the climate, relief, rock or vegetation, or in the groundwater or watercourses.

Agricultural land use has various effects on soil development. The deforestation of central European forests that began in the Subatlantic period, and the subsequent field cultivation reduced the transpiration and thus increased the water infiltration rate, so that dissolved substances were more strongly leached. As a result, the surface runoff on slopes increased and led to a translocation of soil material. **Soil erosion** leads to the partial removal or even the complete elimination of natural soils, while colluvium is piled up preferentially at the foot of the slope and develops into so-called *Colluvisols* according to the German soil classification system (Sect. 7.5.22.2). In the valleys, the rivers often swell and flood the floodplains, leaving fluvial sediments behind.

Plowing destroys the original horizons, creates an artificial Ap horizon, aerates the soil, and therefore accelerates the decomposition of organic matter. In many soils, this reduces the aggregate stability and increases the susceptibility to soil surface sealing and erosion, which is called **soil degradation**.

The soil nutrient contents are increased through **fertilization** and the pH values through **liming**. This counteracts natural and anthropogenic acidification and slows down weathering processes. Especially the dynamics of *Podzols* are strongly modified and adopt the dynamics of *Cambisols*, which is called **regradation**.

The **drainage** of soils affected by groundwater or waterlogging improves the aeration, so that stagnization and gleying are inhibited and groundwater-affected soils can be converted into terrestrial soils.

Forestry also influences soil development. Spruce monoculture results e.g. in shading and poorly decomposable litter, which reduces the number of soil organisms, and increases the tendency to form raw humus and podzolization in nutrient-poor soils. In waterlogged soils, spruce monoculture can lead to compaction of the topsoil and to increased mottling by water stagnation of the subsoils. **Forest fertilization** has similar effect to fertilization of arable fields, mainly accelerating the decomposition of humus.

In all types of soils, a rise in the groundwater table, irrigation and flooding (e.g. in paddy rice cultivation) often lead to gleying, which can also be associated with **salinization** in semi-arid to arid regions. The eutrophication of waters due to the disposal of nutrient-loaded sewage changes the development of subhydric soils, which particularly promotes the formation of sapropel (Sect. 7.5.19.1). Groundwater-affected soils in river valleys are enriched with carbonates and other salts by flooding and infiltration of river water.

In Central Europe, **waste gas from** industry, power plants, vehicle traffic and domestic fuel as well as from intensive agriculture, have led to an accumulation of SO_2, NO_3 and NH_3 in the atmosphere, which reach the soil as acids with precipitation and intensify the acidification (see Sect. 10.2.1).

At the roadsides, in contrast, rubbish, carbonate dusts, and the applications of NaCl (road salt) in the winter result in nutrient inputs and a rise in pH (Fig. 7.4), which, in acidic forest soils, promote the decomposition of humus and inhibit weathering and podzolization.

The climate is also strongly changed by **urban industrial areas**, where temperatures are generally 1–3 °C warmer than in the surrounding areas, leading to an acceleration of weathering and decomposition processes. At the same time, a new parent rock was created by various human technical activities. Here, a distinction is made between relocated **natural** substrates incurring from construction pits, public roads or from the extraction of mineral resources, and **artificial** (or technogenic) substrates such as building rubble,

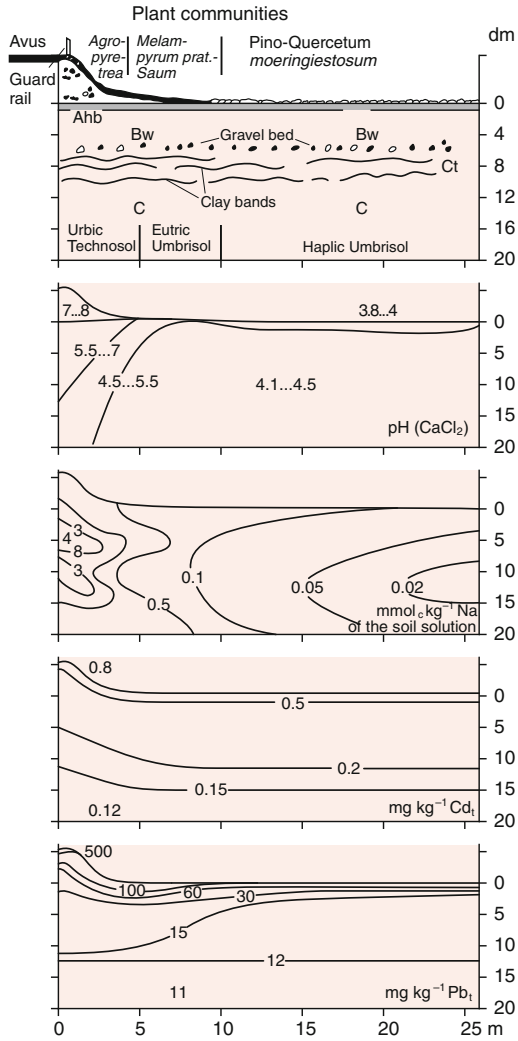

Fig. 7.4 Changing of vegetation, soil units, pH values, Na concentration of soil solution (in relation to 1 kg soil); Cd and Pb contents in relation to the distance of a motor way (Avus in Berlin, Germany; Blume 1996: Fig. 10)

bed ash, ash and urban waste (see Sect. 8.2.1). These deposited substrates (e.g. harbor sludge, loess) are also subject to soil development. In urban waste and sludge landfills, with wastewater irrigation and with fuel infiltrations, high contents of readily decomposable organic matter cause oxygen deficiency and produce *Reductic Technosols* (see Sect. 7.5.9). The same happens through leakage of gas pipelines.

Completely new, **anthropogenic soils** are also formed following the harvest of peat from bogs, deep plowing of *Podzols*, high additions of compost or sewage sludge, peat or plaggen sods, through deep infiltration ditches, terracing etc. In these anthropogenic soils, the character of the natural soil is lost to such an extent that they are described as special soil groups referring to the natural soils (Sect. 7.5.22).

7.1.7 Time

Time is the essence of every process taking place in nature. The longer the climatic, hydrological, biological and anthropogenic factors act on the parent rock and the developing soil, the stronger the change from the original state.

For this reason, age is of great significance for the soil's properties. In this respect, the soils of Central Europe, which have mainly formed only since the Pleistocene, mostly even after the late glacial period, i.e. since ca. 14,000 years, differ fundamentally from many soils in older land surfaces in the subtropics and tropics, which are millions of years old. In Central Europe, the depth of soil formation is generally limited to a few meters, while that of older land surfaces can reach several decameters. The older the soil, the more changes can be expected in the factors affecting soil development, such as the climate, which then influences its genesis. Seacoasts, river plains, and many dunes generally have very young and therefore poorly developed soils, because their development is interrupted by erosion/sedimentation processes.

In different phases of soil development, equal periods of time can lead to different extents of change. Most often, they change greatly at the beginning, and only change minimally later after reaching a certain equilibrium between the environment and the soil or between the environment and the soil-biocenosis system. For this reason, in terms of soil development, time must also be considered as a historical category, as a concrete developmental process.

7.2 Processes of Soil Development

Substance transformations and translocations are continuously taking place in the soil, and are associated with the conversion of energy. These transformations and translocations consist of numerous individual chemical, physical and biological processes that take place simultaneously and successively, mainly induced by the climate and soil organisms and defining the soil dynamics as a whole.

Recurring changes in the soil temperature during the course of a day or a year (Sect. 6.6) and of the soil moisture as a result of precipitation and evaporation or infiltration (Sect. 6.4.5) are observed. Soil aggregates are formed and degraded through shrinking or animals like earthworms, and swelling, associated with cyclical compaction and loosening (Sect. 6.2.2). The properties of the soil solution, such as the soil reaction (Sect. 5.6), the redox potential (Sect. 5.7), or the type and concentration of ions (Sect. 5.1.2), are subject to constant change under the influence of precipitation, water movement and molecular diffusion, exchange processes with mineral, humus and root surfaces, as well as organism activities (Sect. 4.3). The same is true for the amount and type of soil organic matter through decomposition and humification (Sect. 3.5), and for the mineral composition through dissolution and crystallization (Sect. 2.4.2).

On the one hand, cyclical substance translocations take place in the soil, e.g. soluble salts shuttle between the topsoil and subsoil in alternate dry and moist climates. On the other, they also take place between the soil and the plants. Ultimately, it is a large-scale matter cycle like water and element precipitation, associated with water and element translocations. Humans can also be involved in these processes, e.g. through the removal of plant material at harvest and fertilization (Sect. 9.5).

Many of these processes are not completely reversible, which results in small permanent changes that add up to larger changes over the course of time. Provided that this results in characteristic soil properties or soil horizons, it is referred to as profile-formative or soil-forming processes, which as a whole determine the course of pedogenesis. The soil development factors determine the type and intensity of pedogenic processes (Sect. 7.1).

On the one hand, new soil horizons and changes occur through conversion processes (transformations) such as weathering and mineral formation, decomposition and humification, and structure formation, and on the other, through transport processes (translocation), where percolating, ascending or also laterally moving water leads to a redistribution of substances. Accumulation processes act externally; in doing so, the addition of carbon (and nitrogen) through plant assimilation leads to the formation of organic matter. Furthermore, particles (dusts) and dissolved substances are added from precipitation and sometimes also groundwater. Depletion processes are mass losses through erosion and especially dissolved substances though leaching.

These horizon-formative processes are accompanied by horizon-blurring processes or **turbations**, through which material from different soil depths or soil horizons are mixed by alternate wetting and drying, periodic freezing, burrowing soil fauna, or also plowing.

Some of the above-mentioned processes, particularly the substance transformations, were already described in Chaps. 2–6; still, they will be discussed here again briefly to demonstrate their influence on profile differentiation. In principle, the individual profile-formative processes cannot be observed in isolation from one another because they influence each other mutually, and because only the various interactions between them lead to soil formation (and to the development of very different soils).

7.2.1 Transformations and Depletions of the Mineral Body

References: Ollier (1984), Campbel and Claridge (1987), Duchaufour (1998) and Wilding (2000).

Weathering and **mineral formation** are physical, chemical and biological processes (Chap. 4). These result in profile differentiation, because they take place at different intensities in the individual horizons, and lead to the formation of different new minerals to various extents.

Physical weathering (Sect. 2.4.1) causes solid rock, called R layer, to be broken into fragments and loosened. This leads to the formation of a C horizon through transformation. Chemical weathering (Sect. 2.4.2) partly or completely dissolves the minerals. Especially in humid climates, it is associated with the leaching of dissolved weathering products as well as dealkalization (Sect. 2.4.2.2) and acidification. Weathering is often coupled with the formation of new minerals from the dissolution products: Clay minerals (Sect. 2.2.5) and iron oxides (Sect. 2.2.6.3), among others, are formed, which ultimately lead to the formation of a B horizon in the subsoil.

Moisture penetration and temperature essentially control the type and rate of weathering and mineral formation. Their dependence on the climate leads to typical forms of these two processes in the various climatic zones on Earth, which are described in the following.

7.2.1.1 Frost, Temperature and Salt Splitting

The alternation of freezing and thawing of soil water causes **frost splitting** or **cryoclastics** (Sect. 2.4.1) and plays a role in profile formation, especially in the permafrost soils of cool climates and the thaw zone of permafrost soils. The minerals in the topsoil are fragmented more intensively the more frequent the alternation between freezing and thawing, which depends on the depth of the summer thawing (0.2–1.5 m). For this reason, it is stronger in Subarctic or subalpine than in Arctic or alpine regions. In cooler regions, especially the slopes facing the sun are affected, because here the frozen soil thaws more frequently and deeply, and in warmer regions often the shady slopes, because the heat-insulating vegetation cover is lacking for a longer period of time. High amounts of precipitation reduce cryoclastic processes, because a thick snow cover compensates for temperature differences, just as with very low amounts of precipitation, because the soils are then too dry. Many rocks in German low mountain ranges were deeply fragmented and loosened in the periglacial area through cryoclastics during the Pleistocene glacial period.

A rapid change in temperature can also lead to fragmentation of the mineral particles without freezing and thawing of the soil water. It is then called temperature splitting or thermoclastics. It plays an important role mainly in continental hot deserts such as the inner Sahara, where daily temperature fluctuations of 30–50 °C were measured. In soils, the fragmentation of rock and minerals by **heat splitting** reaches a depth of about 50 cm. It is supplemented by **salt splitting**, which can already be triggered by nocturnal dewdrops and was even observed in cold deserts.

7.2.1.2 Brunification and Loamification

The weathering of minerals containing iron with the formation of iron oxides is of great significance for the extent of profile differentiation. The liberation of iron from silicates containing Fe(II), such as biotites, olivines, amphiboles or pyroxenes, only reaches a greater extent after decalcification and lowering of the pH value below 7. In temperate and cool climates, it leads to the formation of brown-colored iron oxides, especially **goethite**, which sometimes accumulate at the surface of primary minerals. This **brunification** results in the transformation of a C into a Bw horizon. Especially in humic topsoils, the reaction of iron with organic acids also forms organometallic complexes, which (due to strong Ca occupancy, among other things) are immobile, and also coat mineral particles and cement finer particles together to form aggregates. Brunification is the profile-formative process in many soils in temperate climates.

Brunification is often associated with the formation of clay minerals, which is called **loamification**. Table 7.3 shows examples of the intensity of clay formation.

Brunification and loamification were favored in soils of Central Europe, because intense

Table 7.3 Intensity of clay formation and clay migration in soils of Germany, New Zealand and USA (data in kg m^{-2}, age in years; after Jenny 1980; Kussmaul and Niederbudde 1979; Blume 1981)

Soil unit	Material	Landscape	Age of soil	Clay formation	Clay migration	Authors
Luvisols	Boulder marl	NW Germany	12/13,000	34–70	66–112	Blume
Stagnic Luvisols	Boulder marl	NW Germany	12/13,000	28	44–64	Blume
Luvisols	Loess	Lower Saxony	15,000	88–117	42–91	Meyer
Alisols	Loess	Bavaria	15,000	63–98	35–51	Kussmaul
Andosols	Volcanic ash	Palatinate	11,000	72		Jenny
Brunic Arenosols	Dune sand	New Zealand	10,000	72		Syers and Walker
			3000	18		
Podzols	Dune sand	Michigan	10,000	15–18		Franzmeier and Whiteside
			3000	7		

cryoclastic weathering took place during the glacial periods. The boundary of intense brunification today often coincides with the thawing depth (developed through cryoclastic and cryoturbic change) of the periglacial permafrost soil, which partly leads to the conclusion that brunification also occurred already in the Pleistocene.

7.2.1.3 Ferrallitization and Desilification

Under the intense weathering conditions found in the humid tropics, soils are strongly depleted of silicium (desilification), while Fe and Al oxides accumulate in addition to kaolinite and Al chlorite as stable weathering products. This process is called **ferralitization** and results in a ferric horizon (definition see Sect. 7.3).

In the initial stages of tropical weathering (or in the contact area to the unweathered rock), silicates such as feldspars and biotite are dissolved and result in loosening of the rock structure, whereby alkaline and alkaline earth metal ions are already partly removed. In permeable soils, these minerals are later also dissolved, associated with a strong removal of the dissolution products in the sequence Ca > Na > Mg > K > Si. At the same time, Fe oxides are formed, and also hematite in addition to goethite (in the case of higher mean annual temperatures and an extensive lack of organic matter).

Gibbsite is often formed from alkaline igneous rocks; the same is true for Si-rich rocks with strong silicic acid leaching; otherwise kaolinite can be formed. If quartz is also finally dissolved, only very few very stable primary minerals remain, such as zircon, tourmaline, anatase and rutile. Kaolinite can then also be decomposed, because the required Si is missing. This leads to mass losses of up to 90 %. Because the outer shape of the primary minerals is often maintained for a long time (structure retention in saprolites), and therefore no subsidence occurs, ferrallitization is often associated with a strong reduction in the bulk density.

During the course of millions of years, weathering in the humid tropics has reached depths of 40–60 m (in contrast, weathered soil covers with a depth of several hundred meters are mostly formed by translocations). In doing so, individual rock boulders often remain unweathered; they form separate blocks, which then later cover the land surface as erosion residues.

Under humid climate conditions, the deeper soil layers are often water-saturated for long periods of time. This prevents the oxidation of the iron liberated from silicates, so that it is

removed laterally and accumulates at the edges of slopes. Under alternate wetting and drying conditions, the water moves upwards with capillary rise and also leads to an absolute accumulation of iron in the topsoil (f.e. plinthite formation). Figure 7.26 shows an example of a tropical soil with very strong deep weathering and desilification.

7.2.2 Humus Accumulation—Development of Humus Forms

References: Boden (2005), Beyer (1996), Blume et al. (2011: p. 39ff), Jahn et al. (2006: p. 67ff) and Soil Survey Staff (1999: p. 21ff).

The greater portion of organic matter entering the soil when plants, plant parts or animals die, as well as in the form of animal and plant excretion products, is mineralized. Generally, only part of it is transformed into humic substances that remain in the soil over longer periods of time. Together with litter residues, humic substances represent (in Germany) the **humus body** of the soil.

The type and quantity of litter and humic substances composing the humus body depend mainly on the quantity and composition of the annually produced litter (Sect. 3.3.1), i.e. it essentially depends on the vegetation. This is accompanied by the capacities of the soil organisms that decompose, humify and mix the organic matter with the mineral substance, depending on their living conditions (Chap. 4). This means that the heat, water, air and nutrient conditions of a site are decisive.

The humus body can be morphologically divided into humus horizons that differ in terms of the humus texture (type, fraction and properties of the basic macroscopic organic constituents) and the humus structure (packing type and density of the basic constituents). The humus horizons are layered on top of each other or are mixed with mineral soil horizons. All of the humus horizons together represent the humus form, and the vertical section is the humus profile.

According to the environment, a distinction is made between terrestrial humus forms, which are formed under predominantly aerobic conditions, and hydromorphic and subhydric forms, which are formed under intermittent to constant anoxic conditions.

7.2.2.1 Terrestrial Humus Forms

Terrestrial humus forms develop without the effects of groundwater or surface waters. A distinction is made between the organic layers with more than 30 % organic matter (the O horizon) and the humus horizons in the mineral soil profile. If the incorporation of incoming organic matter is inhibited (because of the absence of soil mixing organisms), the humus layers on many forest sites are divided into the following horizons from top to bottom (symbols after Jahn et al. 2006).

The **litter layer** (or Oi horizon) consists of nearly undecomposed leaves or needles, seeds and twigs from trees, herbs and shrubs. The leaves and needles sometimes have irregular spots, are cracked and partly chewed on, which may have already happened on the plant. A small amount (<10 %) of **fine humus** (humic substances and crushed litter without macroscopically visible tissue structures) sometimes adheres to the litter as animal excrements.

The **coarse humus horizon** (or Oe horizon) consists of half-decomposed leaves or needles and small animal excrements. Fine humus accounts for 10–70 % of the soil organic matter. The **fine humus horizon** (or Oa horizon) mainly consists of fine humus and only small amounts of crushed litter residues with visible tissue structure (<30 %). With fine humus, a distinction is also made according to the aggregate size and consistence between crumbly **worm humus** (contains trapped mineral particles), fine crumbly **mor humus** (usually feces from arthropods and Enchytraeidae without mineral particles) and greasy **pitch humus** (fully decomposed droppings).

The Ah horizon, follows underneath these organic layers. It contains little coarse humus or only in the form of dead roots (residues) and dead animal bodies; the fine humus dominates here. The latter either forms its own aggregates,

which are deposited by small arthropods as fecal pellets, are silted by rain, or are mixed with mineral particles by soil mixers (burrowing soil animals). If there is also low base saturation (BS < 50 %), it is an **umbric Ah**. With high base saturation (>50 %), it is called a **mollic Ah** or worm humus horizon, (especially in Chernozems and Phaeozems), where (with higher earthworm populations) the humic substances are combined with mineral particles to form crumbs. A crypto-humus horizon is present when the Ah horizon, because of low humus contents, is relatively light in color and the soil structure was produced abiotically (singular, polyhedral), whereby there is usually no humus layer.

The **humus forms** therefore represent combinations of the described humus horizons. The most important are raw humus, mor and mull.

Raw humus is generally characterized by a thick (5–30 cm) organic layer. A humic A horizon is lacking or is thin compared to the organic layer. Humic substances are often leached into the subsoil through podzolization (see Sect. 7.2.4.2). The organic layer is divided into coarse and fine humus horizons. The transitions between the individual horizons are abrupt. Humic substances are present as mite and Collembola feces, which are riddled with fungal hyphae. The humus body is characterized by a broad C/N ratio of 30–40 in the Oe and 25 in the Oa, and low pH values (under 4). Raw humus is formed particularly in extremely nutrient-poor and coarse-grained soils, with a vegetation cover that supplies poorly decomposable and nutrient-poor litter, such as heathland (*Calluna*, *Erica*, *Vaccinium*, *Rhododendron*) or conifers (*Picea*, *Pinus*). Dense, low-light spruce or European beech forests without an herbaceous understory promote the formation of raw humus, just as is the case with a cool humid climate. Raw humus is classified as *umbric* epipedon after Soil Survey Staff (1999, 2014).

Mostly all of the organic layers are also present in **mor humus**, but with a lesser thickness. However, the transitions are diffuse, the horizons are much more entangled in each other, and a clearly pronounced humic mineral soil follows underneath. Coprogenic aggregates (i.e. fecal pellets) are found in the organic layer and in the upper mineral soil originating from Enchytraeidae and numerous arthropods, which have strong populations in moder humus. A strong 'musty' smell characterizes the moder as well as a looser packing of the humic horizons compared to raw humus. The C/N ratio is of 20, the pH values in soils developed from silicate rocks are of 3–4, and in those developed from carbonate rock also >4. Moder is mainly formed in soils under deciduous and coniferous forests with sparse herbaceous undergrowth that developed from relatively nutrient-poor rocks, under monocultures or under cool humid climate conditions.

(German) ***Pechmoder*** (**pitch humus**), which is only found on the wettest sites in high alpine landscapes, has Oa horizons with a thickness of up to 20 cm mainly originating from Collembola droppings, and with a deep black appearance.

Mull completely lacks an organic layer, or it disappears under deciduous forests a few months after the litter falls to the ground, i.e., it is not always present. It is typical for a *mollic* epipedon after Soil Survey Staff (1999, 2014). In the case of mor-mull a thinner Oe horizon is observed all year round (Fig. 7.5). The Ah horizon is often quite thick and is almost completely lacking in litter substances. The humus body is rather composed almost solely of brown-grey to black fine humus that is closely associated with clay minerals as a component of crumb aggregates. Many burrowing and soil-eating soil animals like large earthworms are present. In mull humus, which has a characteristic fresh 'earthy' smell, the soil flora mainly consists of bacteria and Actinomycetes. The C/N ratio in the Humus body lies between 7 and 15, and the soil reaction is weakly acidic to alkaline. Mull is formed in soils under favorable water and air conditions and relatively high nutrient contents, where the litter is rapidly broken down and decomposed. Mull requires vegetation that supplies nutrient-rich, readily decomposable litter. This means that it is mainly formed under steppe vegetation and deciduous forests with a rich herbaceous understory.

In subalpine dwarf-shrub regions and high montane forests, the **Tangel humus** form is

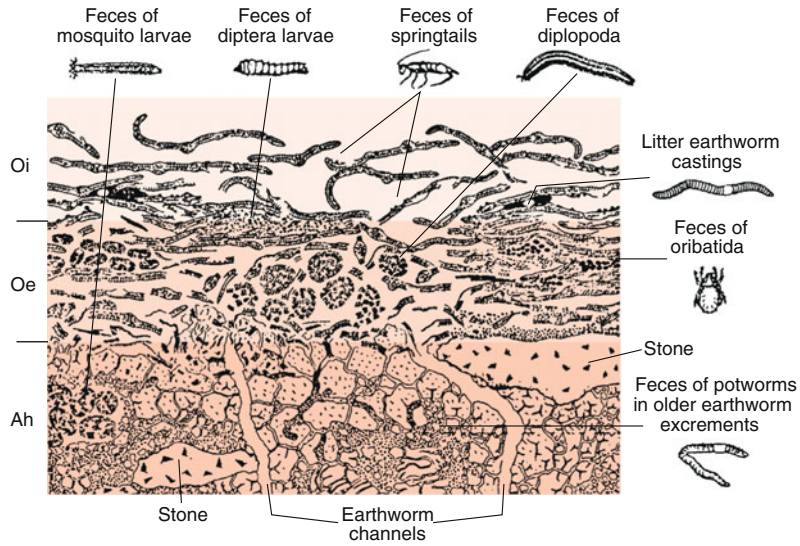

Fig. 7.5 Humus body of a forest soil with relatively good conditions of decomposition and humification with soil animal feces (Oi with slightly decomposed litter of beech trees; Oe moderately decomposed litter, Ah mineral layer with strongly humified organic matter) (after ZACHARIAE, modified)

found on carbonate rocks under the influence of a cool humid climate, which is characterized by humus layers with a thickness of up to 1 m. Here also, there is a visible division of the organic layer into a litter-rich, acidic Oe horizon and a humic substance-rich Oa horizon. Compared to raw humus, however, the horizon transitions are less abrupt. The humic A horizon (Ah) is generally clearly developed and even often contains earthworm casts.

7.2.2.2 Hydromorphic Humus Forms

In wet soils, the lack of oxygen inhibits decomposition and therefore leads to an accumulation of organic matter. Soils that are only wet to water saturation in the winter, while in the summer, are aerated from the top due to water evaporation, have humus forms similar to terrestrial soils with slightly higher humus contents as a result of the slower decomposition. They are called **hydromorphic humus forms**, whereby a distinction is made between hydromorphic mull, hydromorphic mor and hydromorphic raw humus. If mineralization or also the cutting of litter by animals is even more strongly inhibited by oxygen deficiency, half-fens or peats are formed as **wet humus forms** or **bog humus forms**.

Especially in nutrient-rich mineral soils, year-round high groundwater levels lead to humus contents between 15 and 30 %, and are called Aa horizons (according to the German soil classification system). If such soils do not have a humus layer, it is a half-fen. In **half-fens** (German *Anmoor*), humic substances dominate that are formed by aquatic animals and facultative anaerobic microorganisms. At medium water contents, half-fens have an 'earthy' structure, which becomes 'muddy' with persistent water saturation. The humic horizons together have a thickness of 20–40 cm and have a neutral to weakly acidic reaction.

On nutrient-poor sites with high groundwater levels and on more nutrient-rich sites that are subject to persistent or year-round flooding, the decomposition of litter by animals is strongly reduced so that humus layers with more than 30 % organic matter are formed, which are called **peats**. Here, a distinction is made between fen, transitional and bog peats, which can be further classified according to the type of predominant vegetation residues as well as the degree of humification.

The subhydric humus forms **dy**, **gyttja** and **sapropel**, are found at the bottom of lakes. Because their properties also represent the

significant characteristics of their soils (subhydric soils), and the genesis of their humus bodies is equivalent to the genesis of the soil type, they will be explained individually in Sect. 7.5.19.1.

7.2.2.3 The Classification of Humus Forms

After Blume (2011), Blume et al. (2012), the German natural scientist **Christian Ehrenberg** (1795–1876) described between 1818 and 1856 the (micro)morphology, mineralogy and organisms (microbes and animals) of >1000 soils (mainly A horizons but also some profiles) of all continents, and documented the results with several colored paintings: *Chernozems*, *Cambisols*, *Leptosols*, *Arenosols*, *Cryosols*, *Gleysols*, *Limnic* and *Tidalic Fluvisols* were studied, among others. In 1837, **Charles Darwin** (1809–1882) gave a lecture in London *On the Formation of Mould,* talking about the effects of earthworms on the soil under meadows. This was done based on morphological studies of soils in the field and microscopic studies of earthworms and their excrements in the lab. In the year 1862, the Swedish quaternary geologist and pedologist **Hampus van Post** (1822–1911) was the first to describe, investigate and classify the **forms of humus** *mylla* (Engl. mull), *torf* (peat), as well as dy (or peat mud) and gyttja (or eutrophic mud). In the years 1870/80, the Danish forest pedologist **Müller** (1840–1926) studied the morphology and chemistry of loamy and sandy forest and heathland soils (organic as well as mineral layers) in Denmark and Norway, and described and classified their humus forms. He described earthworm *muld* (mull), insect *muld* (moder) and *mor* (raw humus). In 1953, the Austrian pedologist **Walter Kubiena** (1897–1970) described different humus forms and published a taxonomy of humus forms.

7.2.3 Structure Formation

Structure formation, i.e. the spatial change in the arrangement of mineral particles and organic substances and their linking to form aggregates (Sect. 6.3), also plays an important role in the differentiation of soil into horizons. Different forms of soil structure are shown in Fig. 6.14a–i.

In **clay soils**, water absorption and the associated swelling often cause layered or slaty rock structure to be transformed into a **coherent structure** (b). Under dry conditions, aggregates are segregated from this structure due to shrinking. Coarse prisms are often formed in the subsoil, and smaller polyhedrons further up in the profile. However, the size and shape of the aggregates also depend on the clay mineral constituents and on the type of the adsorbed cations. In alkaline soils, for example, columns are formed. Water penetration initially produces a coherent structure again; the fissures do not subsequently close again completely, partly due to an alignment of the layered silicates on the aggregate surfaces, so that although the aggregates swell, they retain their shape.

In the biologically active topsoil, the soil fauna produces fecal pellets, which only partly disintegrate when they are wetted, so that subsequent desiccation produces an imperfect separation structure with raw aggregate surfaces, i.e., subangular blocky aggregates. In humus- and nutrient-rich topsoils with strong biological activity, a **crumbly structure** (g) is even formed that remains stable with alternate wetting and drying, and can therefore be maintained for a longer period of time. For this reason, a clear change in the structure form with increasing depth is often observed in clay-rich soils.

Sandy soils generally have a **single grain structure** (a). In the humic topsoil, it is riddled with embedded arthropod and Enchytraeidae feces, i.e. with fine granules. A fine granular structure can also be found in the subsoil, if the few clay particles between the sand grains coagulate to form microaggregates.

A crumbly structure is only formed in the humic A horizon if silt and fine sand dominates and the living conditions are also favorable for earthworms.

In **loamy soils**, the Ah horizon generally has a crumbly structure produced by earthworms. A **subangular blocky** (f) to **prismatic**

(d) structure follows in the subsoil, where the aggregates become coarser with increasing depth due to more infrequent drying.

Substance embedding can lead to the formation of a strongly cemented, **massive structure** (c), which can result in hard banks that cannot be penetrated by roots. Cementing substances include organometallic complexes in the hardpans of *Podzols* (Sect. 7.5.7), iron oxides in bog iron ore of *Petrogleyic Gleysols* (Sect. 7.5.18) and in (*Petro-*)*Plinthic Ferralsols* and *Plinthosols* (Sect. 7.5.12), carbonates or gypsum in *Petric Calcisols* and *Gypsisols* (Sect. 7.5.13), salts in *Petrosalic Solonchaks* (Sect. 7.5.15), and Si oxides in *Petric Durisols* (Sect. 7.5.14).

Some soils have thin **crusts** at the surface. These are mainly formed on vegetation-free, silt-rich soils due to the splashing effect of raindrops. On farmland, these crusts are quickly destroyed again by soil tillage. On desert soils, however, cementing takes place through microorganisms. These 'biological' crusts are even formed on sandy soils, probably because dust is also bound. Stable thin crusts can form under arid climates, but also on groundwater-affected soils due to the capillary rise of dissolved salts. However, many such crusts are also produced from the exposure of cemented subsoils by erosion of the overlying soil.

Special structural forms such as concretions, mottles or coatings are usually a result of specific translocation processes and will be explained there.

7.2.4 Translocations

7.2.4.1 Clay Migration

References: Blume (1964) and Fanning and Fanning (1989).

Clay migration or **lessivage** is the downwards transport of small clay particles in a solid state. Mainly constituents of the fine clay fraction (<0.2 μm) such as clay minerals, fine-grained Fe, Al and Si oxides and humic substances that are bound to mineral particles are involved. Clay migration leads to a depletion of the clay content of the upper horizons, while the clay content in the lower horizons increases. Still, a maximum clay content in the subsoil can also have other origins, such as geological stratification (primary rock differences or later sand cover of the soil surface), the formation of new clay minerals or preferential upward movement of larger particles like coarse sand, gravels and/or stones by cryoturbation or peloturbation (Sect. 7.2.6).

Just like any other translocation, clay migration consists of 3 sub-processes: (1) dispersion, (2) transport and (3) deposition of the clay particles.

The process of **dispersion** is necessary because the clay particles are usually combined to form aggregates, and these must first be broken down to primary particles to enable translocation. Dispersion only takes place at very low salt concentrations in the soil solution, and therefore requires that the topsoil be largely desalinized and decalcified. A large number of sodium ions in the sorption complex promotes dispersion as well as a high content of swelling clay minerals like smectites.

The **transport** of clay particles requires rapidly moving seepage water. In contrast to the dissolved substances, clay is only transported over longer distances in **coarse** and **medium-sized pores** (macropore flow), and not in fine pores, because the clay particles are too large and are too strongly attracted by the surface forces of the pore walls. In fine-grained soils, transport is therefore only possible in shrinkage cracks and bio-pores (holes of earthworms). Because shrinkage cracks occur more frequently during longer dry periods, clay migration takes place more intensively in climates with pronounced **alternate wetting and drying** than in regions with high amounts of precipitation that are evenly distributed.

The clay particles are deposited where one or several of the factors promoting dispersion or transport are no longer acting: The clay particles are flocculated at the transition to a subsoil containing carbonates. Secondary pores such as animal tunnels or desiccation cracks end further down. In fine-grained soils, the seepage water then penetrates into the fine-pored aggregates from the sides, whereby the clay particles are deposited on the pore walls (Fig. 7.6). In

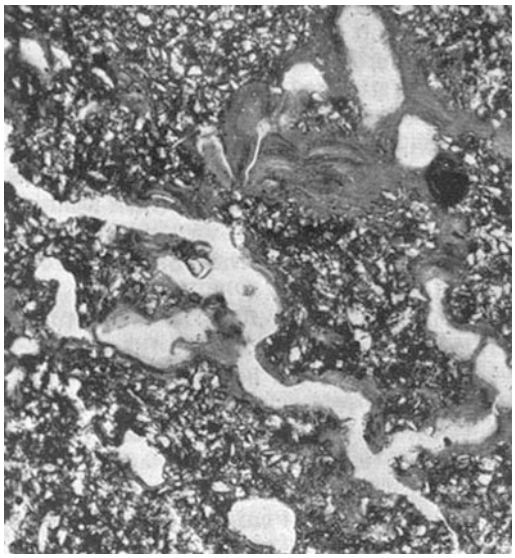

Fig. 7.6 Thin section of the Bt-horizon of a Luvisol. Layered coatings on surfaces of large pores are visible (picture from H-J. Altemüller)

coarse-grained soils, in contrast, the clay particles are often deposited on layers with higher density due to sedimentation or former ice pressing. According to B. Meyer, Göttingen, trapped air can also impede the seepage water front and lead to the formation of thin clay bands in sandy soils.

Considerable amounts of clay can be translocated. In soils developed on loess and calcareous glacial till from the last glaciation, 40–110 kg of clay per m^2 were translocated since the beginning of stronger soil development about 12,000–15,000 years ago (Table 7.3).

However, the clay did not migrate with constant intensity. In soils developed from carbonate rocks, translocation begins as soon as the topsoil is decalcified, and stops again when large amounts of Al ions are released by strong soil acidification. The longer a soil remains in a pH range between 6.5 and 5.0, the more clay can be translocated. Some soils developed from carbonate-free rocks are so rapidly acidified that there is no appreciable clay migration, but *Umbrisols* are formed.

Clay migration is the profile-formative process of *Luvisols* and *Albeluvisols*, as well as *Acrisols* in warm climates. In these soils, it leads to the formation of a pale **eluvial horizon** (E horizon) above a strongly colored **clay-riched** Bt horizon. Clay migration also took place in many other soils in virtually all climate regions: For example, it is responsible for clay bands in many *Hypoluviv Arenosols* in the German lowlands and low mountain ranges, or is involved in the development of the columnar horizons typical for *Solonetzes* (Sects. 6.3.1 and 7.5.16).

Clay migration results in intercalation compaction of the subsoil. This can cause periodic waterlogging, which leads to the formation of stagnic subunits of Albeluvisols and other soils with clay migration. It results in oxygen deficiency for plants. The clay-depleted topsoils are more easily silted up with strong water penetration and are more subject to erosion on slopes. In ecological terms, clay migration also represents a redistribution of nutrients and exchange capacity in the rooting zone.

7.2.4.2 Podzolization

References: Petersen (1976) and Wiechmann (2000).

Podzolization is the downward movement of organic substances in soils, often together with complex-bound aluminum and iron. The translocation takes place with strong acidic reactions, because the nutrient deficiency then inhibits microbial decomposition of the organic ligands. A cool humid climate also inhibits organism activities and can therefore promote podzolization. A distinction is made between mobilization, transport and precipitation.

Among the **organic** substances, mainly low-molecular compounds from throughfall of trees, poorly decomposed plant litter, O horizons and root exudates are translocated. These compounds form **organometallic complexes** with Al and Fe ions from silicate weathering and/or those that were previously absorbed by the vegetation.

The translocated substances are precipitated and accumulate in the subsoil. There are different causes for **precipitation**. The organometallic complexes can flocculate if additional Al or Fe ions are bound during transport, because the solubility decreases with an increasing metal-carbon ratio. A higher pH value or a higher

Ca saturation in the subsoil can also promote precipitation through the disintegration of the organometallic complexes or their floccules. Finally, organic ligands can also be decomposed microbially. Organic metal complexes can be adsorbed onto already precipitated Al and Fe oxides, so that an existing accumulation horizon can then act as a filter itself. Precipitation is also promoted by reduced hydraulic conductivity in subsoils with slightly higher clay contents.

Some of the translocated substances are separated in the illuvial horizons. Organic substances usually accumulate most strongly in the topmost sub-horizon, and Fe, Al and finally Mn oxides in the deeper-lying sub-horizons.

The translocated substances often coat mineral particles and cement them together; they form a **coherent to massive structure** that is typical for the B horizon of *Podzols*. *Podzols* with a massiv B horizon are classified as *Ortsteinic Podzols*. However, thicker coats develop cracks as a result of frequent drying, are fragmented and then often form microaggregates in the interstices of soils with single grain structures.

Podzolization often only initially causes the degradation of organometallic and oxidic coatings on the mineral particles, and thus their bleaching in the topsoil (=**particle bleaching**), whereby iron remains in the neighboring humus aggregates and therefore in the Ah horizon, but aluminum and especially manganese can already be displaced into the B horizon. Stronger podzolization then produces a bleached eluvial horizon (E horizon) over a brownish-black (soft) *orterde* (=friable iron/humus pan) or (hardened) *ortstine* (=hard iron and/or humus pan) illuvial horizon. A humus-enriched B is a Bh horizon, an iron and/or Al enriched B is a Bs (s from sesquioxides) horizon. Podzolization leads to the dislocation of nutrients in the rooting zone, such as Cu, Fe, Mn, Mo and P.

7.2.4.3 Decalcification and Calcification

References: Driessen et al. (2001), Nettleton (1991) and Wilding (2000, 2011).

Under humid (to semiarid) climatic conditions, the carbonates from the parent rock are dissolved by acids from precipitation and soil respiration, and are leached out of the topsoil. In the subsoil, it can then precipitate again and thus cause **calcification**. In doing so, secondary carbonates can be finely distributed and penetrate the matrix, form white coatings on the aggregate surfaces (so-called **pseudomycelia**), or concretions through to hard pans. The symbol k is added for a horizon with secondary carbonate accumulation. Secondary carbonates are generally present as calcite or aragonite. Dolomite is only observed under the effect of water with very high Mg contents.

A slight carbonate accumulation promotes the formation of a loose aggregate structure that is resistant to silting. Stronger carbonate accumulations, in contrast, cause a solid massive structure. Such a consolidated horizon is called *Petrocalcic* horizon, **calcrete** or **caliche**. Carbonate accumulations like calcretes can reach the topsoil through erosion and then form crusts. Groundwater calcification can also directly lead to a crust formation at the soil surface. Calcareous crusts and carbonate beds in the soil inhibit root growth. They must therefore be broken by loosening or plowing.

In terms of genetics, a distinction is made between air borne water, groundwater, slope water and underwater calcification.

Rain water calcification is observed in terrestrial soils. In very moist climates, the hydrogen carbonates formed by the weathering of carbonatic rocks are completely leached out. In drier, alternate wetting and drying climates, they are partly accumulated again in deeper horizons as $CaCO_3$, where the Ca also partly originates from silicate weathering or precipitation. $CaCO_3$ accumulation is then followed by gypsum and then finally salt accumulation further down. In permeable soils, carbonates accumulate in fine and medium-sized pores, initially at the contact points between two minerals. This is later followed by increasing filling of the voids, sometimes in the form of stalk-like calcite crystals. In soils with inhibited water flow, the medium-sized pores also remain moist for longer periods, so that calcite is only formed in the coarse pores that are more aerated (e.g. as **loess puppets**). The $CaCO_3$

accumulation in *Calcisols* (Sect. 7.5.13), which are mainly found in arid climates, is considerable. In soils of rocks without carbonates, earthworms can also cause an accumulation of $CaCO_3$ through their $CaCO_3$-forming gland secretions.

In groundwater-affected soils, hydrogen carbonates are transported upwards and often accumulate as carbonate concretions. In marl or limestone landscapes, even under humid climate conditions, this **groundwater calcification** can lead to the accumulation of large amounts of carbonate as **bog lime** or **meadow chalk**. In soils with lower groundwater tables in arid climates, the $CaCO_3$ will be accumulated in the deeper subsoil. Above it follows an accumulation of gypsum, and above that, water-soluble salts.

Slope water calcification is typical for landscapes with layer sequences with carbonatic rocks of different permeabilities. It is observed where we find a permeable layer on a slope above a less permeable layer (usually clay).

Underwater calcification takes place at the bottom of lakes; here, carbonates mainly accumulate through organisms.

7.2.4.4 Silification

References: Chadwick and Graham (2000/2011) and Nettleton (1991).

Silification is the formation and accumulation of secondary Si oxides in the soil. The chemical weathering of silicates liberates Si, which is leached out into the subsoil as dissolved silicic acid, is absorbed by plant roots, or contributes to the formation of new clay minerals (Sect. 2.2.5). Especially under arid to semi-humid climate conditions, a portion of the dissolved Si can be precipitated in the form of amorphous, hydrous $Si(OH)_4$ polymers, and can be later converted to cristobalite followed by opal due to drainage (Sect. 2.2.6.1). In sandy soils, this takes place at the contact points between the mineral particles, and in clayey soils, on adsorbed $Si(OH)_4$ groups. Drainage and aging of the polymers can then lead to an irreversible cementation of the primary mineral particles. This initially leads to the formation of Si-cemented concretions (durinods), and finally of continuous consolidated beds (**duripans** or silcrete) as typical forms of *Durisols* (Sect. 7.5.14). Consolidation begins already at a Si polymer content of 4 %.

In desert soils, carbonate and Si accumulations are often found in the same horizon, even though in different areas: the former is found mainly in larger voids, and the latter in the soil matrix.

In desert soils, duripans have a platy structure (1–15 cm ∅). In clay-rich soils of Mediterranean climates, it results in hardening of the aggregate surfaces (prismatic structures with 0.3–3 m ∅). Also under humid climates, in soils developed from easily weathered rocks (e.g. volcanic tuff, olivine-rich dunite), a high Si concentration in the soil solution can lead to the formation of silcretes as spring water or groundwater deposits. Bio-opals (Sect. 9.8.1) can accumulate in topsoils. This is especially true for steppe soils, and for sea muds and *Tidalic Fluvisols* (marsh soils), because grasses and diatoms accumulate large amounts of Si.

Duripans impede root penetration into the subsoil and inhibit water movement.

7.2.4.5 Salinization

References: Bresler et al. (1982), Singer (2007) and Yaron et al. (1973).

Salinization is defined as the accumulation of water-soluble salts in soils or soil horizons. A distinction is made between an addition of (air borne) salts through precipitation, which only leads to an accumulation of salts under arid climates (=**rainwater salinization**), and an addition from the groundwater, which is observed at the coasts in arid and humid climates as well (=**groundwater salinization**). Furthermore, fertilization, irrigation or the use of road salt can also lead to an artificial salinization (Sect. 10.2.5).

The most commonly observed salts are NaCl, Na_2SO_4 and Na_2CO_3, and sometimes also $CaCl_2$, nitrates and borates. The salts stabilize the soil structure when drying. Dissolved salts influence the soil pH: The salts of a strong base and acid such as NaCl result at a pH of 7, those of a strong base but a weak acid such as soda have a strong alkaline affect (pH > 8–10), and those of a strong acid, but only a medium-strength base such as gypsum have a weakly acid effect (pH 5.8).

Higher salt contents affect plant growth, because they increase the osmotic potential of the soil water and thus impede water uptake (Sect. 6.4.2). Certain elements can have a direct toxic effect (e.g. Cl, B).

After the eluviation of the Na salts (through climate change, relief position or irrigation), many sodium ions often remain on the exchange surfaces (=alkalization). This increases the pH and destabilizes the soil structure, which promotes topsoil silting and enables clay migration. Such alkalized soils have very unfavourable properties for plant growth and are called *Solonetzes* or sodium soils (Sect. 7.5.16).

Rainwater salinization occurs when the soils are subject to continuous additions of dissolved atmospheric salts with precipitation. They mainly come from the oceans. For this reason, NaCl dominates beside K^+, Mg^{2+}, Ca^{2+}, SO_4^{2-}, NO_3^-, HCO_3^- and $B(OH)_4$ salts. In deserts, salt additions also come from dusts. Atmospheric salts are rapidly leached out of soils in humid climates, in contrast, they accumulate in soils of arid climates (Fig. 7.7a). For this reason, desert soils (e.g. *Gypsisols*, *Calcisols*, *Solonchakes*, *Aridic Arenosols* always contain salts. The amount of accumulated salts depends on the proximity to the ocean, the precipitation rate, the duration of arid climatic conditions, the relief position, and the soil permeability. Sandy soils with high permeability are generally relatively poor in salts, because even the extreme deserts in the world (<20 mm annual precipitation) were subject to more humid conditions during the Holocene, during which the salts were leached out into the subsoil. Soils in depressions, e.g. in a wadi (creek with episodical water flow) can be largely free of salts, because they are more strongly percolated during heavy rainfall events (Fig. 7.7c). In permeable or sandy soils, as well as in semiarid climates, the salts are transported more deeply than in less permeable or clay-rich soils, as well as in pronounced arid climates (Fig. 7.7b). But even in (groundwater-free) soils of extreme deserts, the salt maximum is not observed at the surface, because the salt is translocated during episodical storm rainfalls. Although subsequent dryness lets the salts rise again with the soil water, they do not rise all the way to the surface, because the water only moves in vapor form in the very dry topmost soil layers. Soluble salts are accumulated further down in the soil than the more weakly soluble gypsum and calcite. A distinction is also made among the readily soluble salts according to their solubility: The very mobile nitrates as well as $CaCl_2$ accumulate at the very bottom, and soda accumulates fairly high up (Smettan and Blume 1987).

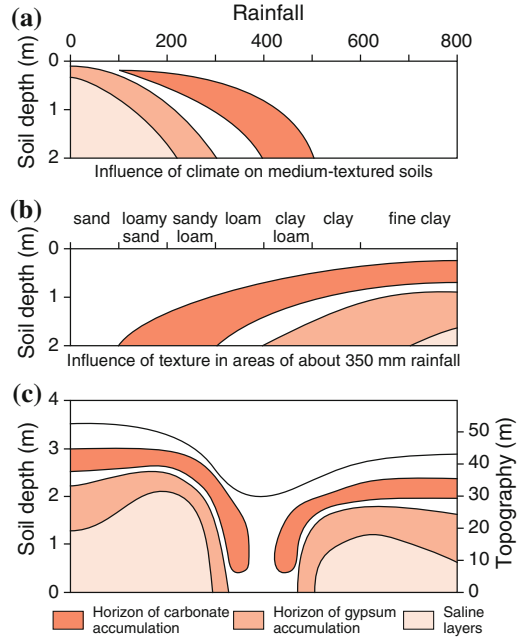

Fig. 7.7 The effect of rainfall, soil texture and topography on soil leaching in arid regions (Yaron et al. 1973: p. 14)

In **humid** climate regions, natural **groundwater salinization** only takes place in areas of influence of the ocean, where the salt content can vary between <1 % (brackish water near estuaries) and 3.5 % (open ocean). Examples of soils that are affected by such salinization are soils in tidal flats and salt meadows that are not diked in. Saline soils are rarely observed inland. They are then associated with surface-near, salt-rich groundwater (e.g. in the area of risen salt stocks or saline springs).

In **arid climates**, however, inland groundwater-affected soils are often enriched with salts. The salts come from saline rocks or

infiltrated rainwater. Under extreme arid conditions, there may be a strong accumulation of salts even with low-salt groundwater. Various salts rise with the capillary water and are then precipitated in the evaporation zone depending on their solubility (Table 2.10): First $CaCO_3$, then gypsum, then soda and Na_2SO_4, and finally Na and Ca chlorides and nitrates at the top. The accumulation can be so strong that it leads to the formation of **salcretes**. **Salt crusts** are formed if the groundwater reaches the soil surface. However, the salts are dissolved again with each rainfall, and may therefore circulate during the course of the year between the topsoil and the subsoil.

On the one hand**, artificial salinization** takes place in soils of humid climates as well due to surface irrigation with Na-rich sewage water, and near roads due to road salt (Fig. 7.4). Furthermore, floodplain soils are contaminated by fluvial water that is enriched with salts due to the discharge of potassium salt from the potash industry. The salts do not remain in the soil, but they lead to an elevated Na saturation on the exchange media, so that clay-rich soils are more readily silted. In arid climates, irrigation can very easily lead to artificial salinization. Especially through furrow irrigation, many areas in India, Iraq, Egypt and the USA have been made fully unproductive. Fluvial water or deep, often fossil groundwater is used for **irrigation**, and although its average salt content is usually below 0.1 %, it can be much higher depending on the season and catchment basin. The salts can then accumulate over the course of the years. The water of the Indus in India, containing only 0.03 % soluble salts, e.g. with an irrigation of 300 mm annually on uncultivated fields, leaves 900 kg of salt behind per ha. Furthermore, irrigation often leads to a strong rise in the groundwater table. The upward movement and evaporation of soil water then leads to an accumulation of salts in the topsoil. **Sprinkler irrigation** strongly promotes salinization, because lots of water already evaporates before it reaches the soil. In contrast, subirrigation (perforated pipes laid close below the soil surface) with plastic sheeting on the soil can prevent salinization to a large extent.

7.2.5 Redoximorphosis

References: Blume (1964), Fanning and Fanning (1989) and Schlichting and Schwertmann (1973).

Redoximorphosis is the formation of redoximorphic characteristics in soils where there is alternation of the oxygen conditions (see Sect. 5.7 for basic principles). The formation of green, blue and/or black reduction colors in case of O_2 deficiency is called **reductomorphosis**, and of those of black metal sulfides are also called sulfide formations. Subsequent aeration causes the formation of brown, red or also yellow oxidation colors, which are observed as concretions or mottles. In doing so, the oxidation of sulfide can lead to the formation of sulfuric acid (**sulfurication**) and may cause soil acidification. Reducing or oxidizing conditions usually develop with the participation of microorganisms. Water saturation favors oxygen deficiency. But even in soils that are not saturated, oxygen deficiency can occur due to O_2 displacement by CO_2 or CH_4 gas through (post)volcanic mofetta (gas springs) or artificial deposits at greater depths of the Earth's crust, damaged gas pipelines, or as a result of strong microbial O_2 consumption in, on and beside urban waste or sewage sludge landfills containing lots of readily decomposable organic matter.

Constantly anoxic soil horizons (then rH values < 12) are often colored black by iron sulfides, especially FeS, or are depleted of iron and manganese and are then bleached white (or colored light yellow by the sulfur). At the same time, the soil air is rich in CO_2 and can also contain methane and traces of H_2S. In oxygen-poor environments (rH values 12–19), Fe^{2+} and Mn^{2+} ions can be detected in the soil solution. Siderite ($Fe^{II}CO_3$) or vivianite [$Fe^{II}_3(PO_4)_2 \cdot 8H_2O$, turns blue when exposed to air] can lead to a grey coloring, or $Fe^{II,III}$ hydroxides to a green to blue (green rust) color of the soil. All characteristics that are typical for rH values < 19 are called **reductomorphic** (and designated with the symbol r in the horizon description).

Sulfides are formed by bacteria such as *Desulfovibrio desulfuricans*, which use sulfate

ions as an electron acceptor in anoxic environments in order to gain energy from the oxidation of organic matter. Furthermore, Fe oxides and other metal oxides are generally reduced for the same reason, so that metal sulfides are then formed. Elemental sulfur is also sometimes formed, apparently when dissolved heavy metal ions are not present. Sulfide formation is particularly strong in *Tidalic Fluvisols* of coastal areas, because these marine sediments contain large amounts of protein-rich, readily decomposable organic matter, mainly originating from dead plankton, and because through the daily flooding by the tides, there is a constant input of sulfates that are dissolved in the sea water. It is therefore a characteristic process for *Sali-Tidalic Fluvisols* at the coasts (Sect. 7.5.19.3). Sulfide formation is less common in the reduction horizons of a typical *Gleysol*, in contrast, it is more common in eutrophic subaquatic soils, the **Sapropels** (Sect. 7.5.19.1). Sulfide formation is also common in the soils of urban industrial areas (leads to the formation of *Reductosols*; Sect. 7.5.9). This is true for urban waste and sewage sludge landfills containing large amounts of readily decomposable organic matter, as well as for soils contaminated with oils and tars (e.g. under gasoline stations) and also for soils over damaged gas pipelines or beside landfills, where the sulfate reducers (Sect. 4.1) use methane as a C source.

Intermittently in soils or horizons with low to zero oxygen contents are characterized by mottles and/or concretions of Fe^{III} and $Mn^{III,IV}$ oxides in addition to bleached horizons. In soil horizons with high water and air conductivity, mainly black to rust-brown **concretions** are formed that are a few mm to several cm in size. In special *Gleysols*, they are also present in the form of continuous consolidated accumulation horizons, so-called **bog iron ore**, which usually consists of goethite and ferrihydrite. Soils with bog iron ores are classified as *Petrogleyic Gleysols*. In horizons with low conductivity, in contrast, mainly **mottles** are formed, which contain less oxides, which are more finely and widely distributed. There are exped and inped Fe/Mn concentrations. **Exped** is used to designate reddish-brown (then usually ferrihydrite and goethite) to black (then also Mn oxides) coatings on the surface of aggregates (as well as the root surfaces of swamp plants) and sheathing of larger voids (e.g. root channels, animal tunnels). **Inped** is used to designate yellowish-brown (then lots of goethite), orange (then lots of lepidocrocite), to brownish-black (then also Mn oxides) concentrations inside the aggregates in the form of mottles or concretions; they are classified as *stagnic color pattern.*

Many **groundwater-affected soils** (*Gleysols*, *Gleyi-Tidalic Fluvisols*, *Solonchaks*) have a constantly wet, reductomorphic subsoil (so called Cr horizons), with an overlying (intermittently) aerated surface soil containing exped Fe/Mn oxides, the Bl horizon (with capillary fring mottlings, caused by ascending groundwater). The process of **gleying** involves the reduction of Fe and Mn oxides in the Cr horizon. The formed Fe and Mn ions migrate upwards into the finer pores following a tension or oxidation gradient, through mass flow or diffusion, or rise with water into the upper, unsaturated soil horizons and form the Bl horizon. They are then oxidized and precipitated as oxides in the vicinity of air-filled coarse pores, or even in these pores themselves. Soils of sanitary landfills have a similar form with an O_2-free, reductomorphic Cr horizon under an exped redoximorphic surface soil containing O_2. The same is true for soil horizons that were strongly compacted by plowing and contain readily decomposable organic matter (e.g. beet leaves). Gleying leads to an accumulation of nutrients in the Bl horizon, however, sometimes in a poorly available form (e.g. P and Mo occluded in bog iron ore).

In contrast, many ***Stagnosols*** or other soils with a **stagnic color pattern** like ***Stagnic Albeluvisols*** exhibit inped Fe/Mn accumulations. In the process of **stagnization**, excess water (e.g. after persistent rainfall) initially causes water saturation in the preferentially rooted coarse pores (e.g. in the aggregate interstices). At the same time, dissolution of the Mn and Fe oxides on the edges of pores begins through reduction, and the ions diffuse into the interior of the aggregates following the flow of water or a redox gradient. Trapped oxygen inside the aggregates can result in repeated oxidation and precipitation of reduced

iron and manganese ions. With subsequent desiccation, the coarse pores are drained again first. Oxygen then penetrates into the aggregates from these pores and oxidizes the Fe^{2+} and Mn^{2+} ions. Therefore, the process of stagnization leads to the formation of mottles and concretions preferentially inside the aggregates. In doing so, the mottles are scattered through the soil matrix, so that even concretions generally consist of more than 80 % trapped silicates. In contrast to gleying, stagnization only leads to a redistribution of nutrients within individual horizons, which preferentially accumulate inside the aggregates and thus in areas far away from the roots.

Sulfate acidification occurs when sulfides (with the participation of microorganisms) are oxidized to form **sulfuric acid** and Fe oxides (usually ferrihydrite). This **sulfurication** begins as soon as a sediment or soil horizon containing sulfides is aerated. If the substrate contains carbonates, the sulfuric acid is neutralized, otherwise the pH value drops severely and often falls below a value of 3. In addition to oxides, other stable minerals can also be formed, namely orange-colored schwertmannite $Fe_8O_8(OH)_6SO_4 \cdot nH_2O$ in the pH-range from 3.0 to 4.5, and yellow jarosite [K, H_3O, Na]Fe_3 $(SO_4)_2(OH)_6$ in the pH-range below 3.5. These minerals are formed as an efflorescence on aggregate surfaces or as tunnel fillings. Especially jarosite (which is generally the constituent of maibolt) is considered as a diagnostic mineral for acid sulfate soils. Sulfurication mainly occurs with the drainage of former *Tidalic Fluvisols* or *Thionic Gleysols* that are carbonate-free or low in carbonates. Acid sulfate soils are found in coastal landscapes of temperate climates. However, they are widespread in lower latitudes, especially after the drainage of mangrove swamps. Landfill substrates from coal or energy production are sometimes also rich in sulfides, so that the corresponding tailings piles also have acid sulfate soils.

7.2.6 Turbations

Turbations (*turbatio* = turbulence) are processes where soil material from one or several soil horizons is mixed and the boundaries between the soil horizons or rock layers are blurred. In addition to **bioturbation**, i.e. mixing by soil organisms, **cryoturbation** induced by soil frost, and **peloturbation** as a result of frequent alternate wetting and drying in clay-rich soils, humans also blur the horizon boundaries or create new horizons through **soil tillage**. As a matter of principle, all substance components are involved in the mixing. Despite this, there is often a sorting of the particles if coarse particles are not included, and this can lead e.g. to the formation of **gravel layers** with bioturbation, and to gravel covers with cryo- and peloturbation. In contrast, stones rising to the surface through soil tillage are collected and removed (Blume 2011).

Earthquakes, the growth of salt crystals or explosive escaping of compressed air after rainfall primarily lead to a destruction of the structure, which can be accompanied by mixing processes. This also includes the blowing of sand into soil cracks (accumulation in cracks), which is widespread in deserts.

7.2.6.1 Bioturbation

Burrowing soil animals break down and mix the litter layer with the upper mineral soil and therefore blur the boundaries between the humus and mineral bodies, and at the same time, they produce a humic A horizon. This sometimes results in a change in the morphology of the soil surface, e.g. by ants, whose activities are a significant cause for the hummock pastures in the Swiss Jura. Some animals, including both rodents such as mice, moles, hamsters and ground squirrels, as well as ants, termites and particularly earthworms, also transport subsoil material and deposit it on or in the topsoil (Table 7.8). These activities can move translocated substances back to the surface again, so that intense animal activities can counteract the translocation of clay or nutrients. In semi-humid climates, this can prevent decalcification. At the same time, however, some of the topsoil material can reach deeper horizons in animal tunnels, as seen in humic rodent **krotovina** and worm burrows. The depth reached strongly depends on the soil and climatic conditions, and can often reach

several meters with earthworms in continental steppe regions, because they burrow deeper into the soil in the summer due to the dryness and in the winter due to the cold (see also Sect. 6.3). Lugworms of *Tidal Fluvisols* in coastal areas and large earthworms (up to 1.5 m lengths) in the tropics transport large amounts of soil (Table 7.8).

Intense bioturbation is only observed in soils with favorable water, air and nutrient conditions, and also in fine-grained soils, because gravels and stones cannot be transported. For the same reason, gravel layers were formed in many tropical soils at a depth of 0.5 to >2 m as a result of intense termite activity. In some cases, soil mixing is also observed due to windthrow of trees or the pressing out of soil pulp when trees are moved by the wind (arboturbation). Vegetation counteracts nutrient translocation by absorbing nutrients from the subsoil and returning a portion to the topsoil through the litter (=**base pump**).

7.2.6.2 Cryoturbation

Water moves towards freezing soil layers along a tension gradient. This leads to an accumulation of water in the freezing layers, while the layers following below are depleted. Slow freezing, especially in fine sandy-silty soils with a high water conductivity, leads to the formation of **ice lamella** or **ice lenses** in the soil, or **needle ice** at the soil surface. In the former case, the overlying soil layers are raised. Frost heaving and subsequent sacking when thawing can also mix the soil layers. This process is particularly intense in periglacial climate regions. Here, frost heaving leads to the formation of mounds with a height of several dm (**hummocks**), which often form a regular **pattern ground of polygons** with a width of several meters. This heaving can result in the rupture of roots and the uprooting of trees. In the Mackenzie Delta of Northern Canada, the constant addition of groundwater led to the formation of mounds consisting of ice with an elevation of up to 45 m and a width of 600 m, so-called **pingos**, within a period of 1000 years. The formation of hummocks is associated with strong mixing of the substrate, so that soil horizons and/or rock layers can have stripes (**brodel** and **pocket formation**). Stones migrate towards the soil surface and the edges of the polygons, leading to the development of **stone circles**. When thawing, the fine earth subsides with respect to the stones, which are still anchored in the frozen substrate. Furthermore, stones cool down faster when freezing due to their higher thermal conductivity (Sect. 6.6.3), so that ice lamellas are more frequently formed on their undersides, which then heave the stones up.

In permafrost soils, i.e. soils with a permanently frozen subsoil, strong mixing takes place when the topsoil, which thaws in the summer, freezes again from the top in the winter, and the associated volume expansion puts pressure on the non-frozen soil. During the glacial periods, many soils of Central Europe were reworked by cryoturbation, the traces of which can often still be observed in the soils today (Bronger 1982).

7.2.6.3 Peloturbation

Peloturbation is defined as the mixing of soil material by repeated shrinking and swelling (Sect. 6.2.2). Especially in warm climates with pronounced alternate wetting and drying, shrinkage cracks develop in clay-rich, smectitic soils in dry periods with a depth of up to 2.5 m and a width of several cm, in which the loose surface material falls. At the same time, the soil surface subsides by 3–7 cm. In doing so, the soil is in constant motion, because the clay minerals swell during the cool morning hours with high relative air humidity, and shrink again after midday, which is associated with a daily heaving and subsidence of the soil surface by 0.03–0.5 mm. This process breaks down the aggregates and is called **self-mulching**. In contrast, rewetting during the rain period causes swelling pressure in the subsoil. Frequent repetition of this process leads to strong mixing of the subsoil and topsoil materials, so that the soil is hardly acidified and often develops a thick humic horizon. The swelling pressure also presses the soil aggregates against each other, causing shiny **slicken sides** due to clay alignment.

These movement processes often result in a microrelief: A regular network of mounds and depressions (**gilgai**) is formed, because the upward motion of soil material dominates at some spots, and downwards motion at others. Gilgai mounds have a height of a few cm to 3 m, and are 2–50 m apart. The formation of gilgais leads to hook growth of trees and to the displacement of fences.

Peloturbation can also cause a certain segregation, because coarser particles are not involved in the daily and seasonal swelling and shrinking of the clay minerals, but rather they migrate slowly upwards.

7.2.6.4 Accumulation in Cracks

Deposited foreign sediments are normally fairly quickly mixed in with the underbed through bio-, cryo- and/or peloturbation, and in cultivated soils also through tillage. In deserts, however, mainly coarse silt and fine sand enter by wind and fill up the soil cracks. The width of the filled cracks ranges from 100 μm up to several dm, and the depth from a few cm up to several m. The cracks form together an irregularly shaped **polygonal network** (Fig. 7.8). The diameter of the polygons ranges from a few cm up to about 30 m. Some of the polygons reach the surface, but are often covered with sands, gravel or rock slabs.

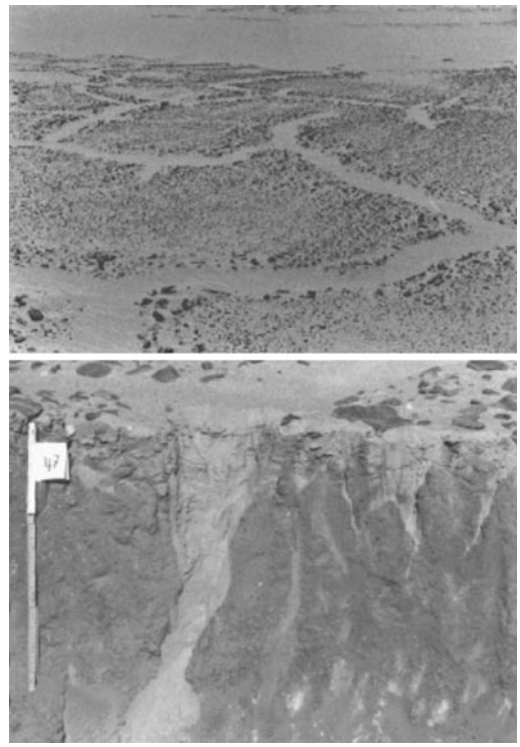

Fig. 7.8 Soil cracks filled with windblown sand of the East Sahara, surface (*above*) and profile (*below*); pictures of F. Alaily

Such accumulations in cracks are a characteristic trait of soils in hot deserts (e.g. Sahara, Negev), but are also observed in cold deserts (e.g. Antarctica). As relicts of cold-arid conditions during the Pleistocene, they are also found in Older **Weichselian** (US: Wisconsinian) and former moraine landscapes of Central Europe, however, they are covered by 2–4 dm of periglacial cover sand (German: *Geschiebedecksand*). The sand wedge networks here can still be seen from an aircraft, because they become visible due to the poor growth of crops attributed to water deficiency.

Cracks are formed in cold deserts through the contraction of the year-round frozen soil at very low temperatures, and in hot deserts, through desiccation after soil wetting (by episodical storm rainfall). As a result of salt cementation, this is even possible in pure sands, because strong soil water evaporation leads to the concentration and precipitation of dissolved salts at the contact points between the sand grains. Blown-in particles fill the cracks, and frequent recurrence may lead to very wide sand cracks. Also in hot deserts, the strong temperature fluctuations during day and night or summer and winter can contribute to the expansion of cracks.

In semiarid cold deserts and in tundras, in contrast, **ice wedge polygons** (with 1–20 m ∅) are formed in permafrost soils. They also can be attributed to cracks, which are formed in the arctic winter by cold contractions and reach a depth of several m, in which hoarfrost sublimates. A rise in temperature due to climate change often caused the melted ice to fill wedges with solifluction deposits (see Sect. 7.2.7.1 for definition). Such **ice wedge pseudomorphoses** are also observed in periglacial loess landscapes of Central Europe.

7.2.7 Soil Landscape Processes

In addition to processes that mainly take place in the soil body and contribute to the development of its horizons, there are translocations that go beyond the boundaries of the individual pedon. They also change the soils of a landscape, because some are depleted of substances, and others accumulate. Translocations in the landscape can involve the movement of entire soil bodies (mass transfer), or soil material is transported by water or wind (soil erosion). Furthermore, dissolved substances are transported by slope water. Normally, dissolution products from weathering leave the profile downwards and only move towards the valley in the deeper subsoil. They then either accumulate in the soils of depressions or leave the landscape in flowing waters. However, translocation sometimes already takes place in the soil itself either laterally or parallel to the surface, so that substances such as Ca or Fe are transported from upper slope to lower slope soils, without leaving the pedosphere.

7.2.7.1 Mass Transfer on Slopes

Mass transfer takes place on slopes under the effect of gravity. Shear resistance forces hold the soil or rock masses on the slope. Spontaneous motion as a rock fall or landslide, or also a slow, continuous creep (Fig. 7.9) occurs when the shear resistance between the roof and the floor decreases and/or when the shear strain increases. Both can occur as a result of water additions, the former also due to a change in temperature, and the latter e.g. due to snow load. The slope inclination, the properties of the roof (clay masses are particularly unstable) and of the floor (smooth layers, joint or cleavage planes that are oriented parallel to the slopes or water-restricting layers facilitate movement) as well as the climatic and vegetation conditions (deforestation promotes transport) determine the type, intensity and frequency of mass transfers.

Landslides or rock falls require a loosening of the rock on the naked, steep rock by physical weathering. Changes in temperature, storm rainfall or also earthquakes then trigger the movement, whereby individual stones, but also large masses of rock can slide down at speeds up to fall velocity.

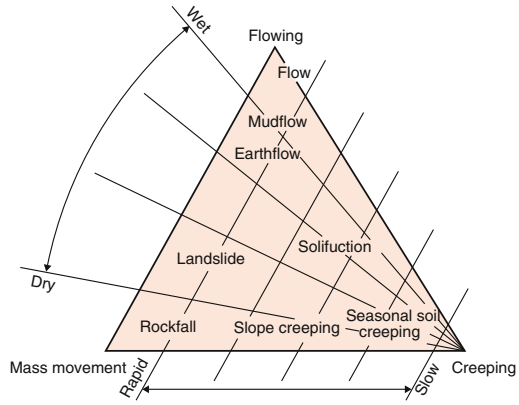

Fig. 7.9 Classification of mass transfer on slopes (after Bauer out of Carson and Kirkby 2009)

Landslides, **mudslides** (wet rubble avalanches) or **mudflows** (e.g. wet Lahar volcanic ashes) move rapidly (up to 200 km/h) and often far into the valley; their degree of moisture differs from the sliding soil masses. They are triggered by strong rainfall, which increases the soil moisture and provides a lubricant, by earthquakes or also by the undercutting of a slope by a stream or a poorly constructed road.

With **mass movement**, a break edge and radial cracks are formed on the upper slope, while soil material is pushed together like stone rolls at the lower slope. With strong wetting and increasing speed, mass movement often turns into a mudflow (or a mudslide), where the deposited soil material is strongly mixed. In high-altitude mountains, mass movement or mudslides are often triggered by avalanches.

Creeping along the slope can also occur under a closed vegetation cover, in fact already beginning at a slope inclination of 2°, provided that plastic swelling soil masses are present. Water often penetrates into the roof through joint or strata water in the floor. Waterlogging or also trampling by grazing animals can trigger the movement, which then often produces breaks and rolls parallel to the slope. With a movement

of only 1–20 mm per year, it is referred to as **soil creep**, and at >20 mm as slope creep. Movement over frozen subsoil is called **solifluction**. It takes place more frequently in regions with permafrost soils where the deeper horizons are permanently frozen, while the upper horizons thaw in the summer.

Creeping can modify certain turbations. With peloturbation on slopes, normal gilgais (Sect. 7.2.6.3) turn into elongated striated gilgais, or cryoturbation leads to the formation of striated soils instead of pattern ground (Sect. 7.2.6.2).

7.2.7.2 Soil Erosion by Water and Wind

In terms of the movement of larger masses of soil on more or less steep slopes, a distinction is made between the transport of soil material by water and by wind, i.e. **soil erosion**. While soil erosion by water requires a slope, wind erosion mainly takes place in wide-open plains.

Erosion by **water** is widespread in arid regions with sparse vegetation and occasional strong rainfall. It also reached great extents in humid regions since the Neolithic, when humans became sedentary and started clearing the forests. Landscapes with long-term agricultural use, such as Central and Southern Europe, China and India, as well as widespread land reclamation regions e.g. in the USA and Russia, exhibit high levels of erosion damage, while they are much lower in forest and grassland regions.

Natural erosion by **wind** (deflation) influences the landscape mainly on plain surfaces that have no or little vegetation cover in arid to semiarid regions, while in humid climates, it is mainly restricted to coastal areas with sandy soils.

The processes and factors involved in soil erosion, as well as the possibilities available for its prevention are described in detail in Sect. 10.7.1. Like with the soil movement described above for slopes, soil erosion by water and wind also strongly affects soil profile development. Soil development ceases completely if erosion continuously removes all of the weathered materials. When soil formation and erosion are roughly equal, the soil permanently remains at a specific development stage. **Top cut profiles** are formed when erosion reaches greater extents only after soil development has already taken place. With water erosion, the removed soil particles are partly deposited at the foot of the slope as **colluvium** and often cover the existing soil profiles. The fertility of the wide valleys of the Nile, Mississippi or Ganges is attributed to the **formation of fluvial loam**. This was also triggered in Central Europe by clear-cutting in the past. **Buried soils** are formed with repeated coverage, when the respectively deposited material is once more subject to profile differentiation.

Especially in hilly loess landscapes, erosion therefore leads to the formation of typical slope sequences: Soils that are on plateau sites or under forest are often still *Luvisols* (Sect. 7.5.6.1), while soil development on the slopes with the most intense erosion are reverberated to the *Calcaric Regosols* (Sect. 7.5.3) stage. All transitional stages are found in between, which can often easily be recognized by the color of the respective topsoils. The depth functions of the substances that were transported down the slope with the soil material also clearly reflect the extent of erosion and reshaping of the soil profile: While eroded profiles on slopes have low phosphate and humus contents, already reaching very low values at shallow depths, colluvial profiles are characterized by high and deep-reaching phosphate and humus contents. This clearly shows how strongly soil erosion can differentiate the productivity of soils on slopes.

Similar phenomena are observed with wind erosion. Here also, the top cut soils at the deflation site correspond to the buried at the deposition site. Soils on dunes often remain e.g. in the immature soil stage, while soils developed at the same time on another site are buried by eolian sand.

7.2.7.3 Slope Water Transport

Dissolved weathering products from terrestrial soils (and salts from precipitation) reach the groundwater with the seepage water, and are then partly accumulated in groundwater-affected soils. Thus, in dune and lower moraine landscapes of

Northern Germany, Fe, Mn and P are leached out of *Podzols* on hills and accumulated in soils of depressions as **bog iron ore**. In loess and upper moraine landscapes, in contrast, mainly Ca is translocated as hydrogen carbonate, which can lead to the formation of **meadow chalk** in depressions.

If there are poorly permeable rock strata in the profile, translocated substances may already accumulate on slope soils. In the Southern German Highlands, for example, consolidated Fe and Mn oxides at the base of mudflows are accumulated where jointed sandstone crops out over impervious granite. The same is true for Ca, where jointed limestone crops out over marl near the surface: Here, the Ca from *Rendzic Leptosols* is translocated in *Vertisols* or *Vertic Cambisols* located further down in the valley and accumulates as $CaCO_3$.

In the humid tropics, in addition to alkaline earth metal ions, Fe and Si are often also translocated in larger quantities and accumulate on the slope step or toe as **plinthite** (Fe) or **silcrete** (Si). In arid regions, salts even accumulate in the depressions of a landscape, so that saline soils are formed.

Slope water seepage and substance deposits can occur punctually as spring formations or also along a longer slope section. If the hydraulic conductivity already strongly decreases with depth in the slope soils, translocation takes place near the surface in the soils themselves (interflow). Fe and Mn are then preferentially leached out of soils that are wet almost year-round and where longer-term reducing conditions dominate, like in *Stagnosols* (Sect. 7.5.8.1). Such conditions, for example, can lead to **wet bleaching** in sandy A horizons of multi-layered soils on shallow slopes of the Sandstone Black Forest. This is followed by Fe precipitation in neighboring soils with stronger slope inclinations and/or smaller difference in texture (see e.g. Fig. 8.3). In subarctic regions, such translocations apparently take place over frozen subsoils.

Transport with slope water also leads to the formation of **eluvial** and **illuvial soils** beside each other in the landscape. In the former case, slope water intensifies weathering and translocation processes, which can simultaneously inhibit humification and structure formation due to the increased leaching of nutrients. In illuvial soils, the addition of substances retards weathering and often simultaneously stabilizes the soil structure. Both Ca and Fe deposits result in a loose structure rich in coarse and medium pores, which increases the capacity for air and available water. With higher mass input, however, the accumulation horizons are hardened and **calcretes** or **ferricretes** are formed.

The substances that are added to a depression in dissolved form are generally not accumulated at the lowest position of the landscape, but rather mainly form a **precipitation seam** at the lower slope, the location of which is determined by the groundwater level in the depression. Furthermore, in dry periods, additional substances are transported with groundwater out of the depressions into slightly more elevated areas. This was observed particularly in saline soil landscapes of arid climates, even though this form of lateral substance transport only takes place over short distances.

Lateral substance transports can also have a decisive effect on pedogenesis.

7.2.8 Profile Differentiation

The described processes do not take place in the soil isolated from each other, but rather more or less simultaneously, although several of the processes always dominate. These processes also interact with each other. It is only the interaction of many processes that leads to soil formation. These change its properties over the course of time: it goes through stages of development. The longer the pedogenic factors have time to evolve, the more the soil can develop and the stronger the differentiation into horizons with distinct properties. This will be described using the example of two development series or successions of dune sand (Fig. 7.10, above) and calcareous glacial till (Fig. 7.10, below) (see Sect. 7.4.1 for an explanation of the soil names).

Soil formation on dune sand (e.g. 80 % quartz, 15 % feldspars, 5 % mica): The sand was colonized by tundra vegetation after its deposition in the late glacial, leading to the development of an immature soil. Decomposition, humification and mixing resulted in a fine crumbly, humic A horizon. Cryoclastic weathering during the fading glacial period broke down mainly the micas. Especially during the Holocene, this enabled rapid brunification up to a depth of 60–100 cm, whereby 1–2 % clay was also formed. At pH values of 7–5, this clay (probably also added as Sahara dust) was partly displaced and deposited at a depth of 1–2 m in the form of thin strips, while a mor developed as a humus form. Under the cool humid climate of the Subatlantic, increasing acidification and nutrient depletion under oak/birch forests delayed litter decomposition; this led to a translocation of Al and later also Fe in organic complexing ligands. Due to litter raking and deforestation, raw humus formation and podzolization increased under *Calluna* heathland, so that pronounced humus and Fe/Al accumulation horizons were eventually formed, which reached deep into the soil particularly through former root channels, and were partly cemented to form hardpans. At the same time, the hardly biologically active E-horizon was compacted through subsidence, while acidification reached depths of more than 2 m. Even after reforestation with pine, podzolization continued and the pH of the surface soil dropped below 3, partly due to sulfuric acid from human air pollution, among other things. Parallel to this, there was extreme silicate weathering and nutrient depletion.

Soil formation on calcareous glacial till: Through litter production and the intense burrowing activities of soil fauna in the early Holocene, a thick humic topsoil containing carbonates and with a loose crumbly structure was formed on calcareous glacial till (e.g. 40 % quartz, 20 % respectively carbonate and clay minerals, and 10 % respectively feldspars and micas). Carbonate dissolution, which already started before the colonization by organisms, led to a continuous

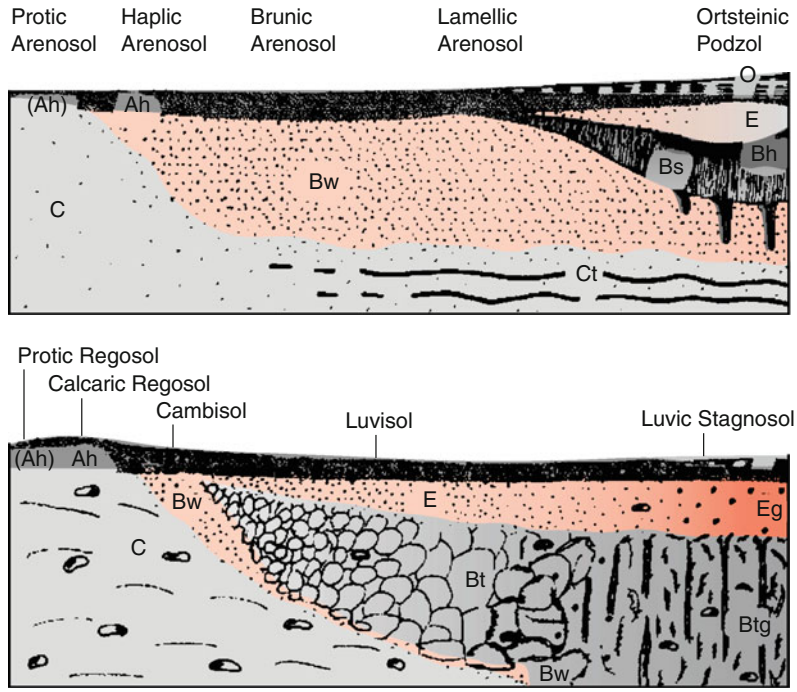

Fig. 7.10 Possible soil development from dune sand (*above*), and Pleistocene calcareous glacial till (*below*) in NW Germany

deepening of the soil, even if the intensity of carbonate leaching decreased with time, because the topsoil was crossed by more rain water than the subsoil. Decalcification was followed by brunification and clay formation, mainly from the weathering of micas. At the same time, in the subsoil with low levels of biological activity, and relative (through decalcification) and absolute clay accumulation, the coherent structure of the till was periodically transformed into a subangular blocky structure. Furthermore, clay migration began, which was probably very intense under the more continental climatic conditions of the Boreal (due to a lower water table of the oceans resulted in a longer distance of the coast), and later also included fine silt, but has largely come to a stop today due to strong soil acidification (Sect. 7.2.4.1). Because the calcareous glacial till itself is often densely packed (due to a former ice cover of several 100 m), and is subject to subsidence compaction (as a result of decalcification) and pedogenic compaction due to clay infiltration, this led to intermittent water retention under the relatively cool humid climate conditions of the Subatlantic. The subsoil was marbled and the topsoil developed Fe/Mn concretions (redoximorphosis). Lower biological activity, caused by increasing nutrient depletion and intermittent O_2 deficiency, reduced the thickness of the humic topsoil and sometimes led to the development of a platy structure as well as a beginning of weak podzolization.

Terrestrial soils in Central Europe probably went through the stages shown in Fig. 7.11, however, not always up to the end, because there was often only 10,500 years of time since the retreat of the ice (Table A.2 in the Appendix) and erosion interrupted their development.

In addition to **recent soils**, which developed under the current constellation of pedogenic factors, there are soils that were formed in earlier geological eras under different conditions. If they were covered by new sediments and interrupted in their further development, these ***Paleosols*** either remained unchanged as **fossil soils** (Bronger 1982), or are found at the surface as

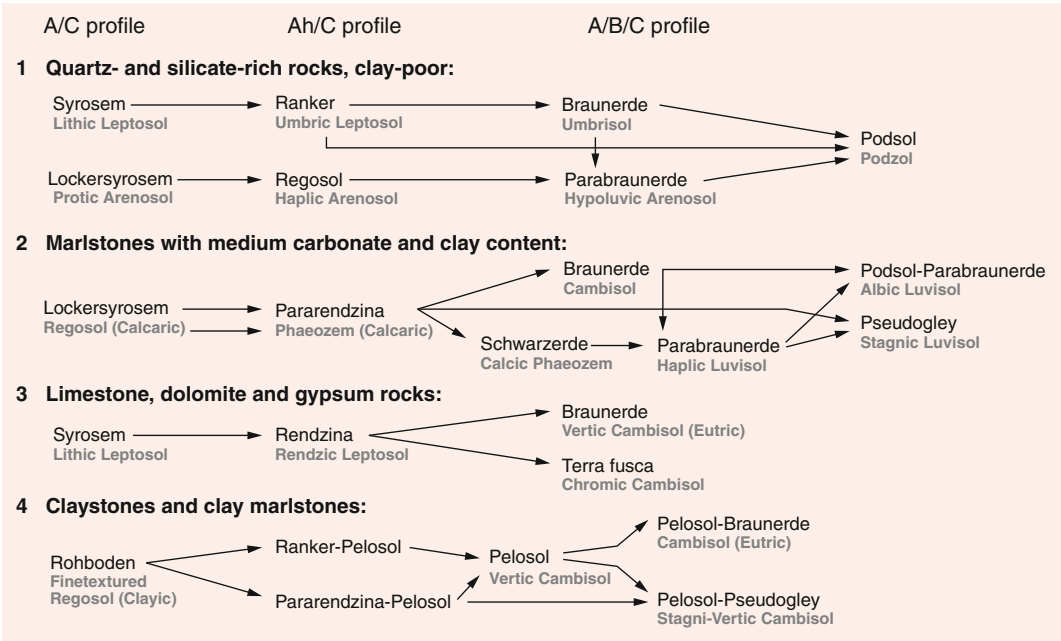

Fig. 7.11 Soil development in Central Europe in relation to the parent rock (German names in *black*, WRB in *grey*)

relict soils and are now subject to soil development under the present conditions (**polygenetic soils).** This either largely eliminated the formerly developed soil characteristics (in Central Europe, e.g. often because of strong clay migration), or preserved them due to their stability to such an extent that the former soil type can still be clearly identified.

Old land surfaces, some of which were already present in the Tertiary or in earlier epochs, are still found today e.g. at higher elevations in tropical regions, or also in temperate humid climate regions, e.g. in large parts of the Rhenish Slate Mountains and other German low mountain ranges. On such land surfaces, the constellation of pedogenic factors changed several times over the course of time, sometimes dramatically. In this way, some of the soils found at these sites were formed by different climate and/or relief conditions. As a product of such **polycyclic** development, the genesis of many soils in the tropics and subtropics is very difficult to identify. Also in Central Europe, there are still remains of soils that were formed during the tropical and subtropical climate periods of the Cretaceous and Early Tertiary (e.g. *Ferralsol* relicts). However, provided that they were not covered, they were subject to renewed pedogenesis under different conditions in the Pleistocene and the Holocene.

During the warm interglacial periods and the shorter interstadial periods of the **Pleistocene** (Table A.1 in the Appendix), soils were formed again in Central Europe, where in many cases, they were covered again during the subsequent glacial period by glacial till deposits, eolian loess deposits or solifluction deposits and were thus fossilized. These ***Paleosols*** are often buried under thick loess deposits, and serve today for research on the geological course of the Pleistocene.

Also on geologically very young deposits, the course of soil development was not undisturbed, as can be seen on the examples of **dune sand** and **calcareous glacial till** (see above). The climate only reached two weak warm maximums during the **late glacials** in the Bölling and Allerød (Table A.2 in the Appendix), which can be identified in the soils of several parts of Central Europe. In the warmest and simultaneously driest period of the Holocene, the Boreal (8800–7500 BP), *Chernozems* and *Phaeozems* were formed on some sites instead of *Luvisols* on loess and calcareous glacial till. The development of these soils has stopped since the beginning of the more humid Atlantikum and was replaced by pedogenic processes of more humid climates.

7.3 Diagnostic Criteria of Soils

References: Boden (2005), IUSS/ISRIC/FAO (2006/2007), Jahn et al. (2006) and Soil Survey Staff (1999, 2014).

In the international classification systems *WRB* and *US Soil Taxonomy,* soils are classified according to their **diagnostic horizons**, **properties** and **materials** (Tables 7.4 and 7.5). In Germany, soils are classified according to their special combinations of soil horizons with depth. In the following, the soil horizon designations and the definitions of diagnostic horizons, properties and materials will be presented.

7.3.1 Soil Horizon Designation

The **soil horizon designation** summarizes many observations of the soil description and gives an impression of the genetic processes involved in forming a soil. Horizon symbols consist of one or two capital letters for the master horizon and lower case letter suffixes for subordinate distinctions, with or without a figure suffix.

International symbols are given first (Jahn et al. 2006), followed by the symbols for the US and Germany (see a, b, c).

Table 7.4 Summary of dominating characteristics and thickness for diagnostic horizons (IUSS/ISRIC/FAO 2006/7)

Horizon (explanation)	**Characteristics** (partly simplified); **hor** horizon; color = Munsell color: hue, value, chroma, moist, dry; **R** rock; **TOC** total organic carbon; **TRB** total supply of bases; soil structure: **CR** crumbly, **CO** columnar; **S** sand, **L** loam, **LS** loamy sand; **SL** sandy loam; **X** skelettic;**vol** volume; **pedo** pedogenetic; further abbreviations see Annex 10.3)	**Thickness** (cm)
Albic (Latin white)	E hor, dry chroma ≤ 3 + value ≥ 7; moist chroma ≤ 4 + value ≥ 6	≥1
Anthric	Ap like mollic, but with a plough pan or lumps of applied lime or ≥ 0.15 % citric acid soluble P_2O_5 + < 5 % vol. animal pores below Ap	≥20
Anthropedogenic:		
Anthraquic	Ap with hue 7.5YR or 10YR 2.5Y 5Y GY B BG, overlying a dense, mottled plow pan	≥20
Hortic	Value + chroma moist ≤ 3; BS ≥ 50 %; ≥1 % TOC ≥ 0.01 % mobile P_2O_5; ≥25 % vol., traces of animal activity	≥20
Terric	Raised surface; color of sediment; BS ≥ 50 %; <20 % vol. artifacts	≥20
Plaggic	Raised surface by plaggen = sods; moist value ≤ 4 chroma ≤ 2; S-L; TOC > 0.6 %; <20 % vol. artifacts	≥20
Irragric	Irrigated with sediments; TOC ≥ 0.5—↓ 0.3 %; more clay than below; ≥ 25 vol.% animal pores	≥20
Hydragric	Subsoil of wet cultivation with Fe/Mn coating or concretions, or > 2 times Fed or >4 times Mnd as Ah., or mottled or wet-bleached	≥10
Argic (lessivage)	LS or finer, at least >8 % clay; >3 %/>1/5/8 % clay than topsoil with < 15 / 15–40/ > 40 % clay; if clay coatings on ped surfaces, higher clay contents have to be found within 15 cm or 30 cm from the next hor	≥7.5
Calcic (pedo lime) Petrocalcic	≥15 % lime + ≥ 5 % pedo lime or more as next hor; strong reaction with 10 % HCl; very hard	≥15 ≥10
Cambic	SL to clay; CEC_{clay} > 16 $cmol_c$/kg or >10 % weatherable minerals or TRB > 40 $cmol_c$/kg, pedo aggregates or decarbonated or brownified	≥15
Cryic (Greec ice)	Continuously frozen soil or ice wedges or soil temp. <−0 °C in case of dry soil	≥5
Duric (Latin hard)	>10 (petroduric ≥ 1 cm, duripan > 50) % vol. silcrete pebbles with > 1 cm ∅, not dispersed in hot concentrated KOH and HCl	≥10
Ferralic (Latin iron)	SL or finer; < 80 % vol. X + nodules, CEC_{clay} < 16 $cmol_c$/kg and < 10 % weatherable clay and not andic or vitric	≥30
Ferric (Latin iron)	≥15 % red mottles, or ≥5 % > 2 mm ∅ Fe nodules (exped more red than inped), and < 40 % vol. hard nodules or ferricrete	≥15
Folic (Latin leaf)	Dry org. surface layer: >20 % TOC, wet < 30 days/year	≥10
Fragic (Latin to break)	Prismatic or blocky, dispersed in water, d_B > upper hor, < 0.5 % TOC	≥15
Fulvic (Latin dark yellow)	See andic properties	
Gypsic (Greek gypsum)	≥5 % gypsum, and >1 % vol. as pseudomycelia, crystals or powder (>50 % = hypergypsic); Petrogypsic very hard gypsum layer	≥15

(continued)

Table 7.4 (continued)

Horizon (explanation)	**Characteristics** (partly simplified); **hor** horizon; color = Munsell color: hue, value, chroma, moist, dry; **R** rock; **TOC** total organic carbon; **TRB** total supply of bases; soil structure: **CR** crumbly, **CO** columnar; **S** sand, **L** loam, **LS** loamy sand; **SL** sandy loam; **X** skelettic;**vol** volume; **pedo** pedogenetic; further abbreviations see Annex 10.3)	**Thickness** (cm)
Histic (Greek tissue)	Wet org. hor: >12 % TOC (if sand), >18 % (if clay), other >13–17 %; wet for >30 consecutive d/a	≥10
Melanic (Greek black)	As andic, and value + chroma (moist) < 2 and melanic index[a]) < 1.7[b] and ≥6 % TOC	≥30
Mollic (Latin soft)	Ah with dry value and chroma ≤ 5, moist ≤ 3; 0.6–12 % TOC (20 in relation to folic); CR, loose, BS > 50 %	≥25 ≥10/R
Natric (> Na^+)	Like argic, and CO; BS_{Na} > 15 % or BS_{Na+Mg} > BS_{Ca+H} (at pH 8.2)	≥7.5
Nitic (Latin shiny)	B with nutty structure and shiny surface; < 20 % clay with < 1/5 ↑ in 12 cm in relation to the upper and lower hor; at least 30 % clay, not redoximorphic; Fe_o/Fe_d > 0.05	≥30
Plinthic (Greek brick)	>15 % red/white mottled mixture of Fe oxides and kaolinite (or gibbsite), drying is followed by irreversible hardening; > 2.5 % Fe_d or > 10 % in mottles; Fe_o/Fe_d < 0.1	≥15
Petroplinthic Pisoplinthic	Similar to plinthic, but very hard ≥40 vol% hard, red to black nodules with > 2 mm Ø	≥10 ≥15
Salic (Latin salt)	EC of GBL (equilibrium soil solution) > 15 mS/cm or > 8 at pH > 8.5	≥15
Sombric (French dark)	Bt with migrated humus; BS < 50 %; in highlands of the (sub)tropics only	≥15
Spodic (Greek wood ash)	pH (H_2O) < 5.9 or cultivated; color 7.5YR or more red, value ≤ 5, chroma ≤ 4; or 10YR, value ≤ 3, chroma ≤ 2; Al_o + ½ Fe_o > 0.5 % and > 2 of the A/E hor; or ODOE > 0.25 and > 2 of the A/E hor; deeper than 1 dm from the soil surface org. C > 0.5 %	≥2.5
Takyric (Turkic barren land)	Aridic properties; CL, SiCl or finer; platy or massive struct.; cracks when dry; EC of GBL < 4 mS/cm or < than subsoil	
Thionic (Greek sulfar)	With sulfuric acid; pH (1:1 in water) < 4.0; and yellow jarosite or yellowish-brown schwertmannite mottles or coatings, or direct superposition on sulfidic material, or > 0.05 % water soluble sulfates	≥15
Umbric (Latin shade)	Ah like mollic, but BS < 50 %	Mollic
Vertic (Latin to turn)	≥30 % clay; slicken sides or wedge-shaped or parallel piped; COLE > 0.06	≥25
Voronic (Russian black)	Like mollic, but black; > 50 vol.% worm casts + (filled) worm burrows; ≥ 1.5 % org. C; BS ≥ 80 %	≥35
Yermic (Spanish desert)	Aridic properties and stone layer with patina, and/or vesicular structure below a silty layer; and/or polygon net of sand-filled cracks (see Fig. 7.30)	≥2

[a]Extractable with 0.5 M $NaHCO_3$
[b]Melanic index: Shake sample with 0.5 M NaOH, measure color at 450 and 520 nm: take the quotient of both

Table 7.5 Dominating characteristics of diagnostic properties and materials (abbreviations see Table 7.4) after IUSS/ISRIC/FAO (2006) and Jahn et al. (2006)

Property	Characteristics
Abrupt textural change (ATC)	20 % > clay within 7.5 cm, if topsoil < 20 % clay; 1/5 > clay, if topsoil > 20 % clay
Albeluvic tonguing	Penetrations of an albic E hor into an argic B hor
Alic (>Al^{3+})	Argic hor with CEC_{clay} > 24 $cmol_c$/kg
Andic	weathered volcanic tuffs
Sil-andic	Si_o > 0.6 %, Al_p/Al_o < 0.5 %
Alu-andic	Si_o < 0.6 %, Al_p/Al_o > 0.5 %
Aric	Disturbed by deep ploughing
Aridic	Upper 20 cm ≤ 0.6 % TOC (S ≤ 0.2 %); BS > 75 %; value > 3, chroma < 2 (both moist); extremely dry
Continuous rock	Consolidated material underlying the soil; exclusive of cemented
Dystric	BS ≤ 50 % at 20–100 cm, or 20 cm/hard rock
Eutric	BS > 50 % at 20–100 cm, or 20 cm/hard rock
Ferralic	CEC_{clay} < 16 $cmol_c$/kg clay, or CEC < 4 $cmol_c$/kg fine earth, partly in B hor
Geric	CEC_{eff} < 1.5 $cmol_c$ kg^{-1} clay, pH ($CaCl_2$) > pH(H_2O)
Gleyic color pattern	Wet due to groundwater, and then Fe^{2+} ions; >90 % reductomorphic color N1-N8 or 2.5Y, 5Y, 5G or 5B, or >5 % mottles
Humic	Mean TOC upper 50 cm min. hor. ≥1 %, Ferralsols + Nitisols 1.4, Leptosols upper 25 cm ≥ 2 %
Hyperhumic	Mean TOC upper 50 cm min. hor. ≥5 %
Lithological discontinuity	Significant changes in particle distribution with soil depth
Reducing conditions	rH value < 13 or presence of Fe^{2+} or the presence of iron sulfide or the presence of methane
Secondary carbonates	Precipitated lime in form of concretions, or above surfaces of peds
Stagnic colour pattern	At least occasional water saturation and then reducing conditions; >50 % redoximorphism in the upper 100 cm of mineral soil
Turbic	Having cryoturbation features (mixed material, frost heave, cracks or pattern ground) in 100 cm
Vermic	>50 % vol. worm holes, karst or filled animal burrows in the upper 100 cm or above hard rock
Vitric	≥5 % volcanic glass
Material	**Characteristics**
Artefacts	Man-made materials like bricks, pottery, glass, industrial waste, garbage
Calcaric	≥2 % carbonates with strongly effervescences with 1 M HCl, at least between 20 and 50 cm
Colluvic	Human-induced erosion, humic Ah material, particularly in down slope sites
Fibric	Hardly humified org. matter in H or O hor (>2/3 plant tissue)
Fluvic	Young fluviatile, lacustrine or marine sediments with >25 % vol. visible layering and changing humus contents down to 100 cm depth
Garbic	Layer with >35 % org. wastes
Gelic	Permafrost in the upper 2 m
Glacic	>30 cm soil with >95 % ice starting at a depth of 1 m, and a cryic hor.
Gypsiric	≥5 vol% gypsum
Hemic	Medium humified H or O hor (2/3–1/6 plant tissue)

(continued)

Table 7.5 (continued)

Material	Characteristics
Hyperskeletic	>90 % gravel + stones down to 75 cm or R layer
Limnic	Subaquatic deposit in form of coprogenous earth, diatomaceous earth, strongly calcareous, or green-colored gyttja > 10 cm in 50 cm
Lithic	R = hard rock within the first 10 cm
Organic	Fine earth ≥ 20 % org. C or mostly water saturated unless drained + 12 ≥ % org. C + (% clay ×0.1)
Ornithogenic	Remnants of birds (bones, feathers, excrement) or activity of birds (sorted stones), and ≥0.25 % P_2O_5 extractable with citric acid
Rendzic	Mollic hor with/above calcaric material (>40 % $CaCO_3$)
Sapric	Strongly humified H or O hor (<1/6 plant tissue)
Sulphidic	pH (H_2O) ≥ 4 + ≥ 0.75 % S (no to <3 equivalent of $CaCO_3$)
Spolic	>35 % anthropogenic layer of natural materials
Technic hard rock	Men made consolidated material (e.g. remains of destroyed brick house)
Tephric	>30 % vol. not weathered tephric material; Al_o + 1/2 Fe_o < 0.4 % (vitric > 0.4 %)
Transportic	Top soil with ≥ 20 cm of soil material transported by humans, e.g. to build walls or other constructions
Toxic	Toxic substances of plant growth within the top 50 cm in addition to Al, Fe, Na, Ca, Mg
Urbic	Having a layer ≥20 cm thick within 100 cm with ≥35 % of rubble and refuse from human settlements

(a) Master Horizons and Layers

I	U	G	International, US, German symbols
L	L	F	Limnic hor, beneath lake water (L = limnic material)
W	W		Water layer beneath floating peat
H		H	Water-saturated organic hor (unless drained)
		hH	With pieces of *Sphagnum, Eriophorum, Drosera* or other peat-forming plants
		nH	With pieces of *Phragmites*, *Typha*, *Carex*, *Hypnum*, *Alnus, Salix* or other fen forming plants
O	O	O	Organic hor consisting of partly to strongly decomposed litter
		L	Litter that is not decomposed
A	A	A	Upper mineral hor, mainly with humus
E	E	Al, Ae	Bleached upper mineral hor beneath the A due to translocation of clay, humus or iron oxides
B	B	B	Subsurface mineral hor with a lower pH and/or a more brown or red color, without lime in relation to the following BC, C or R hor due to weathering, mineral formation and/or clay migration
C	C	C	Subsurface mineral hor, not weathered, mainly similar to the parent material of A and B (unless 2 C)
I			Ice lenses and wedges of permafrost soils
R	R	mC	Bedrock (like granite, lime stone; not hardened soil hor)

A/B, A/E, E/B, B/C and C/R are transition horizons with characteristics of two horizons

(b) Subordinate Characteristics within Master Horizons

Lower case letters are used as suffixes to designate specific kinds of master horizons. In

Germany, they have a more precise definition due to their diagnostic character (Boden 2005; Wittmann et al. 1997).

I	U	G	International, US, German symbols	
a	a	h	Highly decomposed humus	H and O hor
b	b		Buried horizon	Mineral hor
c	c	k	Concretions or nodules	Mineral hor
c	co		Coprogenic earth	L horizon
d	d	m	Dense layer (physically root restriction)	Mineral hor
d	di		Diatomaceous earth	L horizon
e	e	f	Moderately decomposed humus	(H) and O hor
f	ff		Frozen soil	Not in I and R hor
g		w, d	stagnic conditions	No restriction
h	h	h	Accumulation/ Illuviation of humus	Mineral soils
i	ss		Slickensides	Mineral hor
i	i	f	Slightly decomposed humus	H and O hor
k	k	c	Accumulation of pedogenic carbonates	No restriction
l		o	Capillary fringe mottling (gleying)	No restriction
m	m	m	Pedogenic cementation	Mineral hor
n	n		Pedogenic accumulation of exchangeable Na^+	No restriction
o	o	o	Pedogenic accumulation of sesquioxides	No restriction
p	p	p	Ploughing	No restriction
q	q		Pedogenic accumulation of silica	No restriction
r	g	r	Strong reduction	No restriction
s	s	s	Illuvial accumulation of sesquioxides	B hor
t	t	t	Illuvial accumulation of silicate clay (+iron oxide coatings)	B, C hor
u	u		Human made material	no restriction
w	w	v	Pedogenic development of color or structure	B hor
x	x		Fragipan characteristics	No restrictions
y	y		Pedogenic accumulation of gypsum	No restrictions
z	z	z	Pedogenic accumulation of salts more soluble than gypsum	No restriction
@	jj		Evidence of cryoturbation	No restrictions
		a	High humus content (15–30 % org. matter)	A hor
		d	Dense	S hor
		e	Acid bleaching	A hor
		f	Soft structure	B hor
		i	Initial	F, A hor
		n	Not weathered	C hor
		q	Dense, marsh soil	S hor
		w	Filled with groundwater	F, H, G hor
		x	Biogenic mixed	A, E hor

(c) **Special German Master Horizons and Subordinate Characteristics**

Left WRB, right German.

B/C	P	Diagn. B hor of *Pelosole* (>45 % clay of clay stone) with prisms, mainly with slickensides like *Vertisols*
Bw	T	Diagn. B hor of *Terrae calcis* (>65 % clay of limestone) with angular blocky structure
Eg/Bg	Sw/Sd	Diagn. hor of *Stauwasserböden* (=*Stagnosols*)
Bl/Cr	Go/Gr	Diagn. hor of a *Gley* (=*Gleysol*)
	M	Soil of colluvic material (of eroded Ap horizons) transported by water or wind; diagn. hor of a *Colluvisol*
	E	Diagn. hor of a *Plaggenesch,* formed from plaggen (Ap + E > 4 dm)
	R	Diagn. hor of a *Rigosol*, formed by deep ploughing (Ap + R > 4 dm)
	Y	Diagn. hor of a *Reductosol,* influenced by reducting gases (CO_2, CH_4, H_2S)
2,3	II, III	Layers for which upper layers are not formed

Lower case letters before master letters

a	Stratified humic layers due to cyclic flooding of river water
c	Parent mat. consisting of >75 % $CaCO_3$ or $CaSO_4$
e	Parent mat. consisting of 2–75 % $CaCO_3$
f	Fossil horizon
i	Parent mat. consisting of 0–2 % $CaCO_3$
j	Natural substrates transported by humans
l	Loosen packed parent material
m	Massive material
o	With lithogenic org. material
q	Being flooded with spring water
r	Relict horizon
s	Being moistened by slope water
t	Periodically flooded by tide water
tm	Flooded by tidal marine water of the North Sea, EC value ≥ 15 mS/cm
tb	Flooded by tidal brackish water of the Baltic Sea and river mouths EC 15-0.75
tp	Flooded by tidal river water EC < 0.75

Lower case letters before master letters

x	>95 % coarse gravel and stones
y	Anthropogenic parent material (e.g. building rubble, petrol, plastic, slag, sludge, wastes)
z	Influenced by salty sea water (> 0.75 mS/cm)

7.3.2 Diagnostic Horizons, Properties and Materials

The **IUSS** Working Group *World Reference Base for Soil Resources* (WRB) defined special terms for diagnostic horizons, properties and materials to classify soils. Similar definitions and terms were used in the *US Soil Taxonomy* and in the legends of *FAO World Soil Maps.*

Definitions and thickness for **diagnostic horizons** can be found in Table 7.4, and for some **diagnostic properties** and **materials** in Table 7.5.

7.4 Soil Classification

References: Boden (2005), ISSU/ISRIC/FAO (2006/7), Guidelines for Soil Description of Jahn et al. (2006), Soil Survey Staff (1975/1999/2002/2012/2014), Wittmann et al. (1997).

Soils are classified according to their properties. They can be genetically classified as natural bodies, or effectively in relation to their use. Simple effective concepts exist since ancient times (Blume 2003a, b). But effective classifications only exist for special forms of land use like agriculture, forestry or gardening (see Chap. 11).

The following classifications are mainly based on genetic concepts, but sometimes also include ecological concepts in their lower categories. Most modern genetic classifications have their roots in Dokuchaev (1883/1899) and Hilgard (1892/1906), who classified soils as natural bodies according to their parent rock, their climate and therefore also their natural vegetation, and their relief (concept of soil zones). Later on, soils were classified according to their properties, which resulted from special soil-forming processes (Sect. 7.2).

7.4.1 Soil Classification According to the WRB

The *World Reference Base for Soil Resources* (WRB) is an international system to classify soils as *natural bodies,* developed since 1979 for the IUSS under the leadership of the German Ernst Schlichting and later mainly of the Belgians Rudi Dudal/Seppe Deckers, Dutch Otto Spaargaren and German Peter Schad.

The WRB classification is based on soil properties defined in terms of **diagnostic horizons**, **properties** and **materials**, which should be measurable and observable in the field to the greatest extent possible (Sect. 7.3). The selection of diagnostic characteristics takes account of their relation with soil-forming processes (Sect. 7.2). To the extent possible at a high level of generalization, diagnostic features are selected that are of significance for soil management (Jahn et al. 2006).

Main Soil Units of the WRB,
Supplemented with the most important **prefix** and **suffix qualifiers**; definitions were sometimes simplified.
() symbol; explanations in Tables 7.4 and 7.5; hor = horizon

Histosols (HS): with org. hor > 4 dm; > 1/R
Prefix: *Folic*, *Limnic*, *Fibric*, *Hemic*, *Sapric*, *Technic*, *Cryic*, *Andic*, *Salic*, *Calcic*
Suffix: *Thionic*, *Turbic*, *Gelic*, *Tidalic*

Anthrosols (AT): with **anthropedogenic** hor > 5 dm
Prefix: *Hydragric*, *Irragric*, *Terric*, *Plaggic*, *Hortic*, *Technic*, *Fluvic*, *Salic*, *Gleyic*
Suffix: *Sodic*, *Alcalic*, *Dystric*, *Eutric*, *Oxaquic*

Technosols (TC): >20 % vol. artifacts ≤ 10 dm/R, or constructed geomembrane or ≤5 cm / technic hard rock (>95 %)
Prefix: *Ekranic*, *Linic*, *Urbic*, *Spolic*, *Garbic*, *Cryic*, *Fluvic*, *Gleyic*
Suffix: *Calcaric*, *Toxic*, *Reductic*, *Densic*, *Skeletic*

Cryosols (CR): with permafrost in the first m / permafrost in 2 m + cryoturbation phenomena
Prefix: *Glacic*, *Turbic*, *Folic*, *Histic*, *Technic*, *Leptic*, *Salic*, *Spodic*, *Mollic*, *Umbric*, *Cambic*, *Haplic*
Suffix: *Calcaric*, *Ornithic*, *Reductaquic*, *Oxyaquic*, *Thixotropic*

Leptosols (LP): with ≤25 cm/R, or first 7.5 dm/R < 20 % vol. fine soil
Prefix: *Nudilithic*, *Lithic*, *Hyperskeletic*, *Rendzic*, *Folic*, *Histic*, *Technic*, *Salic*, *Mollic*, *Umbric*, *Cambic*, *Haplic*
Suffix: *Gypsiric*, *Ornithic*, *Tephric*, *Gelic*

Vertisols (VR): with *Vertic* starting within 1 m
Prefix: *Grumic*, *Mazic*, *Salic*, *Gleyic*, *Sodic*, *Stagnic*, *Gypsic*, *Duric*, *Calcic*
Suffix: *Albic*, *Gypsiric*, *Pellic*, *Chromic*

Fluvisols (FL): with *Fluvic* at least between 25 and 50 cm
Prefix: *Subaquatic*, *Tidalic*, *Limnic*, *Folic*, *Histic*, *Technic*, *Salic*, *Gleyic*, *Stagnic*, *Mollic*, *Umbric*, *Haplic*
Suffix: *Thionic*, *Anthric*, *Gypsiric*, *Calcaric*, *Tephric*, *Gelic*, *Yermic*, *Aridic*, *Drainic*

Solonetz (SN): with *Natric* starting within 1 m
Prefix: *Vertic*, *Gleyic*, *Salic*, *Stagnic*, *Gypsic*, *Calcic*, *Haplic*
Suffix: *Glossalbic*, *Albic*, *Abruptic*, *Colluvic*, *Ruptic*, *Magnesic*, *Yermic*, *Aridic*

Solonchaks (SC): with *Salic* starting within 5 dm; without *Thionic*
Prefix: *Petrosalic*, *Hypersalic*, *Puffic*, *Folic*, *Histic*, *Technic*, *Gleyic*, *Stagnic*, *Gypsic*, *Duric*, *Calcic*, *Haplic*
Suffix: *Sodic*, *Aceric*, *Chloridic*, *Sulphatic*, *Carbonatic*, *Gelic*, *Densic*, *Drainic*

Gleysols (GL): reducing conditions within 5 dm + *Gleyic* color pattern
Prefix: *Folic*, *Histic*, *Anthraquic*, *Technic*, *Fluvic*, *Endosalic*, *Spodic*, *Plinthic*, *Mollic*, *Gypsic*, *Calcic*, *Umbric*, *Haplic*
Suffix: *Thionic*, *Calcaric*, *Colluvic*, *Sodic*, *Toxic*, *Gelic*, *Drainic*

Andosols (AN): soils developed from volcanic ashes with *Andic* or *Vitric* properties

Prefix: *Vitric*, *Aluandic*, *Silandic*, *Melanic*, *Folic*, *Histic*, *Gleyic*, *Haplic*
Suffix: *Anthric*, *Colluvic*, *Sodic*, *Gelic*

Podzols (PZ): with *Spodic* B within 2 m
Prefix: *Placic*, *Ortsteinic*, *Carbic*, *Rustic*, *Albic*, *Folic*, *Histic*, *Leptic*, *Gleyic*, *Stagnic*, *Umbric*, *Haplic*
Suffix: *Hortic*, *Plaggic*, *Terric*, *Anthric*, *Ornithic*, *Turbic*, *Gelic*, *Drainic*

Plinthosols (PT): *Plinthic* hor starting <5 dm
Prefix: *Petric*, *Pisolithic*, *Gibbsic*, *Posic*, *Geric*, *Vetic*, *Stagnic*
Suffixe: *Albic*, *Ferric*, *Alumic*

Nitisols (NT): with *Nitic* hor starting <1 m (without *Ferric*, *Plinthic*, *Vertic*; not redoximorphic)
Prefix: *Vetic*, *Alic*, *Acric*, *Luvic*, *Lixic*
Suffix: *Alumic*, *Colluvic*, *Rhodic*

Ferralsols (FR): with *Ferralic*, no *Argic*
Prefix: *Gibbsic*, *Posic*, *Geric*, *Vetic*, *Plinthic*, *Haplic*
Suffix: *Ferric*, *Colluvic*, *Alumic*, *Rhodic*, *Xanthic*

Planosols (PL): similar to *Stagnosols* but with abrupt textural change (ATC)
Prefix and suffix similar to *Stagnosols*

Stagnosols (ST): similar to *Planosols* but no ATC, *Reductic* within 5 dm
Prefix: *Folic*, *Histic*, *Vertic*, *Endogleyic*, *Mollic*, *Luvic*, *Umbric*, *Haplic*
Suffix: *Thionic*, *Albic*, *Ferric*, *Ruptic*, *Geric*, *Calcaric*, *Sodic*, *Alumic*, *Gelic*, *Placic*, *Drainic*

Chernozems (CH): with ≥2 dm very dark to black *Mollic* A + pedogenic carbonate or *Calcic* hor
Prefix: *Voronic*, *Vermic*, *Leptic*, *Gleyic*, *Stagnic*, *Gypsic*, *Calcic*, *Luvic*, *Haplic*
Suffix: *Anthric*, *Glossic*, *Sodic*, *Pachic*, *Greyic*

Kastanozems (KS): lighter *Mollic* A, similar to *Chernozem*
Prefix and suffix: similar to Chernozem

Phaeozems (PH): *Mollic* A but no lime, similar to *Kastanozem*
Prefix and suffix similar to Chernozem

Gypsisols (GY): with (*Petro*)*Gypsic* hor, beginning at <1 m depth
Prefix: *Petric*, *Arcic*, *Endosalic*, *Endogleyic*, (*Petro*)*duric*, (*Petro*)*calcic*
Suffix: *Ruptic*, *Sodic*, *Hyperochric*

Durisols (DU): with *(Petro)Duric* hor, beginning at <1 m depth
Prefix and suffix similar to *Gypsisols*

Calcisols (CL): with *(Petro)Calcic* hor, beginning at <1 m depth
Prefix: *Hyper-*, *Hypocalcic*, similar to *Gypsisols*
Suffix: similar to *Gypsisols*

Albeluvisols (AB): *Albeluvic* tonguing/*Argic* hor
Prefix: *Fragic*, *Cutanic*, *Folic*, *Histic*, *Technic*, *Gleyic*, *Stagnic*, *Umbric*, *Cambic, Haplic*
Suffix: *Anthric*, *Alumic*, *Greyic*

Alisols (AL): with *Argic* B with CEC_{clay} ≥ 24 $cmol_c$/kg, >5 dm *Dystric*
Prefix: *Vertic*, *Plinthic*, similar to *Luvisol*
Suffix: similar to *Luvisol*

Acrisols (AC): with *Argic* B with CEC_{clay} < 24 $cmol_c$/kg, >5 dm *Dystric*
Prefix: *Vertic*, *Plinthic*, similar to *Luvisol*
Suffix: similar to *Luvisol*

Luvisols (LV): with *Argic* B with CEC_{clay} ≥ 24 $cmol_c$/kg, > 5 dm *Eutric*
Prefix: *Lamellic*, *Cutanic*, *Albic*, *Escalic*, *Technic*, *Leptic*, *Gleyic*, *Stagnic*, *Haplic*
Suffix: *Anthric*, *Fragic*, *Rhodic*, *Chromic*

Lixisols (LX): with *Argic* B
Prefix: *Vetic*, *Plinthic*, similar to *Luvisol*
Suffix: similar to *Luvisol*

Umbrisols (UM): with *Umbric* A
Prefix: *Folic*, *Histic*, *Leptic*, *Endogleyic,Vitric*, *Andic*, *Ferralic*, *Stagnic*, *Mollic*, *Cambic*
Suffix: *Anthric*, *Albic*, *Brunic*, *Glossic*, *Alumic*, *Turbic*, *Gelic*, *Greyic*, *Laxic*, *Placic*, *Chromic*

Arenosols (AR): developed from loamy sand–sand and < 40 % vol. gravel + stones
Prefix: *Lamellic*, *Hypoluvic*, *Albic*, *Rubic*, *Brunic*, *Protic*, *Endogleyic*
Suffix: *Ornithic*, *Gypsiric*, *Turbic*, *Gelic*, *Placic*

Cambisols (CM): with *Cambic* B
Prefix: *Folic*, *Leptic*, *Vertic*, *Fluvic*, *Endosalic*, *Endogleyic*, *Fragic, Stagnic*, *Haplic*
Suffix: *Ferric*, *Ornithic*, *Colluvic*, *Gypsiric*, *Laxic*, *Gelic*, *Rhodic*, *Chromic*

Regosols (RG): other soils
Prefix: *Aric*, *Colluvic*, *Technic*, *Endogleyic*, *Stagnic*, *Haplic*
Suffix: *Brunic*, *Ornithic*, *Gypsiric*, *Sodic*, *Turbic*, *Gelic*

Example of classification according to the WRB: An eutrophic (BS 60 %), profile derived from loess with silt loam and Fe/Mn concretions in the Eg, but clay loam, clay coatings and mottles in the Btg, is a ***Luvic Stagnosol*** (***Manganiferric***, ***Eutric***, ***Siltic***).

WRB 2014 compared to the former versions of the WRB

1. The Reference Soil Group (RSG) ***Albeluvisol*** is now called ***Retisol.***
2. In the **WRB 2006**, coastal soils were classified as ***Tidalic Fluvisols*** for the first time. In the ***WRB 2014***, the various coastal soils are no longer classified as subunits of a higher unit, but rather as *Tidalic Histosols*, *-Technosols*, *-Cryosols*, *-Leptosols*, *-Solonchaks*, *-Gleysols*, *-Arenosols* and *-Fluvisols.*
3. With the ***Histosols***, a distinction is now also made between *Muusic* (on ice), *Rockic* (on stones) and *Mawic* (between stones) *Histosols*.
4. Until now, **steppe soils** were classified as soils with a ***Mollic*** horizon. *Chernozems* now have a ***Chernic*** horizon as a diagnostic horizon, where the humus body approximately corresponds to the previous *Voronic Chernozem*.
5. ***Technosols*** have been strongly modified. On the one hand, ***Luvic*** and ***Alic Technosols*** have been eliminated as lessivated formations e.g. from thousand year-old walls. They changed to *Luvisols and Alisols* (*Transportic*). On the other hand, other qualifiers such as *Archaic, Dolomitic, Grossartefactic* have been added.
6. A ***Yermic*** horizon consists of a sequence of stone layers with a thickness of two to several cm that are coated with desert varnish, a thin silty, usually biological crust, a layer with porous vesicular structure and a polygon network with fissures filled with eolian sand, reaching depths of 10 cm to 2 m. It is typical for ***Yermosols*** of the FAO World Soil Map. It was abolished and now there is no possibility of forming subunits of ***Yermic Cryosols***, ***-Leptisols***, ***-Fluvisols***, ***-Solonchaks***, ***-Solonetz***, ***-Gypsisols***, ***-Durisols***, ***-Calcisols***, ***-Arenosols*** and *-**Regosols***.

7.4.2 Soil Classification According to the US Soil Taxonomy

References: Soil Survey Staff (1975, 1999, 2002, 2012, 2014).

The soil classification developed by Marbut (1923), mainly based on morphological and chemical soil properties, was the first to be established in the USA. The soils were divided into **zonal** (mainly differentiated by the climate), **intrazonal** (influenced by groundwater or rocks) and **azonal** (hardly developed). These were then classified into **great soil groups** (comparable to the German soil units), **soil series** (local forms being the main mapping unit) as well as (according to the texture) into **soil types**, and finally (according to the productivity) into **soil phases**.

In 1960, the *US Soil Survey Staff* introduced a new system, the ***Soil Taxonomy***, which was completely different from other previous concepts. Except for the names of the soil series, all of the soil designations were redefined, and the composed names originate almost solely from Latin and Greek roots according to their basic combinations of characteristics, reflecting the position of the respective soils in the higher categories, their most important properties and relationships to other soils. Important horizon characteristics were also renamed, introducing precisely defined chemical and morphological differentiation criteria.

This system was based on **diagnostic horizons** and **diagnostic characteristics**, the definition of which was often similar to those from the **WRB 2006/7** shown in Tables 7.4 and 7.5. Finally, specific moisture (Table 7.6) and temperature conditions were also considered as diagnostic characteristics.

The topmost category of the ***Soil Taxonomy*** is the **order**, which always ends with ***-sol***. There are currently 12 orders that are ranked according to a key (e.g. a *Histic* epipedon leads in any case to a Histosol):

1. **Gelisols**: Soils with permafrost (*gelare* [Lat.] = frozen);
2. **Histosols**: Soils with organic soil material. (*histos* [Greek] = tissue);
3. **Spodosols**: Soils with *Spodic* B (*spodos* [Greek] = wood ash);
4. **Andisols**: Soils with *Andic* properties (*an* [Jap.] = dark);
5. **Oxisols**: Soils with *Oxic* B (from oxidic);
6. **Vertisols**: Clay soils with strong swelling/shrinking (*vertere* [Lat.] = turn);
7. **Aridisols**: Soils with arid moisture regime + *Ochric* A or high content of salts (*aridus* [Lat.] = dry);
8. **Ultisols**: Soils with low base sat. (<35 %), *Argillic* or *Kandic* B (*ultimus* [Lat.] = last);
9. **Mollisols**: Soils with *Mollic* A (*mollis* [Lat.] = soft);
10. **Alfisols**: Soils with *Argillic* B (*pedalfa* [American] = lime-free soil);
11. **Inceptisols**: Slightly developed soils with visible horizons (*inceptum* [Lat.] = begin);
12. **Entisols**: Undeveloped soils without visible horizons (*recent* [Engl.] = young).

The characteristic letter complexes for these order names, which are underlined in the preceding list (and, el, ent, ert, ept, id, oll, od, alf, ult, ox, ist), serve to form the names of the next lower category, the suborders. This is accomplished by adding further letter complexes, characterizing the properties of the suborders, in front of the respective order: ***Albic***, ***Anthropic***, ***Aquic*** = wet, ***Argic***, ***Argillic*** (similar to *argic*), ***Calcic***, ***Cambic***, ***Cryic***, ***Duripan***, ***Fibric***, ***Fluvic***, ***Folic***, ***Gypsic***, ***Hemic***, ***Histic***, ***Humic***, ***Orthic*** = normal, ***Perudic*** = wetness, ***Psammic*** = sandy, similar to ***Rendzina***, ***Salic***, ***Sapric***, ***Torric***, ***Turbic***, ***Vitric***,***Wassic*** (covered with water (*Wasser* [German] = water), and ***Udic***, ***Ustic*** and ***Xeric*** moisture regimes.

The **suborders** result from the combination of the two letter complexes. For example, due to their thick, dark, crumbly Ah horizons (*Mollisol* order) and their development in continental regions that are hot in the summer and cold in the winter (letter complex of the suborder: *cry*), the *Chernozems* belong to the *Cryoll* suborder. To equate the following suborders with soil type groups from the WRB system (Sect. 7.4.1) or other classification systems can only be imprecise, because the criteria used to define the groups in the individual classification systems are too different:

Further classification of the suborders leads to the **great soil groups**, which are approximately comparable to the German soil types and are formed by adding more letter complexes in front of the names of the suborders. Normally developed *Chernozems* are called e.g. *Haplocryoll* (hapl from *haplous* [Greek] = simple); *Chernozems* with a clay accumulation horizon under the A horizon are called *Argicryoll* etc.

Further classification (subgroups and families) is possible using adjective addenda. Thus, a *Chernozem* where the subsoil is affected by groundwater is called *Aquic Haplocryoll*, a normally developed *Chernozem* without a B horizon is an *Entic Haplocryoll* (from *Entisol*, i.e. transition to poorly developed soils), and with an Ah horizon with a thickness >50 cm is called *Cumulic Haplocryoll* (from *cumulus* [Lat.] = heap), etc.

The ***Soil Taxonomy*** classification system is used in the USA and several other countries. Because every **order** always includes dry summit soils to wet depression soils, this classification is based on the landscape forms. Developments are continuously updated in the ***Keys to Soil Taxonomy*** (Soil Survey Staff 2014).

The system's deficit is that soil identification according to the *Field Book for Describing and Sampling Soils* (Soil Survey Staff 2002, 2012)

does not require field measurements, e.g. pH-values and redox potentials corresponding to the *Guidelines for Soil Description* of the FAO (Jahn et al. 2006). Furthermore, the diagnostic soil moisture regimes are classified according to the out-dated concepts of *Aquic* and *Peraquic* moisture regimes (Soil Survey Staff 1975): Both generally assume reduced conditions, and therefore oxygen deficiency. For example, this should generally apply to tidal marshes at the coasts, although sandy soils that are flooded twice a day by tidewater often contain oxygen that is dissolved in water all year round. The same is true for some soils in closed, landlocked depressions fed by perennial streams. pH and redox measurements that are easily performed in the field while mapping would enable a distinction between soils that are actually reduced and those that contain oxygen with *Aquic* and *Peraquic* moisture regimes (Table 7.6).

7.4.3 Soil Classification in Germany

References: Boden (2005) and Wittmann et al. (1997).

In the 19th Century, the soils in Germany were mainly classified according to the parent rock. In the 20th Century, following the Russian W. Dokuchaev, H. Stremme was the first to differentiate between vegetation soil types (forest soils, heath soils, steppe soils), lithological soil types (calcic or dolomitic soils, soils of volcanic glasses etc.), wet soil types (floodplain, marsh, peat soils etc.), mountain and slope soils, as well as artificial soils, according to the presence of the individual soil forming factors.

Today, Germany's soils are classified according to a system that focuses on the soil's profile development, reflecting the effects of all soil developing factors or its horizon combination. It is based on Kubiena's (1953) **natural system**, which was modified mainly by E. Mückenhausen and is continuously being expanded by the Working Group for Soil Systematics of the German Soil Science Society. It is based on the following classification for the soils of Central Europe.

The **orders** are the topmost category of this system, which are divided according to the water regime into **terrestrial** soils, **semiterrestrial** or **groundwater-affected** soils, and **(semi-)subhydric** soils. There are also the **peat soils**, which only have a humus body.

1. **Fundamental Principles**
   The German Soil Classification is divided into following hierarchical categories:
   - ***Abteilungen*** **(orders)**
     Differentiated according to their water regime
   - ***Klassen*** **(suborders)**
     Differentiated according to soil dynamics and morphological properties caused by specific dominant pedological processes
   - ***Typen*** **(types)**
     Differentiated according to characteristic horizon sequences (Sect. 7.3), for raised bogs and minor developed soils after geogenic characteristics of the H or C horizon
   - ***Subtypen*** **(subtypes)**
     Norm subtype: has characteristic horizon sequence and properties of the type
     Deviation suptype: with significant supplementary properties
     Transition subtype: additionally with intermediate properties to other soil units
   - ***Varietäten*** **(varieties)**
     Qualitative modifications of a subtype with additional horizon properties deviating from the subtype [e.g. humus form (Sect. 7.2.2), base sat. (like WRB)].

2. **Soil Classification Units** (examples)

   Here is a list describing the units of the German Soil Classification and their typical sequence of diagnostic horizons (partly simplified) as well as their short symbols used in maps. Furthermore some examples are given concerning subtypes.

Table 7.6 Classification of Soil Moisture Regimes (Soil Survey Staff 1999)

Name	Soil temperature	Moisture regime	Period of time	Comments
Peraquic	±>5 °C	Wet	Permanent	Stagnating
Aquic	±>5 °C	Wet	Different	Stagnating
Perudic		Moist pF < 3	Nearly all the time	Perhumic climate
Udic	–	Moist	Σ > 90 d/a	Humic climate
	T_M < 22 °C + ΔT_M ≥ 6 °C	Moist	45 consecutive days in 4 months after the middle of summer in 6 of 10 a	Mostly soil air, if T_M > 5 °C
Ustic	T_M ≥ 22 °C	Dry	≥90 d/a	
	ΔT_M < 6 °C	Moist	>180 d/a or 90 consecutive days	
	T_M = 8–22 °C	Dry	>90 d/a	
	ΔT_M ≥ 6 °C	Sometimes moist	½ time T_M > 5 °C + moist on 45 consecutive d in 4 months following the middle of summer in 6 of 10 years	E.g. in trop. + subtrop. or monsoon zones
Aridic	≥5 °C	Dry	>½ of the time > 5 °C	In aridic zones
Torric	≥8 °C	Dry or partly moist	>90 consecutive days > 8 °C	Sometimes soluble salts
Xeric	T_M < 22 °C	Dry	≥45 consecutive d in 4 months after midsummer in 6 of 10 a	Mediterranean climate
	ΔT_M ≥ 6 °C	Moist	>½ of d with T_M > 6 °C or in 6 of 10 a > 90 d/a with T_M > 8 °C	

d day, *a* year; °*C* temp. of soil in 50 cm depth; T_M annual mean temperature
ΔT_M difference of summer (June–Aug.) and winter (Dec.–Feb.) mean temperatures
Depth of soil moisture determination in silt and clay soils = 1–3 dm, loam + loamy sand = 2–6 dm, sandy soils = 3–9 dm
Soil moisture dry: pF ≥ 4,2; moist: pF < 4,2; wet = water saturated

German Soil Classification Units (examples)

1 ***Terrestrische Böden*** **(terrestrial soils)**

Mineral soils that are unaffected by groundwater, at least in the first 40 cm

F **1.1** ***O/C-Böden*** **(O/C soils)**

Soils with an org. layer (>30 % org. matter)

FF Type: *Felshumusboden* (rock-humus soil)

O/mC profile on solid rock

FS Type: *Skeletthumusboden* (skeletic humus soil)

xC + O/C profile of/on gravel and stones, organic matter in cavities

O **1.2** ***Terrestrische Rohböden*** **(terrestrial immature soils)**

Initial stadium of soil formation, characterized by low org. matter accumulation and very low chemical weathering

OO Type: *Syrosem* (Kubiena 1953)

Ai/mC profile on/of solid carbonate, sulfate (gypsum), siliceous or silicate rock

OL Type: *Lockersyrosem*

Ai/lC profile of carbonate, sulfate (gypsum), siliceous or silicate unconsolidated rock

R **1.3** ***Ah/C-Böden*** **(Ah/C soils)** (Ah < 40 cm)

RN Type: *Ranker* (Kubiena 1953)

Ah/imC profile of solid rock with little (<2 %) or no carbonates, Ah ≥ 2 cm, C < 30 cm beneath surface

RQ Type: *Regosol*

Ah/ilC profile with little (<2 wt%) or no carbonate. Unconsolidated siliceous (quartz) or silicate rock with >3 dm thickness, Ah 2–40 cm

RR Type: *Rendzina* (Kubiena 1953)

Ah/cC profile of consolidated or unconsolidated carbonate rock (>75 % carbonate) or sulfate (gypsum) rock; Ah 2–40 cm

RZ Type: *Pararendzina* (Kubiena 1953)

Ah/eC profile of unconsolidated or solid siliceous or silicate rock with 2–75 % carbonate; Ah 2–40 cm

T **1.4 *Schwarzerden* (steppe soils)**

Includes all soils with Axh horizons with >4 dm thickness. The Axh horizons have a Munsell chroma <3.5 and value <4 (transition units <5)

TT Type: *Tschernosem* (*Chernozem*)

With Axh/Axh + lC(c)/C(c) profile; Axh > 4 dm. Characteristic is a mixed horizon Axh + lC(c), formed by intensive bioturbation

TC Type: *Kalktschernosem* (*Calcic Chernozem*)

With Acxh/Acxh + elCc/elCc profile; Axh > 4 dm; in contrast to TT, the solum exhibits significant enrichment of secondary carbonate in the form of pseudomycelia

D **1.5 *Pelosols* (clay-rich soils)**

Soils of this class have developed primarily from clay-rich or clayey-marly parent rock. They are characterized by significant swelling and shrinking mechanisms, which cause a distinct structure.

DD Type: *Pelosol*

Ah/P/C profile; P: subsurface hor with >45 % clay, prismatic or angular blocky structure and sometimes >1 cm-wide cracks at 50 cm depth (similar to Vertisols of WRB)

B **1.6 *Braunerden* (brown soils)**

Soils of this class are characterized by a Bw or Bv horizon resulting from brunification and clay formation

BB Type: *Braunerde* (brown earth)

With Ah/Bv/C profile

Norm subtype:

BBn *Normbraunerde* Ah/**Bv**/C profile

Deviation subtypes

BBc *Kalkbraunerde* A(c)h/B**cv**/C(c) profile

BBh *Humusbraunerde* Ah/**Ah**-Bv/(Bv/)C profile, Ah-Bv > 4 dm

BBl *Lockerbraunerde* Ah/B**fv**/C profile; Bfv: pore vol. > 60 %

Transition subtypes

DD-BB *Pelosol* BB: developed of 1.5-3 dm P hor, overlying Bv or C

LL-BB *Parabraunerde* BB: with Al-Bv/Btv, lower textural differentiation than LL

PP-BB *Podsol* BB: *Spodic* horizon up to 1.5 dm depth

SS-BB *Pseudogley* BB: S or transition S from 4 to 8 dm or Sw-Bv, Sd-Bv, then also above 4 dm

GG-BB *Gley* BB: Go and transition horizons from 4 to 8 dm

L **1.7 *Lessives***

Soils of this class are characterized by vertical clay migration, and by variably strong texture differentiation in their profiles

LL Type: *Parabraunerde* with Ah/Al/Bt/C profile

Difference in clay content between Al and Bt hor. (in mass%): ≥3 % at <17 % clay and <50 % silt; ≥5 % at <17 % clay and >50 % silt as well as at 17–45 % clay; ≥8 % at >45 % clay.

LF Type: Fahlerde with Ah/Ael/Ael + Bt/Bt/C profile; stronger textural differentation as LL

P **1.8 *Podsol***

Soils of this class have mostly developed from quartz-rich sands, sandstones, quartzites and siliceous schists. They are characterized by podzolization. The topsoil is extremely impoverished

PP Type: *Podsol* with Ahe/B(s)h/B(h)s/C profile

C **1.9 *Terrae calcis*** (after Kubiena 1953)

Very clay-rich, brightly yellow-brown to brown-red colored soils, developed from solution residues of carbonate rocks

CF Type: *Terra fusca* with Ah/T/cC profile

T horizon >65 mass% clay; high water permeability because of a distinct angular blocky structure and karst drainage

CR Type: *Terra rossa* with Ah/Tu/cC profile

From carbonate rock, mostly low humus content, bright brown-red colored by hematite; normally translocated; rubefication under warmer climates; in Germany fossil or relictic

S **1.10 *Stauwasserböden* (soils with stagnic properties)**

Soils of this class show stagnic properties, caused by rain water stagnation. Significant is a change between wetness and reduction, followed by drought and migration of iron and manganese (bleaching, formation of concretions and mottles), S within 4 dm beneath surface

SS Type: *Pseudogley* with Ah/S(e)w/(II)Sd profile

Often two-layer-profile; the redoximorphic hor begins at a depth <4 dm (concretions above mottles)

SH Type: *Haftpseudogley* Ah/Sg profile

Very fine Sand/Silt-rich; no differences in texture between top- and subsoil

SG Type: *Stagnogley* Sw-Ah/S(e)rw/IISrd profile

With strong redoximorphic properties because of prolonged wetness (reduction bleaching and mottling)

X **1.11 *Reductosols***

Reductosols are formed by gases causing reduction or oxygen deficiency (CH_4, H_2S, CO_2) with a diagnostic Y horizon. The gases evolve from post-volcanic mofettas, CH_4-forming microbes of asphalt lakes and sanitary landfills, or are formed from readily decomposable organic matter under reducing conditions by microbes in garbage, sludge, harbor mud or surrounding leaks in gas pipes or broken oil pipe lines.

Y **1.12 *Terrestrial Kultosols* (Terrestrial anthropogenic soils)**

Soils developed from anthropogenic accumulations are classified as natural soils due to their horizonation. The class of the Kultosols include soils that have been altered so strongly by human activities that the original sequence of soil horizons has been mostly destroyed

YK Type: *Kolluvisol* with Ah/M/II… profile

Ah/M > 4 dm thick; from translocated topsoil material (humus content of Ah horizon) that is washed off slopes by water and deposited at the slope foot, in sinks and small valleys, or eroded and accumulated by wind or by cultivation, respectively through anthropogenic transport

YE Type: *Plaggenesch* with Ap/E/II… profile

Ah/E > 4 dm thick; E from accumulated plaggen material (sods)

YO Type: *Hortisol* with Ap/Ex/(Ex-)C profile

Ap/Ex > 4 dm thick; Ex formed by long term intensive horticulture (frequent additions of organic matter, deep digging, additional water supply, shading)

YY Type: *Rigosol* (e.g. vineyard soils); with R-Ap/R/C profile

R horizon was caused by recurrent trench-ploughing (*Rigolen*) up to a depth of 4 to 10 dm, mostly in vineyards or in fruit orchards

YU Type: *Treposol* (deeply disturbed by subsoiling); with R-Ap/R profile

Normally caused by a single deep ploughing or a single deep trench ploughing; e.g. Ortsteinic Podzols

2 ***Semi-Terrestrische Böden* (semi-terrestrial soils)**

Semi-terrestrial soils are influenced by groundwater

A **2.1 *Auenböden* (floodplain soils)**

In this class, soils from sediments or alluvial sediments in river and creek valleys are combined, which are flooded by (O_2-enriched) river water (or water under pressure behind a dike)

Normally have a fluctuating groundwater table, which is generally connected to the river water level

The upper border of the aG horizon (apart from the transition to Gley) is > 4 or > 8 dm below the soil surface

AO Type: *Rambla* (after Kubiena 1953) (*Auen-Lockersyrosem*) with aAi/alC/aG profile

AQ Type: *Paternia* (Kubiena 1953) (*Auen-Regosol*) with aAh/ailC/aG profile

From recent fluvial deposits with or without <2 % carbonates

AT Type: *Tschernitza* (*Chernozem*-like floodplain soil)

With aAxh/(aM/C)aG profile; aAxh > 4 dm thickness

AB Type: *Vega* (Kubiena 1953) (brown flood plain soil)

aAh/aM/(alC/)aG profile; aAh/aM > 4 dm thick

G **2.2 *Gleye* (groundwater-affected soils)**

This class includes soils influenced by groundwater with redoximorphic features, at least in parts of the upper 40 cm

GG Type: *Gley* with Ah/G profile

Norm subtype:

GGn *Normgley* Ah/Go/Gr profile;

Go upper border above 4 dm, Gr normally deeper at 4–8 dm

Deviation subtypes:

GGx *Oxigley* Ah/**Go** profile; no Gr due to O_2-saturated groundwater

GGe *Brauneisengley* (bog iron gley soil) Ah/**Gso/**Gr profile;

With strong cementation of iron oxides, often with **iron pans** (*Petrogleyic*).

GGi *Bleichgley* (without oximorphic features and iron oxides of quartz sands) Ah/**Gw**/Gr profile

GGw *Wechselgley* (*Gley* with strongly fluctuating groundwater table)

Ah/**Go**/Gor/(Gr) profile; Ah/Go > 8 dm; with strongly fluctuating groundwater, outside of floodplains

GGc *Kalkgley* (*Gley* with secondary carbonate); A(c)h/**Gco**/Gr profile. In perhumid climates (e.g. >1000 mm annual precipitation), *Gleys* can also be found outside of valleys.

GGh *Humusgley* Ah/**Ah-Go/**Gr profile; Ah/AhG > 4 dm, humus content like Ah

GGa *Auengley* (*Gley* with floodplain dynamics in the whole profile); aAh/**aGo/aGr** profile

GGg *Hanggley* (on slopes with >9 % inclination); Ah/**sGo**/sGr profile.

GGq *Quellengley* (formed by water from springs) Ah/**qGo/qG**(o)**r** profile

Transition subtypes (example)

BB-GG Ah/Bv/**Bv-Go**/Go/Gr profile

GN Type: *Nassgley* with Go-Ah/**Gr** profile

Go-Ah < 4 dm deep, long lasting groundwater saturation close to the surface

GM Type: *Anmoorgley* (humic *Gley*) with Go-**Aa**/Gr profile

Go-Aa 1–4 dm thick; long-lasting groundwater near soil surface

GH Type: *Moorgley* (bog *Gley*) with **H**/IIGr profile; H horizon < 3 dm thick

M **2.3 *Marschen* (marsh soils)**

Soils of sediments deposited in **tidal areas**, under natural conditions with high daily fluctuating groundwater table

MR Type: *Rohmarsch* with (z)(e)Go-Ah/(z)(e)Go/(z)(e)Gr profile

Soils from sediments (often with carbonates and sulfides) deposited in tidal areas of the North Sea, Baltic Sea and estuaries with very different salt concentrations of soil solution

Subtypes

MRn *Normrohmarsch* tm(z)eGo-Ah/tmzeGo/tmzeGr profile

MRb *Brackrohmarsch* tbGo-Ah/tbGo/tbGr profile

MRf *Flussrohmarsch* tp(e)Go-Ah/tp(e)Go/tp(e)Gr profile

MC Type: *Kalkmarsch* with (e)Ah /eGo/(z)eGr profile from tidal sediments with carbonates

MN Type: *Kleimarsch* with Ah/Go/(z)(e)Gr profile from tidal sediments; decalcified below 4 dm

MD Type: *Dwogmarsch* with Ah/Sw/IIfAhSd/fGoSd/Go/Gr profile from tidal sediments; upper boundary of carbonates is below 7 dm; layered profile, often with humus and/or iron dwog (=fossil Ah or Go horizons)

MK Type: *Knickmarsch* Ah/Sw/(II)Sq/Gr profile; from tidal sediments; upper boundary of carbonates is below 7 dm; strong compaction (Knick) beginning above 4 dm below the soil surface and >2 dm thick

MO	Type: *Organomarsch* with oAh/oGo/oGr profile from tidal sediments of humic clay; often interlayers of peats and muds; strongly acid, often with maibolt (mineral: jarosite)
Ü	**2.4 *Strandböden* (soils of sandy beaches)**
	>3 dm sand; not flooded by daily high tide, only by storm tide
ÜA	Type: *Strand* with (z)(e)Ai/(z)(e)lC/(z)(e)Gw profile
	Subtypes
ÜAn	*Normstrand* tm(z)(e)Ai/tm(z)(e)lC/tmzeG
ÜAb	*Brackstrand* tb(z)(e)Ai/tb(z)(e)lC/(e)tbzeG profile
ÜAf	*Flussstrand* tp(e)Ai/tp(e)lC/tp(e)G profile
3	***Semisubhydrische* and *Subhydrische Böden* (semi-subhydric and subhydric soils)**
	Soils that are periodically flooded by tidewater, as well as subaquatic soils of lakes
I	**3.1 *Semisubhydrische Böden* (semi-subhydric soils)**
	Soils flooded periodically by tidewater
IA	Type: *Nass-Strand* (sandy soil of a beach) with t(z)(e)Fw/Fr profile
IW	Type: *Watt* (tidal flat) with (z)(e)Fo/(z)(e)Fr profile
	Subtypes
IWn	*Normwatt* tmz(e)Fo/tmzeFr profile
IWb	*Brackwatt* tbz(e)Fo/tbzeFr profile
IWf	*Flusswatt* tp(e)Fo/tp(e)Fr profile
J	**3.2 *Subhydrische Böden* (subhydric soils)** (after Kubiena 1953; Blume 2003a, b)
	Soils of lakes, which are under water permanently (definitions in discussion)
JJP	Protopedon with Fi profile, rH value > 19; org. matter. < 1 %
JG	Gyttja with Fo profile, rH value > 13; org, matter. > 1 %
JS	Sapropel with Fr profile, rH value < 13; org, matter. > 2 %
JD	Dy with Fh profile, rH value 13-19; org, matter. > 30 %
4	***Moore* (peat soils)**
	(>30 % org. matter), >3 dm thickness
H	**4.1 *Natürliche Moore* (natural peat soils)**
HN	Type *Niedermoor* (fen: groundwater peat)
	Subtypes:
HNn	*Normniedermoor*, (normal fen, base-rich) with **n**Hw/**n**Hr/(IIFr) profile
HNc	*Kalkniedermoor* (calcareous fen) with nH**c**w/nH**c**r/(IIFr/) profile
HNu	*Übergangsmoor* (transition fen) with **u**Hw/(uHr)/(nHr)(IIFr) profile
HH	Type: *Hochmoor* (raised bog from moss peat)
	Subtype:
HHn	*Normhochmoor* with **h**Hw/**h**Hr/(uHr)/(nHr/)(IIFr) profile
K	**4.2 *Erd- und Mulmmoore* (earthy peat soils, drained)**
KV	Type: *Erdniedermoor* (earthy peat soils, fen)
KM	Type: *Mulmniedermoor* (strong earthy peat soils, fen)
KH	Type: *Erdhochmoor* (earthy peat soils, raised bog)
	4.3 *Moorkultosole* (cultivated peat soils)
	1. *Niedermoor-Schwarzkultur* (black fen cultivation)
	2. *Sanddeckkultur* (sand covering cultivation (1–2 dm) of bog)
	3. *Moordammkultur* (peatland embankment cultivation)
	4. *Sandmischkultur* (sand mixed cultivation of bog with 1.8–2.5 m deep ploughing)
	5. *Tiefpflugsanddeckkultur* (similar to 2, in combination with deep ploughing).

7.5 Representative Soil Units

Literature with color soil profiles and their properties can be found in de Bakker (1979), van Baren et al. (1987), Bridges et al. (1998), Brozek and Zwydak (2003), Duchaufour (1998), Kubiena (1953), Mückenhausen (1977), Rehfuess (1990), Richard et al. (1972–1983), Singer (2007), and Zech and Hintermaier (2002).

The following describes important soils of the Earth as well as their morphology, classification, ecological characteristics and distribution. The descriptions and classifications in the English translation of this book follow those of the last German edition from 2010; however, they take account of the *Guidelines for Soil Description* (Jahn et al. 2006) and put the international classification according to the IUSS/ISRIC/FAO (2006/7) ahead of the last German classification from 2005 (Boden 2005). In addition, the German names as well as the names from the US Soil Taxonomy are also given for the Reference Soil Groups (RSG) (Sect. 7.4); however, their definitions are not always fully consistent with those of the WRB system. In the following chapter especially the RSG of the WRB are used. However, a simplified notation is adapted to characterize the RSG: all qualifiers are prefixed to facilitate the readability in a soil science textbook. Additional qualifiers, which are not defined for special RSG, but are considered as necessary in this chapter, are quoted.

For natural *"Reductosols"*, as well as some subhydric and coastal soils, cultivated soils of the mudflat coast and drained peat soils, suggestions for improvement were made for the WRB classification based on the German soil taxonomy. The same is true for soils of low mountain ranges, which were altered in the Weichselian period due to cryoturbation under permafrost conditions, but do not exhibit permafrost today. They are classified as *"Turbic" Leptosols*, for example.

Furthermore, there is the problem that the majority of international and national soil taxonomies today restrict their classification to properties in the topmost 2 m, which is not the case with other natural body sciences. Today, we know that many land surfaces still have biological activity at depths of much more than 2 m, and are therefore soils. For example, in *Spodic Gleysols* of northern Germany developed from meltwater sands, there is microbial weathering of silicate minerals at a depth of 3 m, and therefore soil formation is taking place. Particularly soils of older land surfaces may reach thicknesses of 40 m, and forest soils may have deeper rooting and microbial activity, so that an adequate classification is not always possible. For example, the diagnostic B horizons of tropical *Podzols* begin at depths below 2 m, and they are then classified as *Albic Arenosols*. Similarly, in many *Durisols* of the moist tropics, the diagnostic horizon often only begins below a depth of 5 m, so that the existence of these soils can only be recognized when their diagnostic horizon is observed in neighboring slope soils at a lesser depth. In contrast to lithology, petrography, geology and biology, soil science is the only natural body discipline in the world today that restricts the thickness of the objects to be classified. Kubiena (1953) demonstrated that there are also other possible ways.

The classification often follows a pedogenic approach: It begins with the hardly developed soils, then the more strongly developed terrestrial soils, followed by soils affected by groundwater, later also by surface water in the lowlands, river banks and coasts, and finally the moors formed under the influence of water surplus and therefore oxygen deficiency. The classification finishes with the permafrost-affected *Cryosols*, soils formed by specific animals such as penguins, or soils that were deeply mixed by termites or ants, *Anthrosols* and *Technosols* that were deeply altered by human activities, as well as (extra) terrestrial Paleosols.

7.5.1 Leptosols (LP)

Leptosols (shallow soils, from [Greek] *leptos* = thin) are soils that are either limited in depth by continuous rock within 25 cm from the soil surface, or contain more than 80 % vol. of gravel and stones over a depth of 75 cm (or to continuous rock). Important subunits are *Lithic Leptosols* and *Rendzic Leptosols*, amongst others.

7.5.1.1 Lithic Leptosols and Foli-Lithic Leptosols

Profile. A *Lithic Leptosol* (German: *Syrosem*) is a hardly developed soil consisting of hard rock. It is only found in patches and has a very thin humic top soil lying directly on the solid rock,

which is broken down mechanically to a maximum depth of 25 cm. A *Nudilithic Leptosol* (German: *Protosyrosem*) has outcrops of hard rock at the surface and only the topmost mm were altered by pedogenesis (Chen et al. 2000). A *Foli-Nudilithic LP* (*German: Felshumusboden*) has a thin O horizon above hard rock. In the US system, they are *Lithic* subunits of *Entisols*.

Development. The *Lithic Leptosol* represents an initial stage of soil formation, where a small amount of humus was formed from dead lichens on otherwise bare rock. The fungal hyphae of the lichen also penetrated into cracks of the topmost mm of rock and initiated chemical weathering with their exudates. This made nutrient elements available to the lichens and at the same time, the cohesion of the firmly bound minerals was loosened, and the rock in the topmost mm corrodes. On limestone, it leads over to the *Rendzi-Lithic Leptosols* and on silicate rocks to *Haplic Leptosols* (German: *Syrosem-Ranker*).

Properties. *Lithic Leptosols* are subject to extreme alternate drying and moistening conditions, *Foli-Lithic LP* are somewhat better. Their properties are otherwise closely related to those of the rock: Neutral soil pH values are found on limestone, and more acidic values are found on silicate rocks. Sometimes the upper cm of the solid rock are also depleted of substances. Pioneer plants (often mosses and lichens) excrete acids and complexing ligands that dissolve and extract nutrients, which can be seen by a bleaching of ferrous silicates. In other cases, the solid rock only forms the base, on which eolian dust and humus from vegetation can accumulate to a depth of a few mm, and therefore a very thin Ah horizon (which is called Ai horizon in Germany) or a thin O horizon is formed.

Distribution. *Lithic Leptosols* are found on eroded surfaces of mountainous regions. On low mountain ranges, they are usually restricted to a few rock ledges, but are found more frequently in high-altitude mountains. *Foli-Lithic Leptosols* are found on surfaces that are hardly at risk of erosion in high-altitude mountains. *Lithic Leptosols* are often found in small areas on walls and roofs of buildings. On the other hand, in continental Antarctica, where the land is mainly covered in ice, the only soils in some areas are on large stones, which are free of snow for 4 weeks annually and therefore exhibit a dense cover of fruticose lichens growing to heights of up to 20 cm. Neighboring fine earth soils are covered for longer periods with snow and cryoturbation prevents colonization by long-lived plants (Beyer and Bölter 2002: p. 94ff, 235ff).

Land use. Due to their limited depth and frequent desiccation, the use of *Lithic Leptosols* is possible at the most as a reindeer pasture in subpolar regions.

7.5.1.2 Rendzic Leptosols

Profile. A typical *Rendzic Leptosol* (German: *Rendzina*) (Fig. 7.12) often has a humus- and skeleton-rich, crumbly Ah horizon over solid limestone or dolomite (Fig. 7.13). The upper rock horizon is often cracked by frost weathering and is enriched with secondary carbonates.

Name. *Rendzina* is a Polish farmer's name, which describes the sound of many stones scraping on the moldboard of the plough. In the US system, it is a *Rendoll* when there is a *Mollic* A.

Development and properties. *Rendzic Leptosols* develop from limestone or dolomite rock through physical and chemical weathering as well as humus accumulation. Chemical weathering essentially causes the leaching of carbonates into the groundwater, resulting in the liberation of silicates and oxides that form the solum as dissolution residues. The non-carbonate **dissolution residue**, which often only represents 1–5 % in fresh rock, is mostly rich in clay (Fig. 7.13); however, this is not the case with soils from calcareous sandstone. Only these residues are normally available as inorganic material for the formation of the A horizon.

As a subtype, the Ah of *Rendzi-Lithic Leptosols* is only <2 cm thick, while the normal *Rendzic Leptosol* often has a humus-rich, dark and thick Ah horizon. Especially in cool humid regions at high altitudes, at least the upper Ah is fully decalcified and acidified: It is then called a *Dystric* subunit, which also often has a moder layer. As a subtype, the *Molli-Rendzic Leptosol* often has a humus-rich, dark and thick Ah

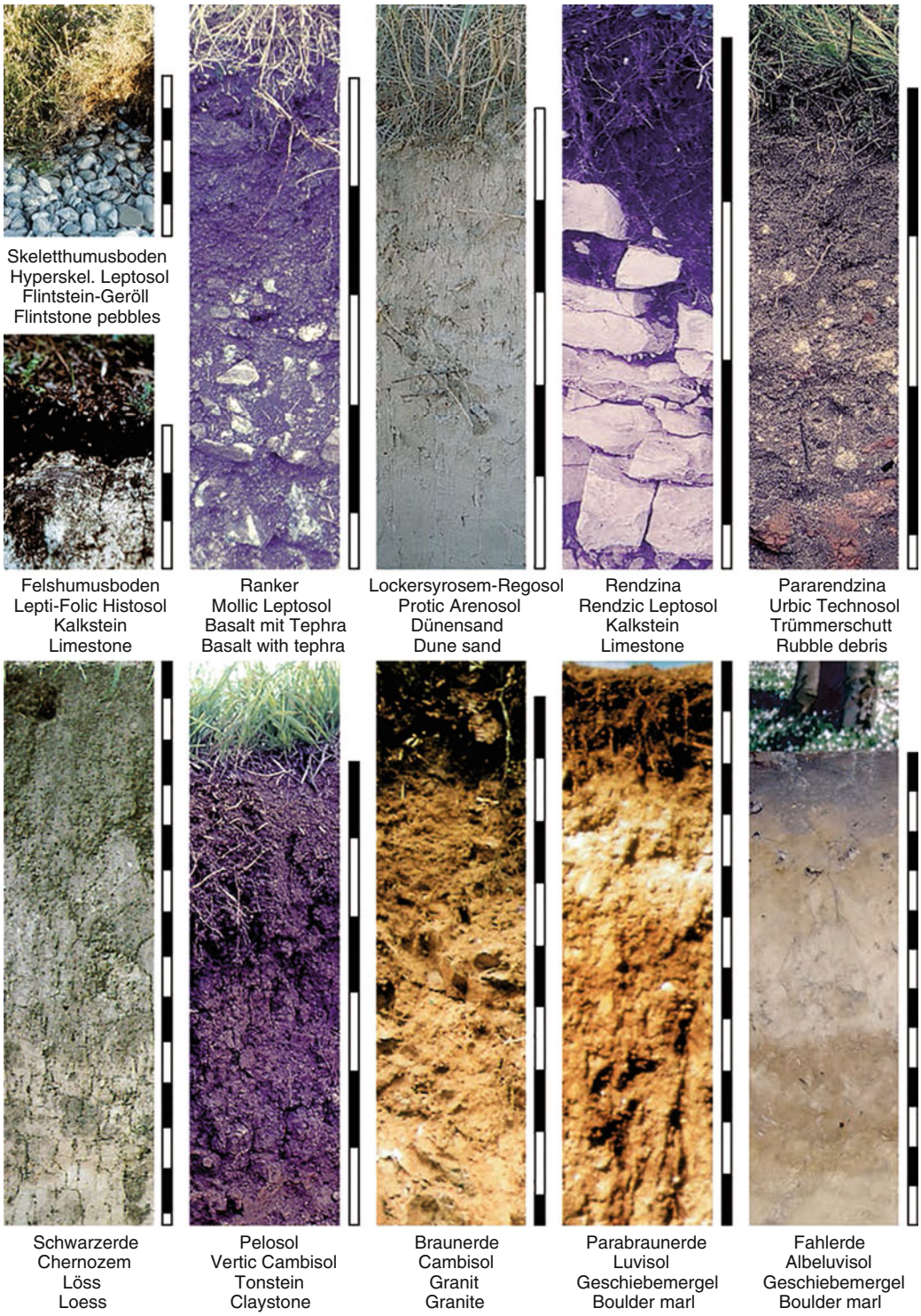

Fig. 7.12 Typical terrestrial soils in Germany (scale in dm; German and international names; draft by H.-P. Blume)

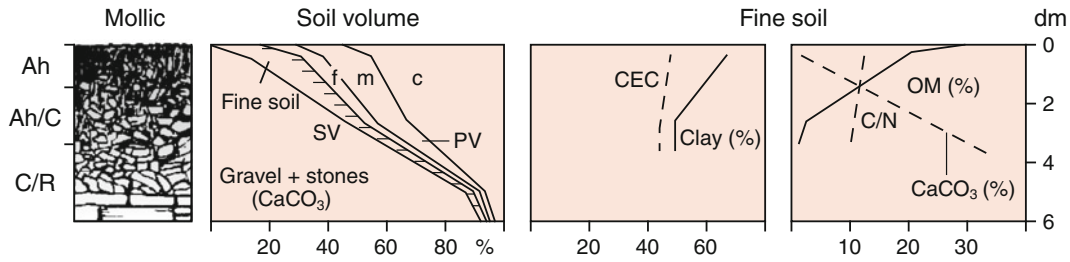

Fig. 7.13 Properties of a *Molli-Rendzic Leptosol* developed from limestone beneath *Fagus silvatica*; South Germany; draft by H.-P. Blume according to analyses by E. Schlichting (Abbreviations see Appendix, CEC in $cmol_c\ kg^{-1}$)

horizon. *Cambi-Rendzic Leptosols* already have a thin Bw horizon, whereby the lack of a polyhedral structure is often caused by an addition of loess (and therefore lower clay contents).

A typical *Rendzic LP.* usually has more than 5 % humus in the Ah horizon and a narrow C/N ratio (Fig. 7.13). The Ah usually contains carbonates and is therefore largely saturated with Ca ions. The silicates are hardly chemically weathered, so that the mineral composition of the soils is closely related to that of the parent rock. Due to the relative accumulation in the dissolution residues, there are more nutrient reserves bound in silicates in the Ah horizon than in the rock. The **high pH** and **high Ca saturation** result in intense biological activity, especially of earthworms. For this reason, the A horizon of *Rendzic L.* mainly consists of water-stable crumbs, which are formed from animal excrements. Therefore, despite high clay contents, *Rendzic Leptosols* are well aerated (also due to slope locations and/or jointed rocks).

Distribution and land use. In Central Europe, *Rendzinas* are mainly found on sedimentary rocks in low mountain ranges and in the Alps. In Mediterranean countries, they are mainly found as *Aridic* subunits, and are low in humus and less biologically active. *Rendzinas* from solid carbonate rocks are usually shallow, and dry on south-facing slopes. For this reason, despite the favorable physical and chemical properties in their rooting zone, they are mainly used for common pasture or forestry. Agriculture is only possible with greater depths to bedrock on level sites and on slopes, which then almost always leads to a strong decrease in the humus content, lightening of the color, and structural deterioration of the topsoil.

7.5.1.3 Silti-"Turbic" Leptosols and Silti-Leptic Cryosols

Literature: Altermann et al. (1999), Beyer and Bölter (2002), Blume et al. (1986: 162ff) and Kimble (2004).

Today, these soils are widely distributed in the high altitude mountains of the world as well as in the permafrost regions of Canada, Eurasia, and ice-free Antarctica. On slopes of the low mountain ranges in Central Europe, which were not covered with glaciers during the Weichselian, solifluction deposits were formed under periglacial conditions as a result of cryoturbation, soil creeping and solifluction. Today, these mudflows often exhibit division into a silt- and stone-rich German: *Decklage* (DL, cover layer), a silt-rich *Mittellage (*ML, middle layer), and a stone-rich *Basislage* (BL, base layer). BL mostly consists of crushed native hard rock, the ML often mainly of loess loam, and DL of loess loam and rocks from the underlying material. During the late glacial in Northern Germany, the loess was transported by wind as fluvioglacial sediment from the present-day North Sea basin, which was dry at the time, and in Southern Germany, in the same way from the Rhine Rift Valley. The high stone contents of the *covering layer* can be attributed to a downwards movement of the rocks from the ML (see Sects. 7.1.1 and 7.2.6.2).

Thin *soils* above native hard rock are called *"Turbic" Leptosols*, and those with high loess loam contents are *Silti-"Turbic" Leptosols*. However, if the *soils* are thicker, they are

classified as *Silti-Leptic Cryosols* (see Sect. 7.1.1 for more details).

Due to the slope locations and the high stone contents, the described soils are mainly used for forestry. Above the timber line in the Alps, they are extensively used as pasture.

7.5.1.4 Foli-Hyperskeletic Leptosol

Profile. A *Foli-Hyperskeletic Leptosol* (Fig. 7.12 top) has a humus layer (without groundwater influence) on rounded gravel with >80 % stones, which is at the most interspersed with mineral-poor humus. In Germany, such soils are called *Skeletthumusboden* (skeletic humus soil). They are lacking an Ah horizon. In the US system, the corresponding soils belong to the *Folists*. In contrast, if there is a humus layer lying directly on hard rock, it is a *Lepti-Folic Histosol* (Fig. 7.12 bottom). In Germany, it is then called a *Fels-Humusboden* (rock humus soil).

Development and properties. *Foli-Hyperskeletic Leptosols* are formed on slope debris, rounded gravel, or scree with little fine earth. For this reason, lichens can act as pioneer plants, and their residues eventually form the rooting zone for higher plants. Frost weathering and chemical dissolution weathering of the rock are much less significant than humus accumulation. The humus layers can reach a thickness of several dm, while joint fillings can reach a depth of up to one meter. Relatively thick, strongly humified Oa horizons generally follow below a thin Oe and Oi horizon. The O horizons are usually strongly acidified and dealkalized, even on base-rich rocks. Such soils are moist (to arid), however, in contrast to peat soils, they are only wet for short periods.

Distribution and land use. *Foli-Hyperskeletic Leptosols* are found in low mountain ranges and even in the lowlands of Northern Germany. For example, under heathland on Rügen, they developed on beach walls made with fluvial gravels of flint stone (Fig. 7.12, top). They are often under forest, however, their exposed location generally does not allow for land use. *Lepti-Folic Histosols* are mainly found in high-altitude mountains, e.g. in the Calcareous Alps, and are associated with *Lithic Leptosols*.

7.5.1.5 Other Leptosols

Profile. Other Leptosols from non calcaric rocks are classified in Germany as *Ranker* (Fig. 7.12). They exhibit a humic, often stony A horizon, which lies on solid, at the most crushed, silicatic, carbonate-free to -poor (<2 %) hard rock. The name *Ranker* (after Kubiena) is from *Rank* ([Austrian] = refuse dump, escarpment). In the US system, *Leptosols* belong to the *Lithic Haplumbrepts*.

Development and distribution. A *Haplic Leptosol* develops from a *Lithic Leptosol* through progressive humus accumulation and rock weathering. It mainly occupies slope positions, where only very thin frost debris layers were held or where erosion impedes further development. In high altitude mountains and low mountain ranges, *Leptosols* are mostly found on hard rock, while neighboring mudflows exhibit *Cambisols, Umbrisols* or *Podzols*.

Properties. Leptosols are generally thin, especially the *Lithic Leptosols*. *Umbric Leptosols* developed from predominantly quartz-rich rocks and are therefore nutrient-poor, and may have a humus layer especially in cool humid low mountain ranges. In contrast, *Mollic LP* developed from mostly quartz-free rocks such as basalt, and are generally rich in available and stored nutrients; in warmer locations, they exhibit especially mull humus forms.

Land use. Because *Leptosols* are usually found on slopes, they are mainly used as extensive grassland or forestry, whereby the trees can often only anchor themselves in jointed rock. In south-exposed locations, e.g. the *Kaiserstuhl*, they are also used for vine growing.

7.5.2 Arenosols (AR)

References: Petermann (1987) and Breckle et al. (2008: p. 65ff, 225ff).

Arenosols are sandy soils ([Latin] arena = sand) with only moderately pronounced horizonation. The texture is (at least in the upper 100 cm) loamy sand or coarser. They mostly have a humus-poor A-horizon, while the sandy texture

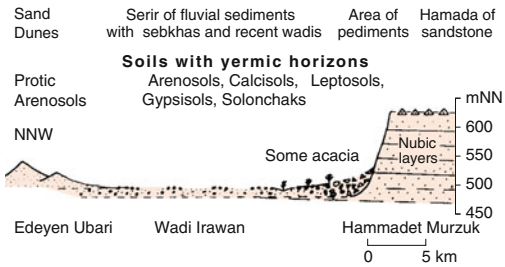

Fig. 7.14 Cross section through the Sahara desert with dunes, serirs and hamadas with different, mainly sandy soils; WSW Ubary, Fezzan, Lybia (H.-P. Blume and Th. Petermann)

only allows for the development of a *Brunic AR*. In the US system, they are called *Psamments*, and in French they are called *sols minéraux bruts*. *Arenosols* primarily develop from eolian sands as well as sandy weathered sandstone.

They are most widely distributed in the deserts of the Earth, for example in the Sahara, where they are formed from and between large sand dunes, but of sandy weathered sandstone of the Hamadas as well (Fig. 7.14). These soils will be described in addition as *Yermic* subunits later with the *Yermosols* in Sect. 7.5.17.

Subunits include, for example: Immature soils, recent dunes, *Protic Arenosol (AR)*, weakly *Calcaric AR*, weakly *Gypsiric AR,* extremely arid and humus-poor *Aridic* and *Yermic AR*, slightly brunified (chroma of the Bw > 4.5 and/or color 10YR or more intensely red) *Brunic* or *Rubic AR* or *Ferralic AR* (if the CEC < 4 $cmol_c$ kg^{-1}), bleached *Albic AR*, weakly lessivated (>3 % clay content difference) *Lamellic AR*, base-poor *Dystric AR* and base-rich *Eutric AR*. In Germany, *Protic AR* are classified as *Lockersyroseme*, *Brunic AR* as *Braunerden* and *Lamellic AR* as *Bänder-Parabraunerden* (*striped Luvisols*). *Arenosols* are only found sporadically in humid climates as stable coastal or interior dunes, while shifting sand dunes are not considered to be soils.

When they have a vegetation cover, *Arenosols* of humid climates contain a small amount of humus (Table 7.7). When they have been decalcified, they are generally acidified and dealkalized.

In Northern Germany, *Brunic Arenosols* developed on sands from the Pleistocene and Holocene are associated with *Podzols*, especially in high-precipitation areas. The coexistence of soils with different degrees of podzolization is due both to differences in texture in the profile and differences in land use, because *Brunic Arenosols* under nature-orientated mixed deciduous forests are also sometimes preserved in the relatively humid Subatlantic, while under heathland or coniferous trees, in contrast, they are more strongly podzolized.

The largest continuous *Arenosol* surface is found in the Sahel zone of West Africa from Senegal to the Sudan. These acidic *AR* are mostly *Lamellic, Rubic, Ferralic* or *Haplic Arenosols*. They are marginal agricultural sites, but in Nigeria, for example, they represent the most important agricultural areas. They mainly exhibit

Table 7.7 *Calcari-Endosalic Arenosol* derived from fluvic material, 2.5 m above sea level, developed from beach wall sand, with *Elymus farctus*, Mellum Island, Germany

Horizon	Depth (cm)	Moist Color	Structure	Texture	Bulk density g cm^{-3}	Moisture	Humus (%)	EC dS m^{-1}	pH H_2O	rH value	Lime (%)
A	0–10	Light grey	Single grain	LS	1.4	Moist	0.1	20	8	25	3
C1	−76	Light grey	Single grain	FS	1.3	Moist	0.1	20	8	25	1
C2	−95	Greyish brown	Single grain	FS		Moist	0.1	>30	8	25	0.5

According to data from H.-P. Blume

extreme P deficiency as well as low contents of all other nutrients.

The low available water and nutrient binding capacity as well as the usually low nutrient reserves of the *Arenosols* allow for use as pasture only above 300 mm annual precipitation, while high-yielding arable farming is only possible above 500 mm along with intensive fertilization. In desert regions, they are preferably used for irrigated agriculture, because their high permeability reduces the risk of secondary salinization.

7.5.3 Regosols (RG)

Regosols are weakly developed soils, which, except for an *Ochric* epipedon (and in desert regions sometimes a *Takyric* and/or *Yermic* horizon) and weakly developed hydromorphic features, only exhibit lithological differences. The name *Regosol* from [Greek] *rhegos* means blanket. The corresponding (sandy) soils are also called *Regosols* in German.

Profile. The *Regosol* is an A/C soil. The texture is loamy sand, loam, silt or clay. The Ah is a <20 cm-thick *Ochric* horizon (i.e. neither *Mollic* nor *Umbric* epipedon).

Development and properties. *Haplic Regosols* developed from carbonate-free to -poor unconsolidated sediments. They are often very deep. However, in contrast to *Arenosols*, the plant-available water binding and nutrient reserves are somewhat higher and even *Dystric* subunits can exhibit some contents of available nutrients. Especially under more humid climate conditions and/or conifers as *Dystric* subunits, they are also base-poor and then often exhibit humus layers with a thickness of up to 10 cm. Humus layers. *Eutric* subunits are more nutrient-rich (BS > 50 %).

Distribution and land use. *Haplic Regosols* are only found in small areas of Central Europe on eroded land surfaces. *Regosols* often develop from soils that were eroded by agricultural use. They then remain susceptible to erosion. They require constant manuring and in arid regions, also sprinkler irrigation if they are to be used for agriculture.

7.5.4 Cambisols (CM) and Umbrisols (UM)

Cambisols and *Umbrisols* are soils that, compared to *Regosols* and *Arenosols*, have stronger humus accumulation in the A horizon and/or exhibit a *Cambic* B horizon. Compared to the C horizon, their Bw horizon is differentiated either only by structure formation (e.g. transformation of a layered or coherent rock structure into an aggregate structure) or moderate silicate weathering, clay and sesquioxide formation have taken place.

Umbrisols are generally characterized by an *Umbric* epipedon, and *Cambisols* usually by a *Cambic* subsoil. In the following, the properties of both forms will be described, and then particularly clay-rich soils as a special form.

7.5.4.1 Cambisols

Profile. *Cambisols* exhibit a humic A horizon with a thickness of at least 20 cm, with a generally smooth transition to a brown-colored Bw horizon (Fig. 7.12). The C horizon follows at a depth of 25 to often 150 cm. There is no *Mollic* horizon.

Name. The term *Cambisol* comes from the Italian language, *cambiare* (to change). The German name *Braunerde* means brown earth. In the US system, these soils belong to the *Ochrepts* or *Umbrepts*.

Development. In temperate-humid climates, *Cambisols* develop from *Leptosols* or *Regosols* as soon as the brunification and loamification caused by silicate weathering (Sect. 7.2.1.2) reach the deeper parts of the profile where there is no humus accumulation. By definition, the structure of the parent rock has been physically modified by swelling and shrinking in the Bw horizon to form segregates (*granular, angular*

blocky, prismatic structure). It is also possible that relatively easily weathered minerals such as gypsum, calcite or olivine have been dissolved and their components have been leached out or oxidized. At least, they are strongly depleted in the Bw compared to the C horizon. At the same time, the BS value is lower compared to the C horizon following below, and the Munsell color is either more intensely red (e.g. 7.5YR instead of 10YR) or intensely yellow in the case of red-colored rock (e.g. mottled sandstone), or the color is brighter (e.g. Munsell 6 instead of 4), or the clay content is higher. On the other hand, the Bw horizon is not as strongly weathered as the diagnostic *Ferralic* horizon for *Ferralsols*: its stone content can be of more than 5 % vol. The exchange capacity of the clay fraction is more than 16 $cmol_c\ kg^{-1}$ or the content of readily weatherable silicates (feldspars, silicates containing Fe or Mg, glass, 2:1 clay minerals) in the fine earth is still more than 3 % or the muscovite content is still above 6 %.

Cambisols (BS value > 50 %) are generally rich in exchangeable Ca and Mg ions and have a stable structure. They can often be quite deep on silicate- and Ca-/Mg-rich igneous rocks (basalt, gabbro etc.). Under forest, they are often more strongly dealkalized (BS 20–50 %) and are then called *Dystric Cambisols*.

Under perhumid climate conditions, the soil development of *Cambisols* may have led to *Stagnosols* or *Gleysols* through *Endogleyic* or *Stagnic* subunits.

Properties. Depending on the parent rock, vegetation, development depth, clay and humus content, bulk density and the acidification, the properties of *Cambisols* vary greatly. *Calcaric CM* are found where groundwater or slope effects, windblow, colluvial deposition or fertilization have caused subsequent carbonate accumulation in an already brunified material. The *CM* normally have an *Ochric* epipedon: Under deciduous and semi-deciduous forests, the mull humus form can also be found on base-rich *CM*, and a *Mollic* epipedon may be lacking because it is too thin (<20 cm) (and it is therefore not a *Phaeozem*). However, forest liming or arable farming with liming after deforestation can also lead to the transformation of an *Umbric* horizon into a *Dystric Cambisol* when acidification of the subsoil is maintained.

The **texture** of *CM* includes very fine sand, loamy sand, silt, loam and clay. Accordingly, the humus and nutrient contents as well as the soil structure vary to a great extent, which can be expressed in the classification by using subunits. *Skeletic CM* are those with 40–80 % vol. of gravel and stones.

Distribution. *Eutric CM* are rare in temperate regions. The opposite is true for *Dystric CM*, which are found e.g. in low mountain ranges with granite, graywacke, slate or sandstone mudflows, and are then associated with *Umbrisols* as well as *Leptosols* from native hard rock, and *Podzols*.

Land use. The agricultural value of *CM* fluctuates across a wide range. Stone-rich *CM* are usually used for forestry. The less fertile *Dystric CM* also serve for forestry in Central and Northern Europe; however, with sufficient fertilization and water additions, they can also very well be used for farming today.

7.5.4.2 Umbrisols

Umbrisols are sandy to clayey A/C soils or A/Bw/C soils with an *Umbric* horizon of a thickness <20 cm, darkly colored by humus (similar to *Mollic*, but BS value < 50 %). Their name comes from the [Latin] *umbra* (shade). In the US system, they belong to the *Umbrepts* or *Humitropepts*; in Germany they are often called *Sauerbraunerden*. Their structure varies with the texture. The humus contents also fluctuate strongly. Sometimes, a thin O horizon is formed (then *Folic UM*).

On silicate-poor rocks such as quartz-rich sands (Fig. 7.15) or sandstones, *UM* developed from *Arenosols* or *Regosols*. *UM* are often weakly podzolized, which can be seen by bleaching of the mineral particles in the Ah, which is the beginning of the formation of an E horizon (then *Albic* UM). There is also a significant decrease in Al, Mn and P in the Ah compared to the subsoil. *UM* are often weakly lessivated, both in those of dune and glacial till sands in Northern Germany and in those

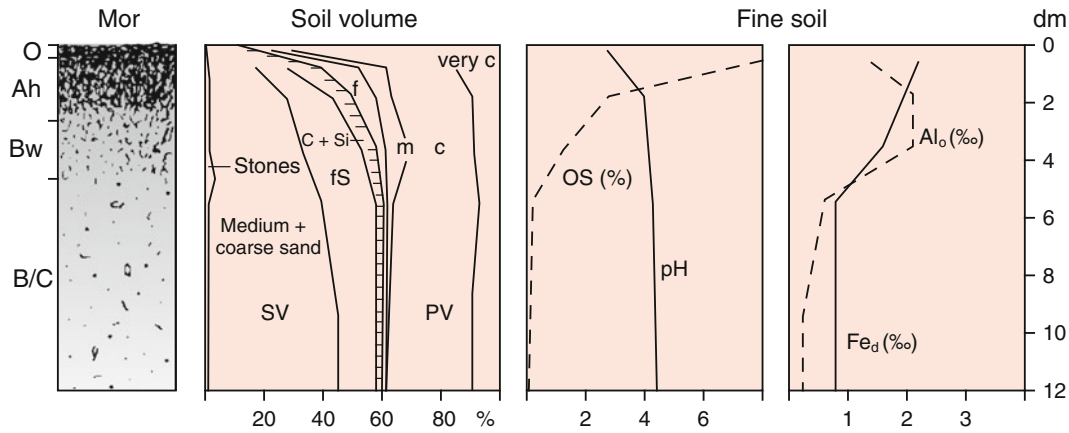

Fig. 7.15 Properties of a *Haplic Umbrisol* developed from boulder sand under semi-deciduous forest; Berlin; draft and analyses by H.-P. Blume (Abbreviations see Appendix)

developed from sandstone or granite mudflows, whereby clay bands are observed at a depth of 1–2 m, among other things (then "*Lamellic*" *UM*).

Hyperdystric Umbrisols (sometimes BS value < 20 %) often have stable aggregates due to the presence of Al ions and/or the adhesive effect of Fe oxides. *Andic Umbrisols* (d_B of the *fine earth fraction* < 0.9 g cm^{-3}) are usually acidic and have a stable structure. They developed at higher mountain locations from igneous rocks. Their looseness is often attributed to an incorporation of volcanic tuffs.

Also, under perhumid climate conditions, the development of *Umbrisols* may have led to *Stagnosols* or *Gleysols* through *Gleyic* or *Stagnic* subunits.

Distribution and land use. *Umbrisols* are often found in low mountain ranges with granite, graywacke, slate or sandstone mudflows under forest, where they are associated with *Leptosols* from native hard rock and *Podzols*. The agricultural value of *Cambisols, Umbrisols* and *Brunic Arenosols* fluctuates across a wide range. Soils that are richer in stones in low mountain ranges are often used for forestry. The *Umbrisols* also often serve for forestry, especially in Northwest Germany; however, with sufficient fertilization and irrigation, they can also very well be used for farming today.

7.5.4.3 Terrae Calcis—Chromic and Rhodic Cambisols

References: Jahn (1997), Jahn and Stahr (1991) and Singer (2007: 91ff).

Terrae calcis represent a special form of the *Cambisols*. They developed over thousands of years from hard, extremely silicate-poor limestone, dolomite or gypsum rocks (<1–5 % clay without silt or sand) through carbonate or gypsum dissolution, and exhibit a very specific morphology.

Profile. On hard limestone, there are soils with a bright yellowish to reddish-brown colored subsoil and high clay contents (>70–80 %), which are classified in Germany as *Terra fusca* or *Terra rossa* (WRB *Chromic* or *Rhodic Cambisol*) (Figs. 7.16 and 7.17). Their B horizon exhibits a dense polyhedral structure with sepic plasma (Sect. 7.2.3).

Name. According to Kubiena (1953), clay-rich, plastic, dense soils from carbonate or gypsum rocks are called *Terrae calcis* (Lat.) and divided into the bright brown *Terra fusca* and the red *Terra rossa*. In the WRB system and the US system, the *Terrae calcis* are not separately classified, but rather the *Terra fusca* as *Chromic or Ferralic Cambisol* (WRB) or *Eutrochrept* (Soil Taxonomy), and the *Terra rossa* often as *Rhodic Cambisol* or *Rhodic Xerochrept*.

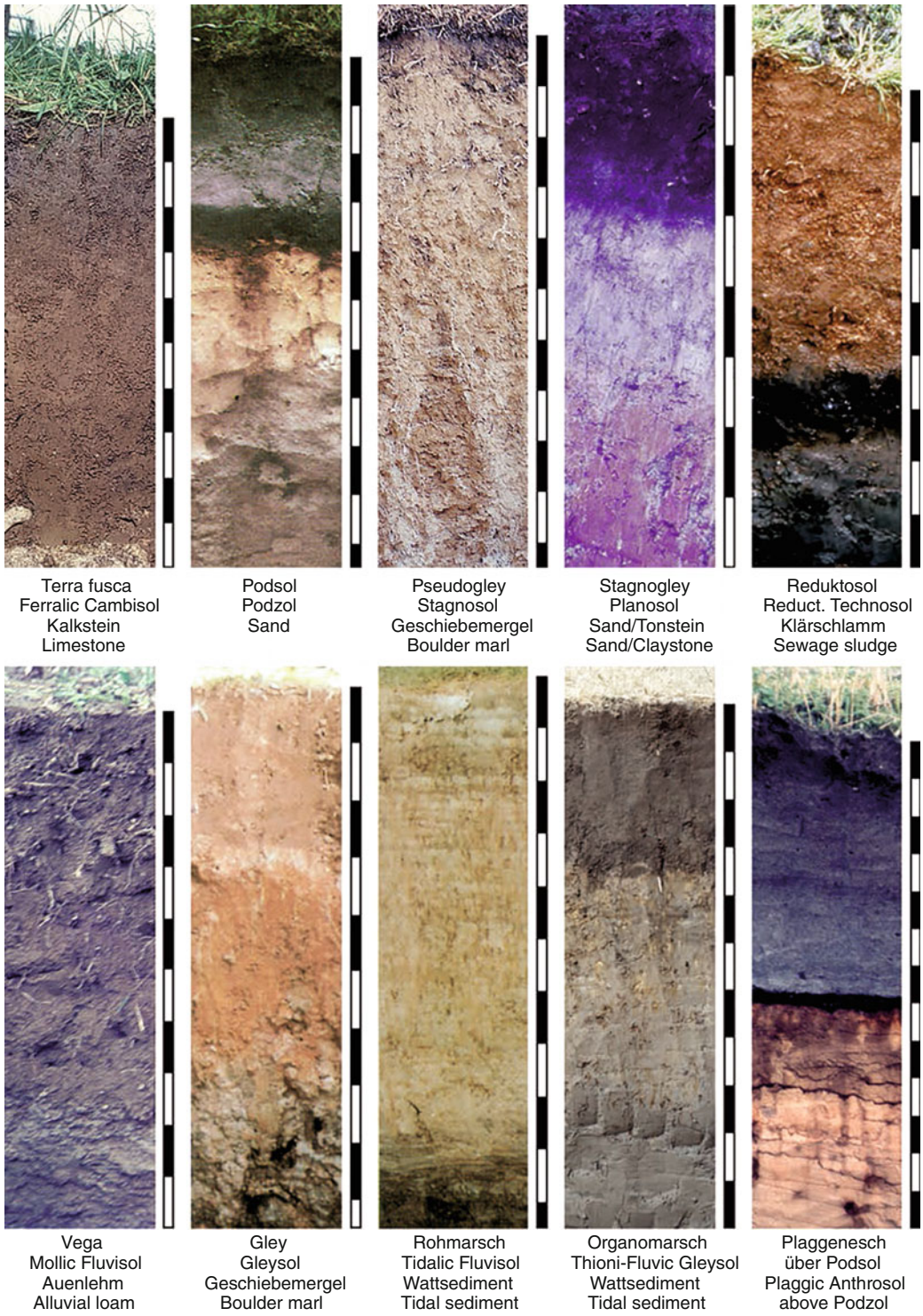

Fig. 7.16 Further terrestrial and groundwater-affected soils of Germany (scale in dm; German and international names)

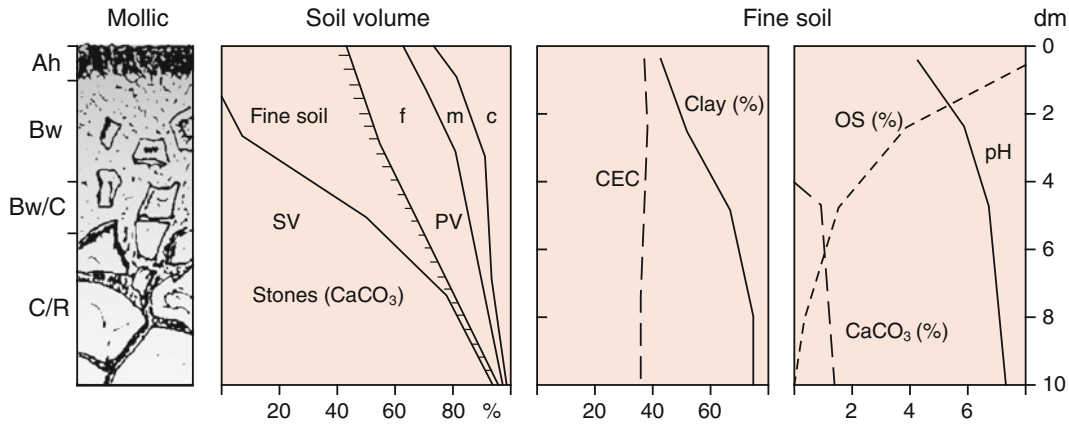

Fig. 7.17 Properties of a *Terra fusca* (*Chromi-Vertic Cambisol*) developed from limestone with loess inputs under spruce; Oberer Lindhof, Württemberg. Draft by H.-P. Blume according to analyses from H. Hemme and E. Schlichting (Abbreviations see Appendix)

Development. *Chromic Cambisols* and *Luvisols* develop from a *Rendzic Leptosol* when the silicate, clay-rich dissolution residues of a very pure (<5 % silicate dissolution residues) limestone, dolomite or gypsum rock (or mudflows of corresponding rocks) are acidified and also become thicker than 10–30 cm, so that the entire solum is no longer mixed with the humus body by the soil fauna. The bright ocher of *Terra fusca* can be from the color of the dissolution residues. However, carbonate- and silicate-bound iron was generally also liberated and oxidized. Therefore, true **brunification** took place. Their silicate mineral composition can broadly correspond to that of the rock and is then often rich in illite, or was altered by weathering and is then usually rich in kaolinite. This genesis is often associated with warm-humid climate conditions during the Tertiary. This is only true for the red *Terra rossa*, colored by hematite formation (=rubefaction). Some *Terrae fuscae* exhibit slight clay migration. However, clay content difference between the topsoil and subsoil are more commonly due to the input of foreign sediments (e.g. loess). Still, when they have striking clay content differences, they are often classified as *Rhodic Luvisols*. The development of *Terra fusca* takes place very slowly, because the dissolution residues of the parent rock are often minimal (often <5 %). Despite high clay contents, stagnization only occurs under perhumid climate conditions, because jointed rocks generally drain the seepage water very quickly.

Properties. *Terrae calcis* are usually moderately to strongly acidified, rich in clay (>65 %), very dense, and plastic in a moist state (Fig. 7.17). Their humus content is generally lower than that of neighboring *Rendzic Leptosols*. The plant-available water holding capacity is 50–100 mm, however, despite the larger rooting zone, it is often hardly higher than in neighboring *Leptosols* due to the very high contents of not available water.

Distribution and land use. In Central Europe, *Chromic* and *Rhodic Cambisols* are only found sporadically mainly on older land surfaces (i.e. Mesozoic to Tertiary) without risk of erosion, developed from carbonate rock (Table 2.9, Fig. 7.17). They are then associated with *Rendzic Leptosols* on the summits and with *Colluvic* subunits of *Cambisols* or *Umbrisols* in the depressions. *Rhodic Cambisols* are more commonly found in Mediterranean countries. They are often eroded or transported. They are mainly used for forestry or pasture. Because of the difficulties associated with tillage and the frequent alternation with shallow, stone-rich soils, they are rarely used for arable farming.

7.5.4.4 Vertic Cambisols

In Central Europe, soils with pronounced separation structures often developed from clay-rich rocks, the morph of which is comparable to the commonly found *Vertisols* in the alternate dry subtropics, and are therefore classified as *Vertic Cambisols*. In Germany, they are called *Pelosols*, derived from the Greek *pelos* (clay).

Profile. *Vertic Cambisols* are soils with pronounced polyhedral to prismatic structures that developed from clay-rich rocks (Figs. 7.12 and 7.18). Clay-rich (>45 % clay) horizons are found between the A horizon and the unaltered C horizon, where the layered structure of the parent rock was dissolved (so-called **maceration horizons**) and transformed into **separation horizons** with angular blocky to prismatic structures. The prismatic structure of the subsoil often exhibits shiny surfaces (=slickensides), and cracks that are often more than 1 cm wide are formed in dry periods, whereby they are comparable to the *Vertisols*.

Development. Swelling of the clay minerals through persistent moisture penetration caused maceration and fragmentation of clay-rich, stratified rock, so that a **coherent structure** was formed. The coherent structure was then transformed by alternate wetting and drying into a **separation structure**: Subangular blocky structures were formed in humic topsoils, with polyhedral and prismatic structures underneath, becoming coarser with increasing depth. The swelling pressure also pressed the soil aggregates against each other, causing clay alignment and the formation of the above-mentioned slickensides. Some *Vertic Cambisols* are brunified and exhibits signs of weak transformation of swelling clay minerals toward Al- or "pedogenic" chlorites. Sometimes, however, only sulfidic and/or carbonate iron is oxidized, even before the decalcification. Especially on level sites, *Vertic Cambisols* often exhibit stagnant water characteristics or have already further developed to *Vertic Stagnosols*. Relatively clay-poor topsoils of many *Pelosols* are attributed to foreign sediment additions (e.g. loess), and only seldom to clay migration. Furthermore, there may be **desilting** due to the rise of coarser particles as a result of swelling and shrinking.

Properties, distribution and land use. When they are dry, *Vertic Cambisols* have strong shrinkage cracks, while when they are wet, they swell so much that air deficiency occurs (Fig. 7.18). Although they often exhibit high water contents, the plant-available water content is low and decreases with desiccation also due to the fact that the remaining water is more strongly bound by shrinkage. Rewetting often also takes place from below due to water seeping into the desiccation cracks.

In Central Europe, *Vertic Cambisols* developed mainly on Mesozoic clays and marl clays,

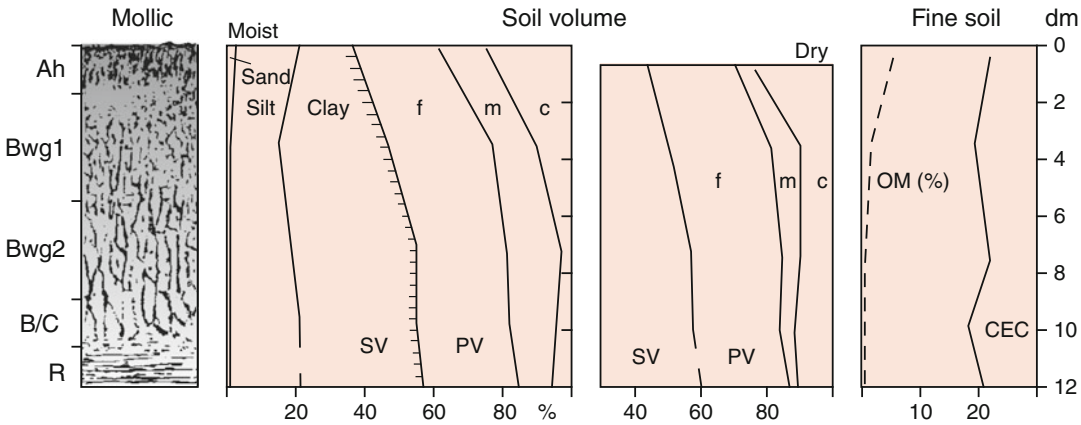

Fig. 7.18 Properties of a *Stagni-Vertic Cambisol* developed from clay under grassland; SW Germany; draft by H.-P. Blume according to analyses from Y. Nagarajarao and E. Schlichting (Abbreviations see Appendix)

and are then associated with "*Vertic*" *Gleysols* in depressions. However, they are also found on Pleistocene glaciolacustrine clay, clay-rich calcareous glacial till and clayey weathered, alkaline volcanites. Due to their high clay contents and therefore strong swelling and shrinking properties—especially in carbonate-free rocks—they are often only used as grassland or forest. In Central Europe, arable farming is generally only possible on *Calcari-Vertic Cambisols*, because here the rootability and air budget are more favorable because of the stabilizing effect of carbonates and ploughing is less difficult. Sometimes *Calcari-Vertic Cambisols* are even better for agriculture because they are too dry for grassland use.

7.5.5 Chernozems (CH), Phaeozems (PH) and Kastanozems (KS)

References: Dokuchaev (1883, 1899), Gehrt (2000) and Bronger (2003).

From the time of their formation, *Chernozems*, *Phaeozems* and *Kastanosems* are steppe soils that developed under pronounced alternating drying and wetting with a strong influence of intense bioturbation by earthworms and steppe mammals (European ground squirrels, hamsters, gophers).

7.5.5.1 Chernozems and Phaeozems

Profile. ***Chernozems*** are soils with a deep, black-colored *Mollic* Ah and accumulation of secondary carbonates in the subsoil, developed from unconsolidated rock of marly composition. They typically exhibit former earthworm burrows and **krotovina** of burrowing rodents filled with humic soil material and reaching depths of several meters because of intense bioturbation (Sect. 7.2.6.1). With a diameter of 10–20 cm in the C horizon, they often contain dark Ah horizon material, and sometimes contain light yellow C horizon material in the topsoil (Fig. 7.12).

Phaeozems are similar: The Ah is somewhat lighter in color and there is no striking pedogenic carbonate accumulation in the subsoil.

Name. The name *Chernozem* comes from the Russian *chernij zemlja* (black earth); *Phaeozem* was derived from the Greek *phaios* and the Russian *zemlja* (dusky earth). In Germany, both units are called *Chernozem* or *Schwarzerde*. In the US system, they belong to the *Vermudolls* (if rich in earthworms) or *Hapludolls*.

Development. In Europe, *Chernozems* and *Phaeozems* were mainly formed from loess or loess loam. A favorable constellation of various factors allowed them to develop beyond a *Calcaric Regosol*. These are mainly the characteristic properties of a calcareous, loose parent rock, the influence of a continental, semi-arid to semi-humid, summer-dry climates, the effect of grass-rich vegetation and the burrowing, mixing activities of soil-dwelling steppe animals.

In marginal areas of the *Chernozem* zone, the soils are often degraded. In addition to topsoil degradation, which is expressed by a lightening of the upper Ah horizon, there may also be decalcification, pH lowering, weathering of primary silicates with the formation of clay minerals and Fe oxides as well as clay migration, which initially affect the Ah horizon and later also the C horizon. These processes lead to the transformation of *Chernozems* into *Phaeozems*. Stages of increasing change often go from *Calci-Veronic* or *Vermic Chernozem* through *Vermic Phaeozem* to *Luvic Phaeozem*. This degradation of former steppe *Chernozems,* taking place extensively under forest since the Atlantic (see Table A.2 in the Appendix), was delayed on sites where humans have been practicing agriculture since the Neolithic (since around 4500 BP).

Properties. Central European *Phaeozems* contain 15–20 % clay (mainly illite) and are usually carbonate-free in the topsoil, and therefore react weakly acidic. The **humus content** is between 2 and 6 %, while Eastern European *Chernozems* can contain more than 10 % humus in the Ah horizon. The org. matter has a high exchange capacity (up to 300 $cmol_c\ k^{-1}$) as well as a narrow C/N (≈10) and C/P ratio (20–100). *Chernozems* and *Phaeozems* generally have a good supply of plant-available micronutrients (B, Cu, Mn, Mo, Zn). Their Ah horizon has a pore volume of ca. 50 % with relatively high

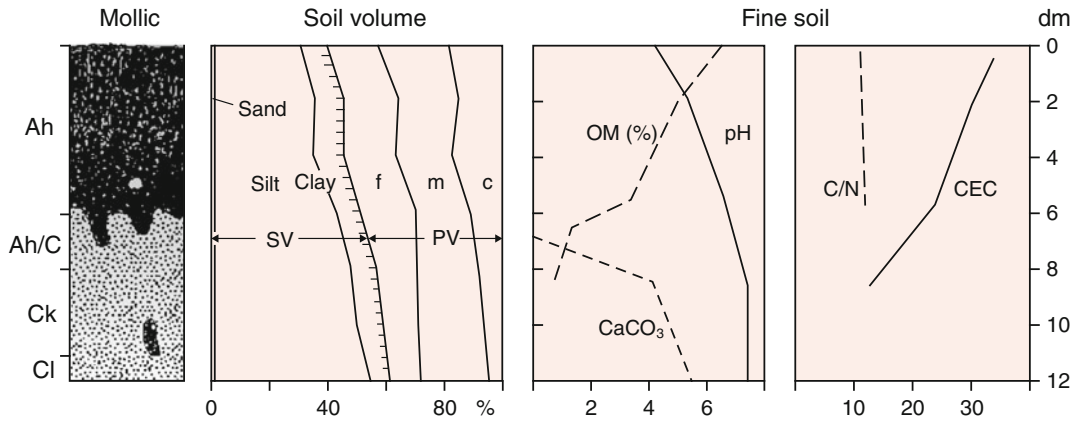

Fig. 7.19 Properties of a *Gleyi-Vermic Phaeozem* developed from loess under deciduous forest; Lower Saxony; draft by H.-P. Blume according to analyses by B. Meyer (Abbreviations see Appendix)

medium-sized and coarse pore fractions (Fig. 7.19). These soils therefore have good rootability and are sufficiently aerated. Corresponding soils developed from loess are capable of storing >200 mm of precipitation in an available form in the upper meter, so that vegetation can survive longer dry periods without damage.

Distribution and land use. In the Erfurt-Halle-Magdeburg region of Germany, there is an extensive *Chernozem-Phaeozem* area that reaches up to Hildesheim. All of the degradation stages can be found here, all the way to the *Luvisols*. In other parts of Germany, only strongly altered *Phaeozem* relicts are otherwise found in isolated areas. Also in the driest areas of the North German and Polish young moraine landscapes (formed during the Weichsel glacial stage), on the Fehmarn and Poel islands, the Uckermark and in the Stettin area, there are soils that are closely related to *Stagnic Phaeozems* or *Gleyic Phaeozems*. *Chernozems* and *Phaeozems* cover large areas mainly in the high-latitude steppes of Eurasia (especially in the Ukraine), North America and in the pampas of Argentina.

Chernozems and *Phaeozems* are very fertile and are therefore excellent field sites. They count among the most important wheat soils on Earth.

7.5.5.2 Kastanozems

Kastanozems (Fig. 7.20) are steppe soils like the *Chernozems* and *Phaeozems*. The name was introduced by Russian soil scientists. In the US system, they are equivalent to *Aridic Borolls* and *Ustolls*. They also have a 40 cm-thick mull A horizon developed through intense animal activity, however, in contrast to the *Chernozems*, they have a more pronounced brown color (Munsell chroma > 2), which is also where their name comes from (the color of chestnuts). There is always a horizon with carbonate accumulation (*Calcic* horizon), even in carbonate-poor rocks. As *Gypsic* or *Petrogypsic KS,* they contain gypsum, which, like lime (*Calcic KS* or *Petrocalcic*), partly consolidates the soil. Compared to the *Chernozems*, the thickness and humus content of the A horizon is generally lower, the carbonate and gypsum accumulation higher up in the profile, and the subsoil can also contain water-soluble salts. These differences result from the lower soil moisture, i.e. less precipitation and/or higher temperatures.

Kastanozems exhibit a neutral soil pH. Silicates are hardly weathered and depending on their parent rock, the clay minerals are dominated by illite, smectite, vermiculite or palygorskite.

Like *Chernozems, Kastanozems* can be very fertile. However, differences in weather conditions from one year to the next result in higher yield fluctuations than with *Chernozems*. Measures to supplement the water reserves, such as fallow, must often be implemented. Wind erosion and also water erosion on slopes are very

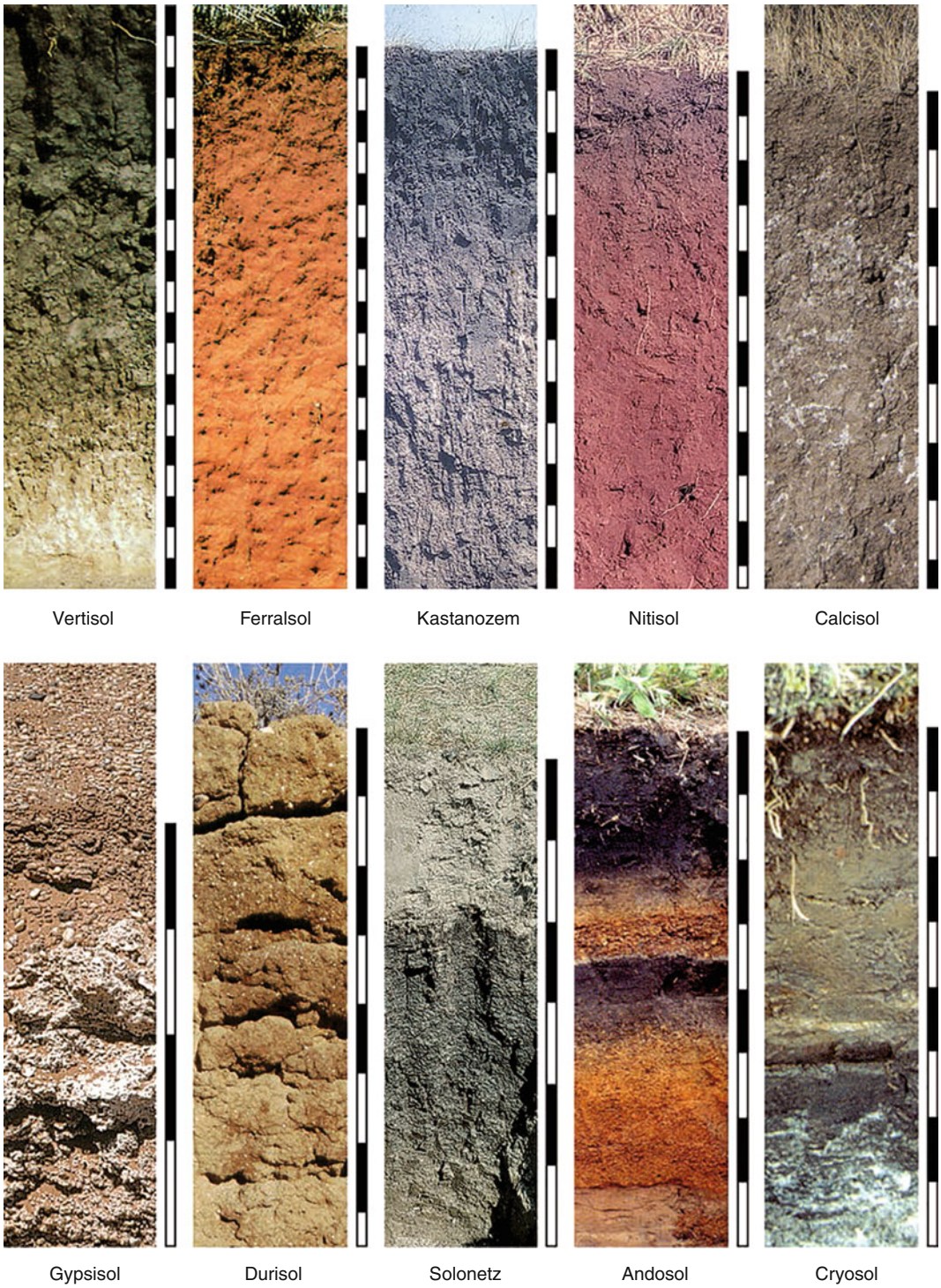

Fig. 7.20 Typical soils of the Earth (scale in dm; names according to the WRB) (draft by H.-P. Blume, *Durisol* P. Schad, *Cryosol* C. Tarnocai)

common. Irrigated agriculture is associated with loss of the *Mollic* Ah and the risk of secondary salinization (Sect. 7.2.4.5).

Kastanozems are commonly found in the continental arid regions of Russia and Central Asia, the drier prairies of North America as well as in Argentina. In Germany, they are only found in the Mainz basin of the Upper Rhine Valley. Because of the brown color, they were formerly called *Brauner Steppenboden* (brown steppe soils) and today, because of their strong accumulations of secondary carbonates, they are called *Kalktschernosem* (Blume et al. 1986: 169ff).

7.5.6 Soils with Clay Migration

A large group of soils is depleted of clay in the topsoil relative to the subsoil as a result of clay migration (see Sect. 7.2.4.1). These soils therefore have an *Argic* B horizon, characterized by clay coatings on the aggregate surfaces or oriented clay bridging between the sand grains in the form of clay bands in sandy subsoils. A distinction is made between four groups, which differ in terms of their clay mineral composition and therefore the CEC in the subsoil, and also in their base saturation (see Sect. 7.4.1): *Alisols* (CEC > 24 $cmol_c$ kg^{-1} clay, base saturation (BS) < 50 %), *Acrisols* (CEC < 24 $cmol_c$ kg^{-1} clay, BS < 50 %), *Luvisols* (CEC > 24 $cmol_c$ kg^{-1} clay, BS > 50 %) and *Lixisols* (CEC < 24 $cmol_c$ kg^{-1} clay, BS > 50 %).

Furthermore, especially in former Tarantian permafrost regions of Central and Eastern Europe as well as Canada, similar soils are found where the topsoil (also more sandy due to the addition of eolian sand) is strongly characterized by cryoturbation. This resulted in a **tonguing transition** between the E and Bt horizon. Such soils are called *Albeluvisols*.

Finally, in the humid tropics and subtropics, there are bright red-colored, lessivated, clay-rich soils that are called *Nitisols*.

In the following, the dominant *Luvisols* and *Albeluvisols* in Central and Eastern Europe will be described in more detail. The former are called *Parabraunerden* in Germany, and the latter are called *Fahlerden* (Wittmann et al. 1997: 253ff). This is followed by a brief description of the properties, development and distribution of *Alisols*, *Acrisols* and *Lixisols*. The *Nitisols* will then be described last.

7.5.6.1 Luvisols (LV) and Albeluvisols (AB)

Profile. ***Luvisols*** exhibit the horizon sequence Ah/E/Bt/C, because clay migrated down the profile (Fig. 7.12). The clay-depleted topsoil horizons can reach depths of up to 60 cm and comprise the crumbly, humic, shallow Ah and the humus-poor, light brown, often platy E horizon. In the deep brown Bt horizons with subangular blocky to prismatic structure following below, which can reach thicknesses between 40 and 120 cm in Central Europe, the clay content is >3, >5, >8 % higher than in the E horizon, depending on the soil texture (German soil classification system). Clay accumulation took place in the form of clay coatings on aggregate surfaces and biopore walls.

In *Albeluvisols*, the clay-depleted topsoil is much lighter in color than the E horizon and the difference in clay content with the Bt is more than 9–12 %, depending on the soil texture (German soil classification system). The E and Bt horizons are generally more clearly differentiated and are thicker than in *Luvisols*. Furthermore, the E horizon has *Glossic* tonguing in the subsoil, which is attributed to periglacial cryoturbation. In Schleswig-Holstein and Brandenburg (states of Germany), temperature cracks filled with eolian sand were even found reaching depths of up to one meter in the subsoil (Sect. 7.2.6.4). There are also often silt-rich coatings on aggregates in the transition to the Bt.

Name. *Luvisol* was derived from the Latin *luere* (to wash); in Germany, it is similar to the *Parabraunerde*. *Albeluvisol* is composed of the Latin words *albus* (white E) and *eluare*. They are called *Podzoluvisols* on the FAO World Soil Map from (1974). In Germany, they correspond to *Fahlerde*. In the US system, both are classified

as *Alfisols*, and the *Albeluvisols* as *Glossudalfs* or *Glossocryalfs* (Greek *glossa* = tongue-shaped).

Development. *Luvisols* and *Albeluvisols* preferentially develop from unconsolidated rock of marly composition, but also from carbonate-free loams and loamy sands. In temperate-humid regions of Europe, they generally developed from *Calcaric Regosols* or *Cambisols*, where the carbonate leaching and weak acidification enabled clay migration (Sect. 7.2.4.1). This is more strongly pronounced in arid, warmer locations than in high-precipitation, cool areas because then the pH remains a longer time between 6.5 and 5, which promotes clay peptization and migration. Furthermore, periodic desiccation in loamy soils leads to better formation of draining shrinkage cracks.

Luvisols and *Albeluvisols* with pronounced clay coatings on aggregate surfaces are called *Cutanic* subunits; soils with sandy subsoils with thin clay bands instead of the clay coatings are called *Lamellic* subunits. In the boundary areas of the Central German *Phaeozem* zones, *Luvisols* sometimes developed from *Phaeozems* through degradation. These *Humic* subunits exhibit dark black clay coatings and the remains of the *Phaeozem* Ah can be seen in the lower Bt horizon.

Stagnic water conditions can occur in *Luvisols* and *Albeluvisols* with strong clay migration or in high-precipitation areas. However, the development than leads to *Luvic Stagnosols* through *Stagnic Luvisols* or *Stagnic Albeluvisols*, where the former E and Bt horizons are so strongly transformed by Fe translocation and mottling that the former *Luvisol* development is hardly morphologically visible in the field.

Properties. The clay migration or lessivage led to differences in clay content between the E and Bt horizon (Fig. 7.21), which can reach up to 20 % clay in *Albeluvisols* of loess regions in Northern Germany. In more continental areas and with layering, the differences can be even greater. The translocated clay minerals, oriented parallel to the void walls, can account for more than 5 % of the soil volume in the Bt horizon.

In Germany, the depth of decalcification in *Luvisols* from Tarantian loess or calcareous glacial tills is usually 0.5–1.5 m; and in *Albeluvisols* from Calabrian glacial till up to depths of 4 m and more. Under forests, *Luvisols* are moderately to strongly acidified.

Luvisols developed from loess or calcareous glacial till exhibit a high potassium supply and fixation capacity. In *Albeluvisols*, a large portion of the illitic clay minerals are depleted of potassium and transformed into soil chlorite. Depending on the rocks and degree of weathering, *Luvisols* and *Albeluvisols* exhibit high to moderate nutrient reserves. Compared to the E and C horizons, the Bt horizon often has fewer coarse pores and usually a higher fine pore content. Nevertheless, the subsoil generally has good rootability and aeration; in *Stagnic* subunits, however, there may be intermittent air deficiencies. *Luvisols* with loamy and silty soil textures have a particularly high plant-available water capacity with 150–200 mm in the first meter.

Distribution and land use. *Luvisols* and *Albeluvisols* belong to the most common soils of the temperate-humid climate regions of Eurasia and America (Bronger 2003; Wiechmann and Blume 2008). In Central Europe, they are mainly found in loess and moraine landscapes. Lessive soils are usually good field sites with high agricultural productivity. However, because of the silting in the lessivated topsoil, soils developed from loess are particularly susceptible to soil surface sealing and are easily eroded on slopes.

7.5.6.2 Acrisols (AC), Alisols (AL) and Lixisols (LX)

Like *Luvisols,* the *Acrisols, Alisols* and *Lixisols* exhibit the horizon sequence Ah/E/Bt/(Bw)/C, and are therefore characterized by clay migration. However, *Acrisols* and *Lixisols* are more strongly weathered than *Luvisols* and *Alisols,* and contain large amounts of kaolinite. In contrast to *Luvisols* and *Alisols,* the CEC of the clay fraction is therefore <24 $cmol_c\ kg^{-1}$. *Acrisols* ([Latin] *acris* = acidic) and *Alisols* are base-poor (BS < 50 %), and in contrast, *Lixisols* ([Latin] *lixivia* = leaching) and *Luvisols* are more base-rich (BS > 50 %).

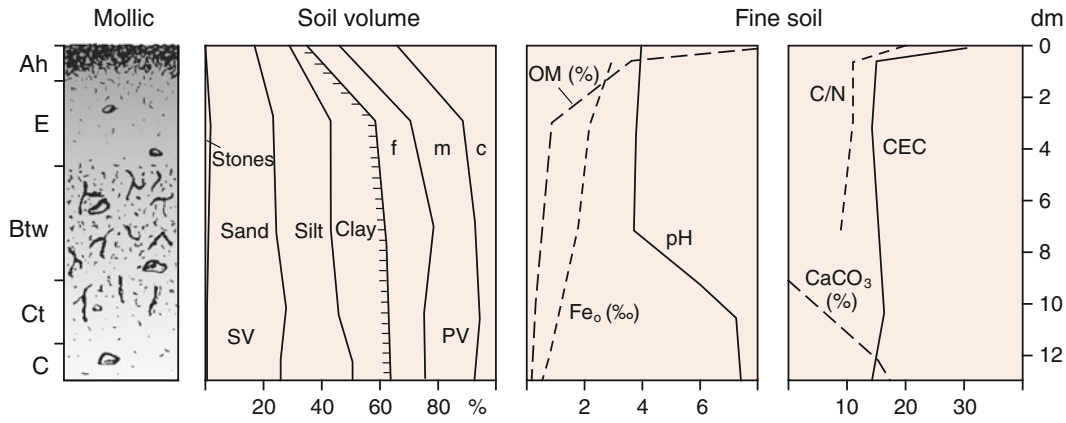

Fig. 7.21 Properties of a *Cutanic Luvisol* developed from calcareous glacial till under deciduous forest; NW Germany. Draft and analyses by H.-P. Blume (Abbreviations see Appendix)

Acrisols are mainly found in the lower latitudes under higher temperatures. In contrast to the *Nitisols*, they are generally formed from quartz-rich rocks, and the differences in clay content between the horizons are more pronounced. *Acrisols* dominate in the more humid tropics and subtropics, whereas the *Lixisols* dominate in the drier savannas and in the Mediterranean. The higher BS values in *Lixisols*, despite stronger weathering, were probably caused by climate change.

Normal *Acrisols*, *Alisols* or *Lixisols* are called *Haplic AC* (or *AL*, *LX*). *Gleyic AC* (*AL*, *LX*) are gleyed in the upper 100 cm, and *Stagnic AC* (*AL*, *LX*) are waterlogged. With the presence of the corresponding diagnostic horizons, other subunits include *Albic AC* (*AL*, *LX*), *Ferric AC* (*AL*, *LX*) and *Plinthic AC* (*AL*, *LX*) (Tables 7.4 and 7.5).

The Soil Taxonomy classifies *Acrisols* with the *Ultisols*, while the *Lixisols* and *Alisols,* like the *Luvisols,* belong to the *Alfisols*.

Like the *Ferralsols*, *Acrisols* generally represent nutrient-poor sites that can only be used for shifting cultivation or have to be fertilized. Due to air deficiency, *Stagnic AC* are generally only used for forestry or pasture, and the same is true for *Plinthic* or *Ferric AC* due to poor rootability.

In contrast, fertilized *Alisols* are better crop sites. *Lixisols* are extensively used as pasture land but also for cotton, Cassava or in the Mediterranean for vine growing, almonds, figs and irrigated citrus. Because they have low nutrient reserves, more intensive use requires corresponding high fertilization.

Acrisols and *Alisols* are more commonly found in Eastern USA, in Southeast China, and in all of Southeast Asia, on Borneo, and in the Amazon basin as well as large parts of West Africa. *Lixisols* dominate in Northeast Brazil, in the savannas of Africa, and also in East and Southeast India and on Mediterranean karst surfaces.

7.5.6.3 Nitisols (NT)

Nitisols (Fig. 7.20) are bright red-colored, lessivated, clay-rich soils of the humid tropics and subtropics. Their name ([Latin] *nitidus* = shiny) refers to the characteristic shiny aggregate surfaces.

Developed from silicate-rich rocks (e.g. basalt, mica schist), *Nitisols* exhibit thick, uniform red colored profiles with stable polyhedral structures and only moderate differences in texture. The clay contents decrease by less than 20 % from their maximum in the upper Bt horizon until a depth of 150 cm. There are no redoximorphic characteristics down to a depth of 100 cm. The silicates in the rock are largely weathered and kaolinite is the dominant clay mineral; in contrast to the *Ferralsols*, however, they still contain weatherable minerals.

Eutric NT have a base saturation >50 % and correspond to the *Paleudalfs* of the US

systematics, while the *Dystric NT* (US: *Rhodudults*) and the more humus-rich (>1 % on average in the upper 18 cm due to the cool-humid high-altitude climate) *Humic NT* (US: *Palehumults*) are more strongly acidified and dealkalized (BS value in the subsoil < 50 %).

Nitisols are loose, deeply rootable plant sites with sufficient aeration, high Plant available water and at least moderate nutrient supply, which enable the cultivation of more demanding crops (e.g. tea, sugar cane and peanut). They count among the most fertile soils of the humid tropics and subtropics. They are mainly found in Nigeria and the Congo, in the coastal regions of India, on the Philippines, in the south of the USA and in Southeast Brazil.

In Germany, fossil *Rotlehme* (red loams, *Fersiallites*) are found on Mount Vogelsberg and in the Westerwald, which developed during the Tertiary under humid tropical conditions from basalt or volcanic tuffs, and can be considered as remains from *Nitisols*.

7.5.7 Podzols (PZ)

References: Blume and Schwertmann (1969), Petersen (1976), Wiechmann (2000).

Podzols are soils that generally have an acid bleached E above a B horizon that has accumulated humus and/or sesquioxides. They are mainly found in cool-humid climates, but also developed from pure sands on tropical coastal sand dunes and are even found in the coastal regions of semiarid, continental Antarctica under lichens on sand where there is no cryoturbation (Blume and Bölter 1993).

Profile. Typical *Podzols* (Figs. 7.16 and 7.22) have the horizon sequence O/Ah/E/Bh/Bs/C, which developed through podzolization, i.e. due to the translocation of Fe and Al with organic matter in the profile (Sect. 7.2.4.2). Under a usually thick humus layer, the bleached E horizon is ash-grey in color and hardly contains any organic matter, but can have a light violet hue, directly or below a thin blackish-grey Ah horizon. Under this eluvial horizon, there is an abrupt transition to the dark **illuvial horizon**, which, depending on the degree of consolidation, is called **hardpan** or **fragipan** and is often brownish-black in the upper humus-rich part (Bh), and rust-brown below (Bs). The transition to the C horizon is diffuse and can occur through a Bw horizon. The **eluvial horizons** have a thickness of 20–60 cm (on slopes of low mountain ranges up to 150 cm). Together, Bh and Bs generally only have a thickness of 10–20 cm, but can bulge down by several dm in depth in the form of hardpan cones or pots. These hardpan cones were formed in zones of preferential water seepage (e.g. in areas surrounding old root channels). The B horizon often has striking panther mottling.

Name. *Podzol* means "***ash soil***" in Russian after Dokućaev (1899), referring to the light grey E horizon. However, Dokuchaev also included today's *Albeluvisols, Planosols* and many *Stagnosols* with the *Podzols* (Glinka 1914). They were also called *Podsols* in Germany; in the US system, they formed the order of the *Spodosols*.

Development. In *Podzols*, weathering and translocation processes reached their maximum extent under the influence of a cold- to temperate-humid climate. *Podzols* develop preferentially from sandy, quartz-rich rocks, with high precipitation and/or low mean annual temperatures under plant species such as coniferous trees, heathland etc. with low nutrient demands and nutrient-poor vegetation residues. Under these conditions, the living conditions of soil fauna and microorganisms deteriorate during the course of acidification and nutrient depletion such that the litter is only slowly and incompletely decomposed, and at the same time, more organic ligands are found in the soil solution, which liberate and translocate Fe and Al (Fig. 7.22). On humid sites, e.g. at the edges of moors, *Erica* heathland vegetation leads to the formation of soft humus pans, while on arid sites with *Calluna* heathland, the Bh and Bs horizon more often develop solid hardpans. They generally develop as **secondary *Podzols*** from *Umbrisols* or *Luvisols*, and under extreme conditions, also directly from *Regosols* or *Leptosols*.

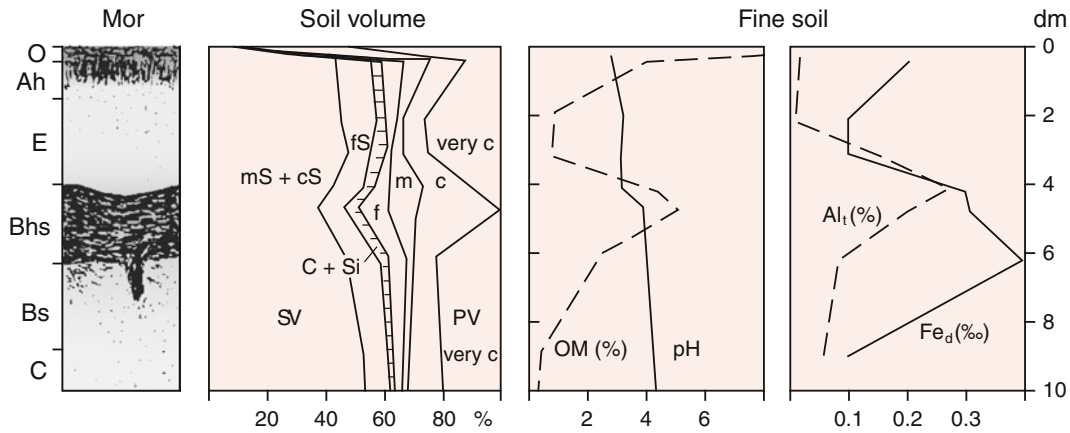

Fig. 7.22 Properties of a *Podzol* developed from sand under pine; Lower Saxony. Draft by H.-P. Blume according to analyses from K.-H. Hartge (Abbreviations see Appendix)

In large areas of Northwest Germany, podzolization was promoted by the harvesting of sod (see Sect. 7.5.22.3), but also by deforestation of the original oak-birch forest as well as its replacement by conifers or heathland vegetation. The development of *Podzols* was often triggered by humans, but in other cases, its development goes back to the Early Holocene. *Podzols* also developed in Central Europe during the Eem interglacial period.

Distribution and development forms. *Podzols* are found wide-spread in cold- to temperate-humid climatic zones (Scandinavia, Northern Russia, Canada). In subpolar, polar and alpine areas, they are found as ***Nanopodzols*** with a thin E horizon (sometimes only a few mm to cm) even on Ca- and Mg-rich rocks (e.g. mica schist mudflows). In the humid tropics, in contrast, they are found as *Bh-Podzols*, sometimes with a more than 2 m-thick bleached E horizon on pure quartz-rich sands.

In Germany, *Podzols* on sandy sediments of the Northwest German Lowlands occur as ***Bhs-Podzols*** and ***Bh-Podzols***. ***Bhs-Podzols*** with particularly thick B horizons are found on deep, arid sands under *Calluna* heath vegetation. Here, the B horizon often leads over to the C horizon with several blackish-brown iron-humus bands. When the groundwater level is high under *Erica* heathland, *Gleyic Podzols* are found that are usually strongly depleted of iron. On mountains, *Podzols* mainly developed from granite and sandstone mudflows. They are preferentially found on slopes where the mudflows are consolidated in the subsoil (e.g. as a *fragipan*) or have slightly higher clay contents due to clay migration and/or stratification. Because of the strong influence of slope water, upper slope *Podzols* often have thick bleached horizons, and lower slope soils, in contrast, have thick accumulation horizons. Podzolization is often more pronounced on south-facing slopes, while on north-facing slopes, the E horizons are wet for longer periods and are darkly colored by infiltrated humic substances. On perhumid high-altitude sites above 800 m in the Black Forest of Germany, *Podzols* are widespread on sandstone mudflows, and have a wavy hard crust with a thickness of l–5 mm at a depth of 30–120 cm, and are therefore called *Placic Podzols*, USA: *Placorthod*, *Placohumod*). These crusts retain water to a large extent, cannot be penetrated by roots, can sometimes be followed continuously over km, and not only appear in soils with *Podzol* morphology, but also in those with *Umbrisol* and *Stagnosol* morphology. They are also found in the Vosges, the Alps, in Scotland and Wales as well as in other perhumid climates (e.g. subarctic, tropics). Softer bands at the upper edge of the B horizon are also observed in lowland *Podzols*.

Properties. The development from predominantly sandy substrates leads to sandy soil textures and generally high quartz contents. Weathering causes an additional accumulation of resistant minerals such as quartz, tourmaline, rutile and zircon. Humus layers with wide C/N ratios (often 30–40) and strong acidification are other distinguishing features and correlate with low nutrient contents (Fig. 7.22). The nutrients involved in podzolization (Fe, Mn, Cu, Co, Zn, indirectly also P) also sometimes slightly accumulate in the subsoil. In cultivated *Podzols,* the humus layer is decomposed, and the nutrient contents and pH are elevated. *Podzols* have a **single grain structure** in the A and E horizon; the B horizon is often cemented with a **massive** structure (then *Ortsteinic PZ*).

Podzols are generally well aerated, but dry. The **pore volume** in the B horizon is often greater than in the E horizon (Fig. 7.22). This is attributed to the fact that there is subsidence in the E horizon because of the removal of finer particles. In the B horizon, the decrease in the total pore volume that would theoretically be expected due to the deposition of these fine particles, is compensated by the formation of new coarse pores from rooting and soil fauna activities and/or through crystallization pressure of oxides at the contact points of the sand grains. If this activity is also suppressed with the hardening of the B horizon into a hardpan, the hardpan horizon can still exhibit a high coarse pore fraction. The hardpan therefore only seldom acts as a retaining body, and even often exhibits higher hydraulic conductivity than the E horizon.

Land use. Strongly developed *Podzols*, which were formerly considered not to be suitable for cultivation, are capable of high yields with artificial irrigation and high fertilization, and are then even capable of productive root crop cultivation. The pH should only be raised up to pH 5.0–5.8, because Mn deficiency occurs at higher pH values. The wide-spread Cu deficiency can be eliminated by adding fertilizers containing Cu, and the Boron deficiency by B fertilization. Hardpan horizons are more detrimental to plant growth the closer they are located near the surface.

7.5.8 Stagnosols (ST) and Planosols (PL)

Stagnosols and *Planosols* are soils with *Stagnic* properties.

7.5.8.1 Stagnosols

References: Blume (1968), Blume and Schwertmann (1969) and Fanning and Fanning (1989).

Profile. *Stagnosols* are soils with deep groundwater tables, where an alternation of stagnant water and desiccation led to the formation of concretions and mottles mainly inside the aggregates, while the aggregate surfaces were bleached (=mottling; Fig. 7.16).

Secondary *Stagnosols*, which often developed from *Luvisols*, exhibit the horizon sequence Ah/Egc/Btg (Fig. 7.23). Under the Ah horizon, there is usually a pale grey, relatively clay-poor Egc horizon containing concretions or weak mottling, often with a platy structure. The concretions are usually blackish-brown and 0.5–50 mm in size, and penetrate into the soil matrix itself. In contrast, the more clay-rich Btg horizons have pale grey/rust brown mottles (often striped) and often have a pronounced polyhedral to prismatic structure.

Primary *Stagnosols*, which developed directly from mostly clay-rich rocks with low hydraulic conductivity, are either stratified (e.g. eolian sand or loess loam over clay) and then clearly divided into Egc and 2Bg, or unstratified and then hardly differentiated into a stagnant area and retaining body. In clay-rich horizons, concretions are less common than mottles. The mottling zone is generally smaller; the orange colors of lepidocrocite dominate in the mottles (Sect. 2.2.5).

Name. The name was derived from the Latin *stagnare* (to flood). In Germany, according to Kubiena (1953), they are called *Pseudogleys*, which also include the *Planosols* and *Stagnic Albeluvisols*. Fanning and Fanning (1989) called them *surface water gleys*. In the US system, they belong to the aquatic subgroups, because no distinction is made between soils affected by stagnant water or by groundwater.

Development. *Stagnosols* develop through **redoximorphosis** under the influence of a

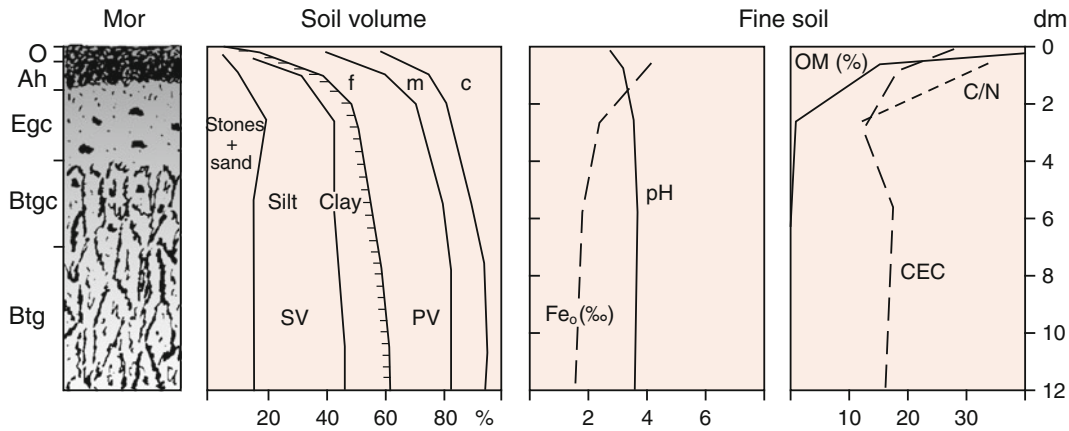

Fig. 7.23 Properties of a *Luvic Stagnosol* developed from calcareous glacial till under spruce; South Germany; draft and analyses by H.-P. Blume (Abbreviations see Appendix)

periodic alternation of waterlogging and desiccation. Temporary stagnant water occurs near the soil surface and usually disappears during the vegetation period. It is caused by dense subsoil layers, which, especially in humid climates and on level sites, retain the rainwater and therefore cause oxygen deficiency, leading to the dissolution and redistribution of iron and manganese within the horizons. In the **stagnant area** (Ec), this mainly leads to the formation of concretions, while the **retaining body** (Bg) is mottled and the aggregate surfaces are bleached, whereas iron accumulates inside the aggregates. The iron is not only present in the form of goethite, but also sometimes **lepidocrocite**. In contrast, silicates are less strongly weathered than in neighboring permeable soils. *Albic Stagnosols* do not contain concretions in the wet bleached E horizon. Transitional forms to other soil textures, where the stagnant water characteristics are only weakly developed or not in all of the horizons, are more common than fully developed *Stagnosols*, because the relatively short wet phases are accompanied by longer dry phases. These include e.g. *Luvic ST*, *Vertic ST*, *Mollic ST* or *Stagnic Phaeozems*, which are strongly mottled in the subsoil. *ST* with uniform mottling in the topsoil and subsoil often develop from sand loess or coarse silt-rich loess in oceanic climates. They largely lack dry phases as well as an abrupt alternation between wet and moist phases. They also have few coarse pores in the topsoil. In Germany, they are called *Haftpseudogleys*.

Properties. *Stagnosols* are temporarily air deficient soils. Their topsoils often dry out more than neighboring permeable soils, because they have a higher root density in the topsoil than in the subsoil. The duration of the wet, moist and dry phases or O_2-poor and O_2-rich phases depends both on the climate and on the hydraulic conductivity of the retaining body, on the thickness of the stagnant area, and on the relief. On level sites, the moist phase often dominates, while the wet phase lasts longest in shallow depressions and the dry phase on slopes.

The hydraulic conductivity of the Bg is generally very low (e.g. <10 cm d^{-1}) and that of the stagnant area higher. Secondary *Stagnosols* are often formations from older land surfaces and are then strongly depleted of nutrients. In contrast, many primary *Stagnosols* are nutrient-rich. In any case, however, redoximorphosis concentrates Fe and Mn, frequently also P, Mo, Cu and Co in concretions and mottles that are poorly available for plant roots. On the other hand, low redox potentials increase the availability of these nutrients.

Distribution. *Luvic Stagnosols* are widespread (common but on small areas) soils of humid climates, and are found both in the cold- and temperate-humid climate regions and in alternate

wetting and drying tropics and subtropics. In Germany, they are found in loess and calcareous glacial till landscapes with more than 700 mm annual precipitation, whereby they are more commonly found on level locations, beside *Haplic Luvisols* on slopes and *Gleysols* in depressions. In drier areas, they only developed on or over older Pleistocene sediments and more strongly silted and compacted sediments, and also on clay. In the low mountain ranges, they are only found in the lower locations, and are represented by *Planosols* in higher, moister positions.

Land use. *Stagnosols* are often good pasture and also forest sites. Because of the long-lasting spring wetness, arable land use is often difficult. Because of the strong binding of water in the soil, pipe or ditch drainage often does not help and is principally also not desirable, because the drained water is then lacking in summer dry periods. Deep loosening is recommended, because this creates air-conducting coarse pores and does not reduce the water reserves. However, it is difficult to maintain the loose packing. The land improvement should therefore be supplemented by the cultivation of deep-rooting crops to minimize the reoccurrence of compaction. Ploughless cultivation is also promising.

7.5.8.2 Planosols

References: Drießen et al. (2001).

Profile. *Planosols* (Fig. 7.16) are soils that are strongly waterlogged with a wet-bleached topsoil and an abrupt transition (Table 7.5) to a significantly more clay-rich subsoil with low hydraulic conductivity. The bleached horizon is depleted of Fe and Mn oxides or they are bound as concretions. The name was derived from the Latin *planus* (=level), because *Planosols* are usually found on intermittently strongly wetted plains. The more clayey subsoil can be due to primary rock stratification or rarely of clay migration. *Ferrolysis* is also suspected of destroying the clay in the topsoil (Brinkman 1979).

Name. The name *Planosol* was derived from the Latin *planus* = flat. In Germany, such soils are called *Stagnogleys*. In the US system, they are sometimes grouped with the *Aqualfs*.

Development and properties. *Planosols* preferably develop under cool humid climate conditions on *Sandkerf*, i.e. sand-rich material above a dense, clay-rich subsoil. Under these conditions, persistent, often year-round waterlogging and low soil temperatures inhibit the microbial decomposition of organic chelating agents and reductors in the soil solution, so that Fe, Mn and heavy metals are dissolved and can be transported laterally in the sandy topsoil over greater distances. The topsoil is therefore wet bleached. There is practically no translocation of the dissolved substances into the subsoil, because it is almost always saturated with stagnant water. The released iron sometimes accumulates below the *Planosols* in areas with stronger slopes (Sect. 7.2.7.3). The difference in texture between the A and B horizon is of lithogenic origin and can be amplified by clay migration. Dudal assumes clay destruction in the topsoil to be the cause of this in *Planosols*. Clay destruction could also play a role in German *PL* (in contrast to *Stagnosols*), because persistent waterlogging may prevent the stabilization of swelling clay minerals through incorporation of Al^{3+} ions. With year-round water saturation close to the soil surface, *Haplic Planosols* turn into *Histic Planosols* and finally into *Histosols*, where the humus layers are thicker and the subsoil is hardly mottled, rather is also bleached.

Some *Planosols* developed from strongly leached *Solonetzes* and are also called *Solod* or *Steppenbleicherde* (steppe bleached earth). Their B horizon then corresponds to that of the *Solonetz*, and is therefore characterized by high Na saturation (e.g. >6 %, hyposodic), a dense columnar structure, often dark color (due to lessivated humus), but significantly higher clay content differences with the topsoil. Such *Planosols* generally developed from *Solonetzes* when the climate became more humid, and are acidified at least in the topsoil. They are often found in shallow depressions, and due to the higher water supply than in the surrounding steppe, they sometimes support the growth of smaller trees and shrubs.

Planosols are moderately deep, air deficient, often strongly acidified sites with nutrient deficiencies in the topsoil.

Distribution and land use. *Planosols* are commonly found on high-altitude plateaus of central European low mountain ranges, on shallow upper slopes or valley heads with springs, as well as in small waterlogged hollows. They are then associated with *Umbrisols* that hardly have any waterlogging. Soils below the *Planosols* often have accumulations of laterally transported iron as "*Oxigleyic*" *Gleysols on slopes* (association see Fig. 8.4: zone 7). In the alternate wetting and drying tropics and subtropics, they are mostly found on small areas.

They are not suitable for agricultural use, and trees also generally only exhibit limited growth.

7.5.9 "Reductosols" and Reductic Technosols (TC)

References: Blume and Felix-Henningsen (2008/2009) and Schulze-Makuch (2010).

The soil classification in this chapter follows the German classification (Wittmann et al. 1997), because 'dry' redoximorphic natural soils cannot be properly classified yet according to the IUSS/ISRIC/FAO (2006/7), only men made ones as *Reductic Technosols*.

Profile. *Reductosols* are soils characterized by gases with a reducing effect or causing oxygen deficiency, such as methane (CH_4), hydrogen sulfide (H_2S) and/or carbon dioxide (CO_2). These gases come from (post)volcanic mofettas or the leakage of gas pipelines, but are also formed in *Reductic Technosols* by microorganisms from readily decomposable organic matter under strongly reducing conditions in urban waste, sewage sludge or harbor sludge deposits as well as in soils where wastewater or petroleum products have penetrated. Soils where reductive gases (or bog gases) are produced by microorganisms due to oxygen deficiency under saturated conditions are not classified as *Reductosols* but rather as "*Reductic*" subunits of *Fluvisols, Gleysols* or *Histosols*.

Many *Reductosols* are divided into Ah/Bo/Br and are often similar to *Gleysols* in their morphology. The Bo horizon is colored reddish-brown by Fe oxides preferentially on the aggregate surfaces, and then only intermittently exhibits elevated CH_4 and/or CO_2 contents and low rH values. The Br horizon exhibits reduction colors. Its air is anoxic, but rich in CH_4 and/or CO_2; its rH value lies below 19.

Name. The name comes from the characteristic reduction colors in these soils. Until now, *Reductosols* only represent an individual unit in the German soil classification. In the WRB and US system, *Reductosols* are not explicitly specified, but rather classified as groundwater-affected soils or *Stagnosols*, and those from anthropogenic substrates such as urban waste or sewage sludge are classified by the WRB system as *Reductic Technosols*.

Development and properties. *Reductosols* in (post)volcanic regions often develop through carbon dioxide (often together with CH_4, NH_3 and/or H_2S) escaping from the interior of the Earth through rock fissures, displacing the soil air and therefore also the atmospheric oxygen. Microbial decomposition takes place anaerobically under such conditions, so that Fe/Mn oxides are reduced and give a bluish-green color to the reduced horizon, e.g. in the form of Fe(II)/Fe(III) mixed oxides, and/or Fe^{2+} ions rise with capillary water during dry periods. In the Bo horizon, in contrast, they are oxidized by atmospheric oxygen and precipitated as ferrihydrite. Because the intensity of escaping gases can fluctuate strongly in the meter range, continuous Fe-depleted *Albic Reductosols*, *Ochric Reductosols* with strong Fe accumulations, as well as *Haplic Reductosols* with a thin Bo horizon often develop beside each other. If sulfates are also reduced in the Br horizon in addition to metal oxides, black metal sulfides are formed.

Reductosols are sites with oxygen deficiency. Their parent materials are often strongly acidified: Those over (post)volcanic mofettas under the influence of high CO_2 concentrations, those under gas plants, where there were inputs of iron sulfides from gas treatment, which led to the oxidative formation of sulfuric acid in the soil. In comparison, *Reductosols* from urban waste, sewage sludge or harbor sludge deposits are alkaline and nutrient-rich.

7.5.9.1 Haplic Reductosols

The first natural *Reductosols* from post-volcanic mofettas were described by Alexander von Humboldt in 1789 in the German Eifel and later also in Baku/Azerbaijan. They occur in punctual areas mainly in regions with strong volcanic activity such as Iceland, Japan or Mexico. In the Eifel/Germany, *Reductosols* from post-volcanic mofettas sometimes form narrow stripes with strong CO_2 liberation on ridges, and were therefore called CO_2 *Gleysols* on old soil maps. Regions with frequent earthquake activity can also promote their development when fissures form in the ground where reductive gases escape, originating from mineral oil, natural gas, coal or bituminous shale.

7.5.9.2 Asphaltic Reductosols

Asphaltic Reductosols represent a special case: They developed from pure asphalt in the upper 2–3 dm of the *Pitch Lake* on the Island of Trinidad as a result of microbial transformation into methane gas. It is said that similar forms are also found in several pitch lakes in California/USA, as well as in Lake Guanoco/Venezuela (Schulze-Makuch 2010).

7.5.9.3 Reductic Technosols

Reductic Technosols have developed since millennia on 'wild' waste deposits and later also on sanitary landfills. Due to intense microbial activity, especially in waste deposits covered with soil material under oxygen deficiency, protein-rich wastes promoted the formation of methane, which escaped upwards as a reductive gas. In the 20th Century, it was used economically in sanitary landfills as a combustion gas.

Since the 19th Century, there are also areas at the edges of many large cities that are used for **wastewater irrigation**, where the high quantities of readily decomposable organic matter led to the development of *Reductic Technosols*.

In urban waste, sewage sludge and harbor sludge, strong microbial transformation under anoxic conditions mainly leads to the formation of methane, which not only displaces atmospheric oxygen in the soil above or beside such landfills, but also consumes oxygen through microbial transformation. This predominantly leads to the formation of Br horizons that are blackened by metal sulfides and later also to reddish brown Bo horizons. The same occurs in soils developing from fills over gas pipeline leaks.

Infiltration of microbially decomposable fuels at roadsides, especially under gasoline stations, as well as oil, tar or other liquid organic substances from (former) commercial or industrial sites can also lead to the development of *Reductic TC*. After the formation of reductive gases subsides (in landfills e.g. after 40–60 years), the Br horizons disappear. Corresponding soils therefore often develop from *Proto-Reductic T.* (horizon sequence A(h)/Br) through *Reductic T.* (Ah + Bo < 4 dm) to *Ocker-Reductic T.* (Ah + Bo > 4 dm), to then finally reach the stage of *Relikt-Reductic T*.

7.5.10 Vertisols (VR)

References: Khalil (1990) and Blockhues (1993).

Vertisols (Figs. 7.20 and 7.24) are clay-rich (>30 %) soils that have deep-reaching shrinkage cracks in dry periods (>1 cm wide at a depth of 50 cm), slickensides on aggregate surfaces and/or a pronounced gilgai terrain.

Vertisols ([Latin] *vertere* = to turn) are soils with intense **peloturbation** caused by strong swelling and shrinking (Sect. 7.2.6.3). These often dark, deeply humic soils (Fig. 7.24) have many synonyms: *Grumosol* in Israel and Australia, *Smonitza* in the Balkans, *Black Cotton Soil* in India and Sudan, and *Tirs* in North Africa.

Vertisols are young or old stable formations of clay-rich sediments or clay-rich weathered Ca silicate-rich rocks (e.g. basalt). They mainly develop in poorly drained depressions or on wide plains in alternate wetting and drying warm climates with pronounced dry months. However, they are also found in temperate climates, e.g. in Southern Germany, where they are associated with *Vertic Cambisols* developed from clay rocks (see Sect. 7.5.4.4). Several German *Pelosols* also fulfill the criteria for *Vertisols*.

During the dry period, *Vertisols* have a pronounced **cracked structure** reaching depths of

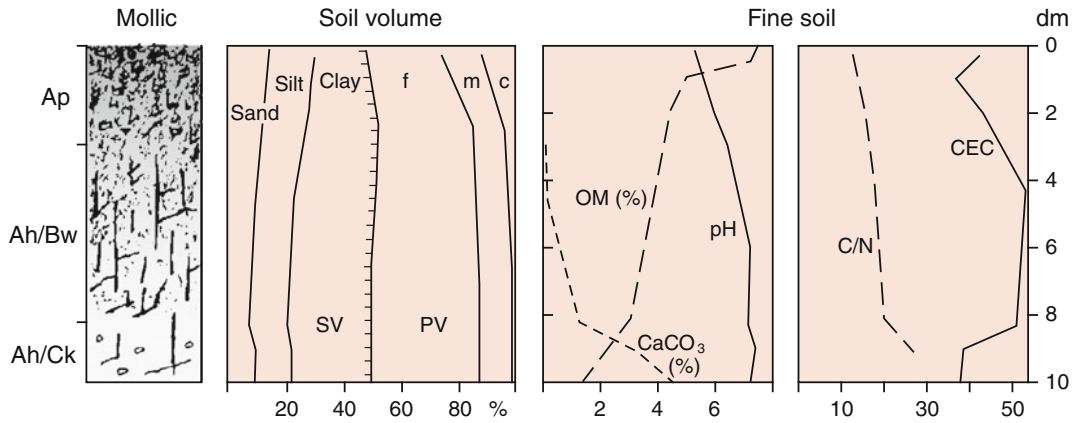

Fig. 7.24 Properties of a *Vertisol* developed from colluviuc material of basalt weathering under grassland; Darling Downs, Queensland (mineral composition of the clay fraction: 60 % smectite, 20 % kaolinite, 20 % quartz); lots of humus in the upper Ap (because of reduced peloturbation during recent years). (According to analyses from CSIRO Australia, drawn by H.-P. Blume) (Abbreviations see Appendix)

up to 1.5 m. Depending on the clay content, clay mineral type and cation occupation (especially the Na fraction), the cracks can be several cm wide. They form a network of polygons at the surface. Coarse prismatic structures dominate in the subsoil, which lead over to rhombic parallelepipeds between a depth of 30 and 100 cm, the aggregate surfaces of which exhibit shiny shear surfaces with aligned clay minerals (**slickensides**). In the upper cm, fine splinters develop through **self-mulching** (Sect. 7.2.6.3), which can be blown into the desiccation cracks along with crushed litter. With the onset of the rainy season, water seeps into the cracks, and as a result, the soil is also wetted from below and the cracks close again through swelling (Blockhuis 1993).

The dominant clay mineral is swelling smectite. The CEC is therefore very high (up to 60 $cmol_c\ kg^{-1}$, Fig. 7.24), whereby the Ca:Mg ratio is narrow. Despite the dark grey color, the humus contents are often less than 4 %; still, the great thickness (>1 m) provides high quantities of humus and N in the solum. Depending on the intensity of peloturbation—for several soils in the Sudan, a complete mixing of the solum within 300 years was reconstructed, otherwise, it is assumed to take more than 5000 years—the humus contents decrease with depth. Their very high base saturation is often not only caused by Ca-rich rocks and inhibited water movement, but also by locations in depressions that enable the input of dissolved substances (Na, K, Ca, Mg, Si, …).

Vertisols in shallow depressions, as *Pellic VR*, are often darker than *Chromic* VR on neighboring ridges. Differences in the parent materials can also cause different colors. Under humid climate conditions, *Vertisols* are often carbonate-free and acidic (*Haplic VR*), whereas under arid climate conditions, they are generally calcareous (*Calcic VR*) and sometimes also contain gypsum (*Gypsic VR*) and are salinized at greater depths. The maximum carbonate content is then in the subsoil at the boundary area of periodic wetting, and is characterized by $CaCO_3$ efflorescences on aggregate surfaces in addition to larger, soft concretions. In this case, there are only small, round and hard calcareous concretions in the topsoil, which probably travelled upwards. Arid climates can also cause higher salt contents (and therefore *Salic VR*) or at least higher Na occupancy in the topsoil, and then lead over to *Solonetzes* as *Sodic VR*.

Particularly in more humid climates, peloturbation causes a pronounced **gilgai terrain** with rounded mounds and depressions on level ground or stripes on slopes. This modifies many soil properties: Soils of depressions swell and shrink to greater depths, and because the water moves laterally, they have more humus

accumulation and salt in the subsoil than soils on summits.

Vertisols are relatively nutrient-rich sites with pronounced alternate wetting and drying. Despite this, P, S, Zn and N deficiencies can restrict plant growth with intensive land use. They are hard to till: they are very hard when they are dry, and very smeary when they are wet, so that they can only be tilled during a short period of medium water contents ("minute soils"). In the savanna, they are used for pasture or rainfed agriculture. With irrigation, they are suitable for the cultivation of cotton, sugar cane, peanut and rice.

Vertisols have a decent soil chemical state, but are catastrophic in terms of their physical properties.

7.5.11 Andosols (AN)

References: Kinloch et al. (1988) and Theng (1980).

Andosols ([Japanese] *ando* = black soil) (Fig. 7.20) usually develop from (young) volcanic ashes and exhibit *Vitric* or *Andic* properties (Sect. 7.3.2).

The topsoil is very loose (d_B < 0.9 g cm^{-3}, andic properties) dark brown to black in color, and rich in humus (up to 25 %). The clay fraction mostly consists of finely grained, spherical **allophane**, stalked **imogolite** and with advanced development, also **halloysite**, i.e. minerals originating from volcanic glasses. In the remaining particle size fractions, fresh glasses dominate in young *Andosols*, while weathering-stable silicates of non-volcanic origins usually accumulate in older soils.

A bright brown to brownish-red Bw horizon or (as a result of repeated ash sedimentation) fossil Ah horizon (Ahb) follow below the A horizon. Under alternate wetting and drying or semiarid climates, the subsoil can be hardened by silicic acid to form a **duripan** (Mexico: tepetate) or silcrete.

The very young, hardly weathered *Vitric AN* consist of >5 % volcanic glasses. The others (andic) are more strongly weathered, allophane-rich and contain >2 % Al_o + ½ Fe_o): As *Silandic AN*, they also contain at least 0.6 % Si_o, as *Aluandic AN* < 0.6 % Si_o and are then also acidic; as *Melanic AN*, they have >6 % by mass SOC. In the US system, the *Andosols* are in the order of the *Andisols*.

Due to their high water holding capacity and their stable, pore-rich structure, *Andosols* are favorable plant sites, provided that there is no hardening (see above). They are characterized by a high variable charge and have a high CEC, and in an acidic state, they have a strong P binding and fixation capacity. In humid climates, they weather rapidly, and therefore have a high nutrient supply capacity and are then often acidified (rarely below pH 5).

Their main distribution is in the Circum-Pacific zone (Japan, Philippines, Indonesia, New Zealand, Chile, Ecuador, Columbia, Mexico, East Africa), and also in Cameroon, the Azores, the Canary Isles and on Iceland; in Germany, they are found in isolated areas of the Eifel (Laacher See volcanism).

7.5.12 Ferralsols (FR) and Plinthosols (PT)

7.5.12.1 Ferralsols

Ferralsols are intensively and deeply weathered soils of the humid tropics. They have a *Ferralic* Bo horizon, i.e. with accumulated Fe and Al oxides (Sect. 7.3.1), often bright red, brown or yellow in color (Fig. 7.20), and no longer contains weatherable silicates (<10 % in the 50–200 μm Ø fraction). The clay fraction has a CEC < 16 $cmol_c$ kg^{-1}, and in addition to the oxides, it practically only consists of kaolinite (Fig. 7.25). Synonyms are *Latosol* or *Oxisol* (Soil Taxonomy) or *sols ferralitique* (French).

As typical forest soils of the humid tropics, *Ferralsols* develop from various silicate rocks, but also from carbonate rocks. High temperatures and strong moisture penetration over long periods of undisturbed development have intensely weathered the silicates, leached the alkaline and alkaline earth metal ions as well as silicic acid (**desilification**), leaving Fe and Al oxides and newly formed kaolinite behind (Sect. 7.2.1.3).

Ferralsols are old land surfaces that have developed over very long periods of time (millions of years). *Umbric FR* have higher humus contents; *Geric* and *Vertic FR* have an extremely low CEC_{eff} (<1.5 or <6 $cmol_c\ kg^{-1}$ of clay) with a relatively high (>5.5) pH; *Acric FR* have less clay in the topsoil; *Rhodic* or *Xanthic FR* have a deeply red- or yellow-colored B horizon. In *Gibbsic FR*, gibbsite (>25 % gibbsite in the fine earth) and other Al oxides dominate instead of kaolinite. This can be attributed to the particularly strong weathering and/or Si leaching in (former) morphological ridge positions.

The red color of many *Ferralsols* comes from the finely distributed hematite and maghemite. In addition, goethite is often found as an Fe oxide. High Fe and/or Al contents cause a stable, earthy aggregate structure (=pseudo-sand), resulting in high hydraulic conductivity and favorable air conditions. Even with higher clay contents, the binding of plant-available water is sometimes only moderate (Fig. 7.25). However, this is more than offset by their great depth. *Ferralsols* often exhibit quartz-rich stone layers in the lower homogenous solum: This is attributed to persistent intense burrowing activity of termites, which transport fine material up to the soil surface (Sect. 7.5.23.3).

In the tropics, *Ferralsols* cover 20 % of the land surface, particularly on the old continental shield of South America and Central Africa. On young land surfaces, they are generally only found on base-rich rocks (e.g. Southeast Asia, Indonesia, Hawaii and several Pacific islands).

Remains from fossil *Ferralsols* in Germany are a product of Tertiary soil development in the Rhenish Slate Mountains, in the Westerwald, Taunus, Palatinate Forest and on basalt in several parts of Mount Vogelsberg, and are called ***Ferrallites***.

Ferralsols are soils with predominantly variable charge. Their AEC is often higher than the CEC_{eff} and then their pH value (KCl) is higher than the pH (H_2O). Their cation binding can therefore be significantly increased by raising the pH, which is important for the Ca, Mg and K supply to plants. Because the *Ferralsols* are usually acidic, raising the pH through liming is also favorable because it immobilizes toxic Al. There is often strong K and Mg and also S deficiency, as well as strong P fixation at very low P contents.

Many *Ferralsols* in South America, Central Africa and Southeast Asia are cultivated with maize, cassava, coffee, cocoa, banana, oil palm etc. However, the crop yields already drop dramatically after a few years, because the humus-bound nutrients are rapidly consumed or leached out after (slash and burn) deforestation and intense humus decomposition, which is attributed to the low nutrient binding capacity of the soil minerals. When agriculture is abandoned, fallow enables regeneration of the nutrient contents in the topsoil, so that crops can be planted again after 8–20 years. The conditions are more favorable for permanent crops; still, here also, higher yields can only be achieved with

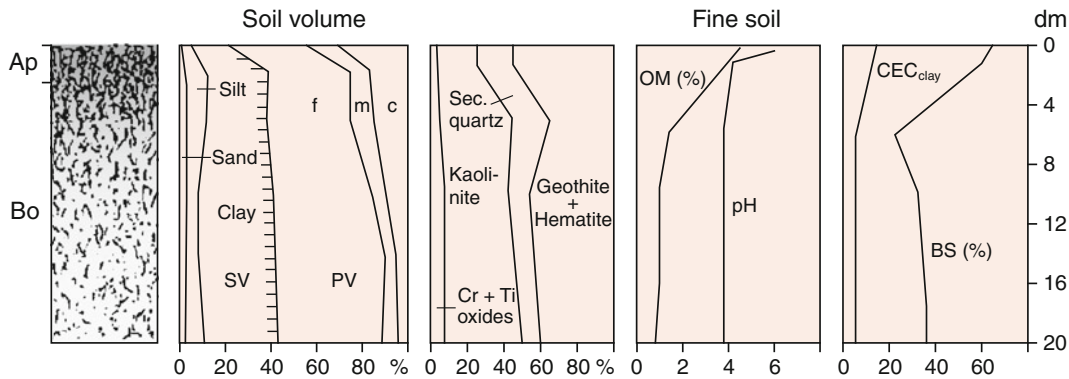

Fig. 7.25 Properties of an *Acric Ferralsol* developed from dunite and nepheline syenite under banana; SW Brazil. (According to analyses by U. Pfisterer and M. Kanig, drawn by H.-P. Blume) (Abbreviations see Appendix)

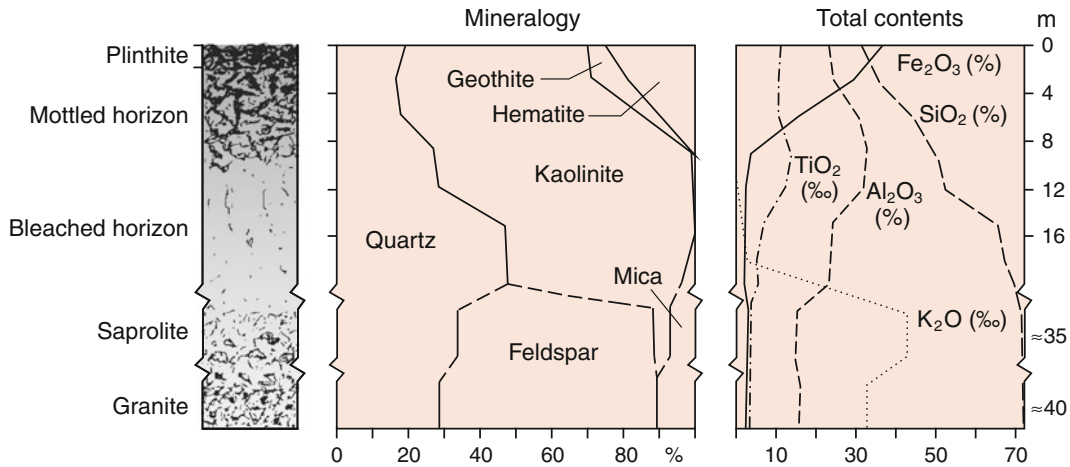

Fig. 7.26 Properties of a Petric Plinthosol, developed from granite as *Inselberg* (due to erosion: see Fig. 7.35), NO Bangalore, India (according to data from H.-P. Blume and H.P. Roeper) (Abbreviations see Appendix)

fertilizers, although their efficacy is reduced by P fixation and K leaching. Because of the favorable bioclimatic conditions, *Ferralsols* developed from ultrabasites can be very productive and allow for high banana yields e.g. in Brazil (Kanig et al. 1989; Pfisterer 1991).

Many *Plinthic FR* are irreversibly hardened after erosion and can therefore no longer be used for agriculture.

7.5.12.2 Plinthosols

Plinthosols (*PT*) are characterized by a plinthic horizon (Table 7.4; [Greek] *plinthos* = bricks). It is found either in the form of an Fe oxide-rich solid bank or crust (=petroplinthic) and/or as a red/white mottled horizon, which is irreversibly hardened with strong desiccation. The latter can be covered by a wet bleached horizon. In this case, a *Plinthosol* has the morph of a *Planosol* and can be a present *Stagnosol*.

Plinthosols are strongly weathered soils found on old land surfaces of the humid and alternate wetting and drying tropics: The white areas of a plinthite or mottled horizon mainly consist of Al oxides and/or kaolinite, and the red areas of Fe oxides (Fig. 7.26). As a result of strong hardening, they are protected from erosion and occupy high terrain positions today.

The poor rootability of *Plinthosols* strongly impedes agricultural use. When the topsoils are eroded, *Plinthosols* are barren land. Humid *Plinthosols* in depressions can be used for pasture.

7.5.13 Calcisols (CL) and Gypsisols (GY)

References: Nettleton (1991) and Petermann (1987).

Calcisols and *Gypsisols* are soils with accumulations of carbonate or gypsum in arid climates, i.e. in semideserts or deserts.

Calcisols (Fig. 7.20) have an at least 15-cm thick horizon with more than 15 % carbonate (and 5 % more than the parent material). The carbonate ($CaCO_3$) is a secondary accumulation and is found as pseudomycelia or in the form of skins on aggregate surfaces, penetrating the soil matrix as soft to hard concretions or forms soft to hard carbonate beds (**calcrete**). The former are called ***Calcic***, and the latter ***Petrocalcic*** horizon. *Calcisols* can develop from calcareous or carbonate-free rocks. The secondary carbonates can come from the weathering of calcareous silicates, from the groundwater, and/or be added with precipitation under arid climate conditions.

Calcisols are typical for semideserts and Mediterranean regions. In deserts, *Gleyic CL* are only found as groundwater formations and there is no decalcification, but rather only carbonate translocation. The *Calcic Gleysols* of humid climates (Sect. 7.5.18) are strongly redoximorphic in the upper 5 dm. The humus contents in the topsoil are low, the soil pH is alkaline, and there is often little gypsum and/or water-soluble salts.

Gypsisols (Fig. 7.20) have a horizon with a thickness of at least 15 cm with >5 % gypsum ($CaSO_4 \cdot 2H_2O$), which, similar to the carbonates in *Calcisols*, can occur in the form of efflorescences on aggregate surfaces or also as harder beds. *Gypsisols* exhibit neutral reaction, are low in humus and often salinized. Transitional forms of *Calcisols* and *Gypsisols* are also often observed: with groundwater formations, the gypsum accumulation is then above the carbonate accumulation, and the opposite is true with surface water formations (see Sect. 7.2.4.5). *Gypsisols* that were not formed by groundwater are only found in semideserts and deserts. In the US system, the *Calcisols* are called *Calcids* and *Gypsisols* are called *Gypsids*.

Many *Calcisols* are used for extensive pasture. Rainfed agriculture with barley, (wheat) and sunflower is also possible; however, higher yields are only achieved with irrigation. In the latter case, due to the low tendency towards surface crusting, furrow irrigation is preferred to flood irrigation. *Gypsisols* can be used for pasture as well as rainfed agriculture, provided that the gypsum content in the topsoil is below 25 % and there is enough precipitation. In contrast, high yields, for example with alfalfa, maize, wheat or also fruit, can be achieved with irrigation—even with high gypsum contents. Hard gypsum or carbonates beds reduce yields or even impede land use because they inhibit root growth.

7.5.14 Durisols (DU)

References: Nettleton (1991).

Durisols (Fig. 7.20) are soils that are hardened by silicic acid. It creates a continuous hardened bed (=duripan) often with a thickness of 0.3–4 m (WRB > 10 cm), or areas of the soil matrix that are hardened by SiO_2 (durinods). Their name was derived from [Latin] *durus* = hard. Dissolved silicic acid from mineral weathering initially forms hydrous, amorphous opal, which is later transformed into microcrystalline cristobalite (Sect. 7.2.4.4).

Durisols mainly developed in semiarid and humid regions from volcanic tuffs. *Petric DU* are characterized by a compact bed. *Calcic* or *Gypsic DU* also exhibit carbonate or gypsum accumulations, which often coincide with a duripan. *Leptic DU* develop from hard rocks, *Arenic DU* from sands; *Yermic* and *Aridic DU* are found in deserts, while *Luvic DU* develop under alternate wetting and drying climate conditions. They are acidified under humid climates, but they otherwise react neutral to alkaline.

In the USA, *Durisols* are mainly classified as *Durids*, and on the FAO World Soil Map, they are called 'duripan phases' mainly of *Xerosols*, *Yermosols*, *Planosols* and *Luvisols*.

Durisols are found extensively in South and Southwest Africa, in West and South Australia, in the South and West of the USA, as well as in parts of the Central Sahara Desert. Because they have only recently been adopted as an individual unit in the WRB system, their distribution pattern and also their genesis still require research.

Agricultural use is generally very difficult because of the poor rootability (if it is not already strongly limited by drought), so that extensive grazing dominates. For irrigated agriculture, hardened areas were sometimes broken mechanically. The broken beds are then used for road construction.

7.5.15 Solonchaks (SC)

References: Sumner (2000): G-3 Salinity and Singer (2007).

Profile. *Solonchakes* are saline soils. They are characterized by a horizon that is at least 15 cm thick with an electr. conductivity of the saturation extract > 15 mS cm^{-1} [EC > 8 mS cm^{-1} suffice at pH (H_2O) > 8.5]. (=*Salic* horizon: see Sect. 7.3.1).

Name and properties. *Solonchaks* (SC; from [Russian] *sol* = salt) are also called *Solonchaks* according to the WRB and in Austria; in the USA, they are grouped with the *Aridisols*, especially the *Salorthids*. The salts can come from the atmosphere (as dust or dissolved in the rainwater), from the ocean or from a saline rock. They were redistributed in the landscape and often accumulate in depressions through groundwater or slope water. According to the cause of salinization, a distinction is made between rain water, groundwater and *anthropogenic Solonchaks* (Sect. 7.2.4.5). In Germany, only groundwater and *anthropogenic Solonchaks* are found. They have not yet been classified in the German Soil Taxonomy.

As desert soils, **rain water *Solonchaks*** are extremely dry almost all year round and have salt accumulation especially at depths of 2–5 dm. They are relatively more clay-rich and therefore less permeable than neighboring *Arenosols* or *Regosols* with *Yermic* properties.

As a matter of principle, **groundwater *Solonchaks*** are associated with high groundwater levels and therefore with depressions; they are wet at least in the subsoil. In deserts, however, they may be dry relicts of formerly high groundwater levels. Here, they also developed in recent years under old tamarisks, the roots of which cause a lowering of the (saline) groundwater by 5–15 m (during the last 5000 years) and excrete salts with their leaves. Especially readily soluble salts are concentrated in the topsoil and sometimes form a salt crust at the surface. ***Anthropogenic Solonchaks*** have a similar morphology, which is caused by artificial irrigation. *Kulto-Solonchaks* are found in Germany as tailings piles from the potassium industry. Furthermore, they can also be found at the edges of urban roads where large amounts of road salt is spread in the winter, so that under semiarid to humid conditions, as they occur e.g. in Berlin, the salts are not fully leached out in the summer (Fig. 7.4).

Gleyic and *Stagnic SC* exhibit redoximorphic characteristics in the upper 100 cm, *Calcic SC* are calcareous, and *Gypsic SC* contain gypsum. *Mollic SC* are characterized by the mull humus form, and *Histic Solonchaks* by a thin peat cover. *Takyric SC* have a takyric structure, *Aridic* and *Yermic SC* are extremely humus-poor and arid, while *Sodic SC* have a strong Na occupation, and are therefore similar to *Solonetzes*. In the US Soil Taxonomy, only saline soils among the *Aridisols* form their own group as *Salorthids*, which are wet in the upper 100 cm (for at least one month), i.e. the groundwater *Solonchaks*.

Due to their high salt contents, *Solonchaks* are generally well aggregated. Their pH is determined by the type of salts: Soda-rich *Solonchaks* are strongly alkaline [pH (H_2O) often >9], chloride-rich are weakly alkaline, while gypsum-rich are neutral (often <7) and therefore have a higher ecological value. The vegetation

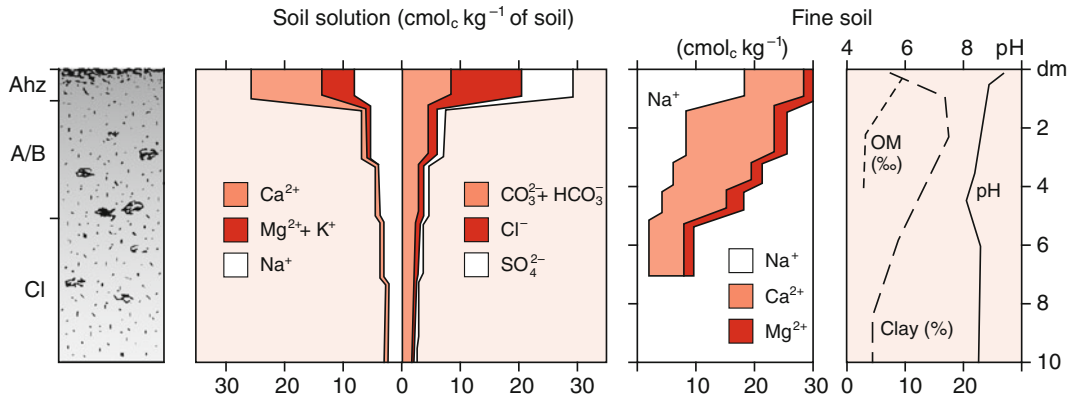

Fig. 7.27 Properties of a *Gleyic Solonchak* developed from river fluvial sand under grassland; Apaj, Hungary; draft by H.-P. Blume according to analyses by Szabolcs and staff (Abbreviations see Appendix)

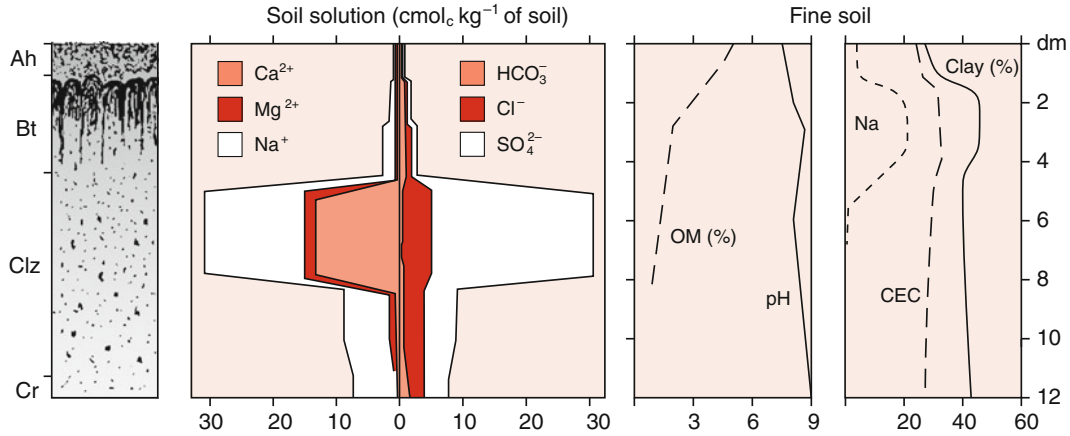

Fig. 7.28 Properties of a *Glossalbi-Gleyic Solonetz* developed from fluvial loam under grassland; Parepa, Rumania; draft by H.-P. Blume according to analyses by M. Nicolsu and V. Josof (Abbreviations see Appendix)

consists of halophile species (e.g. *Suáeda maritima, Lepidium cartilagineum)* and is often hardly developed, which results in low humus contents in the A horizon. Figure 7.27 shows a typical groundwater *Solonchak*.

Distribution. *Solonchaks* are mainly found in semiarid and arid climates (Sects. 8.4.3 and 8.4.4). Because of the climate, in Europe they are restricted to small areas in the southern Ukraine, the Balkans and Spain. In Germany, they are only found where saline springs occur due to salt tectonics, especially in the lowlands of Northern Germany. Small areas of *Histic SC* were described in north-west Germany, *Gleyic SC* in the region of Magdeburg.

Land use. Land use is only possible after the salts have been leached out. This is very difficult to achieve at higher clay contents, and especially in soils with low $CaCO_3$ and $CaSO_4$ contents, it can easily lead to stronger alkalinization and unstable soil structures.

7.5.16 Solonetz (SN)

Reference: Levy (2000).

Profile and name. According to the WRB, *Solonetzes* (*SN*; Russian common name) (Fig. 7.20) are soils of arid climates with a Bt(n) horizon. It is characterized by high Na saturation [>15 % or (Na + Mg) > Ca saturation], a columnar structure, relatively high clay contents (Fig. 7.28), and often also dark color. They are also called alkali soils or **black alkali soils**. In the US Soil Taxonomy, they belong to various orders and are labeled with the syllable *Natr*(*i*).

Development and properties. *Solonetzes* usually develop from *Solonchaks* through desalination caused by groundwater lowering (then as *Gleyic SN* with mottles), a more humid climate (usually the normal *Haplic* SN) or through the effect of groundwater containing Na on steppe soils (then as *Mollic SN* with a mull A). The high Na saturation leads to high pH values between 8.5 and 11 and promotes the downwards translocation of clay and humus (and at the same time, upward movement of silt due to the alternation of swelling and shrinking). This causes the formation of the typical **columnar structure** with the rounded caps.

Salic SN contain salts in higher concentrations, however, they are limited to the subsoil (below the Bt) (Fig. 7.28). *Gypsic SN* or *Calcic SN* exhibit (in the upper 100 cm) strong gypsum or carbonate accumulations, while *Albic SN* are strongly bleached in the topsoil due to clay depletion; *Gleyic* and *Stagnic SN* are at least intermittently wet in the upper meter and have redoximorphic changes. In contrast, *Yermic* and *Aridic SN* are dry and very low in humus.

In a moist state, *Solonetzes* are strongly dispersed, poorly aerated and hardly permeable. In a

dry state, they form hard slabs and are often pervaded by deep shrinkage cracks. Because of these properties, they represent very poor cropping sites.

Distribution. Until now, *Solonetzes* have not been described in Germany, but have been in Austria and the Balkans. They are found extensively particularly east of the Caspian Sea, in West and Central Australia, in Somalia, Canada and North Argentina.

7.5.17 Desert Soils–Soils with a Yermic Horizon and Aridic Properties

References: Kubiena (1953), Blume et al. (1984), Blume (1987), Campbell and Claridge (1987), Petermann (1987), Blume and Berkowicz (1995), Soil Survey Staff (1999, 2014), Alaily (2008) and Breckle et al. (2008).

Soils with a *Yermic* horizon and *Aridic* properties (Tables 7.4 and 7.5) are soils of extreme hot or cold deserts. Because of low, at the most episodic precipitation, at least their topsoil is dry almost year-round and therefore has no plant-available water. For this reason, there are generally no natural plants, apart from a few algae that are capable of living on the morning dew and some adapted grasses with an extensive root system directly under the soil surface, which are supplied with water by the episodical precipitation. In depressions, there may also be natural tree growth extracting groundwater from a depth of several meters. In cold deserts of Antarctica, even lichens do not grow when the soil temperatures are in the negative range all year round. Adapted algae and microorganisms are then the only soil organisms. Because of the lack of bioturbation by animals, the soils have a high bulk density.

Still, especially in hot deserts, there is a wide spectrum of various soils (Fig. 7.14), which were often formed during somewhat more humid phases in the past. Kubiena (1953) was the first to describe them as *Yerma* (from *Yermo* [Spanish] = desert) or immature soils of arid deserts. In the Sahara, during the last period of higher precipitation about 5000 years ago in the Neolithic or in the Weichselian, Paleolithic humans were able to live in the dry savanna, preferentially at the shores of lakes that are dry today (Pachur and Altmann 2006).

Typical soils of Central Libya and SW Egypt, with mean annual rainfall below 10 mm and mean annual temperatures around 20 °C, are extremely dry almost year-round and practically free of organic matter (*Hyper-Ochric* AR with <0.4 % org. C). They are alkaline (pH 7–9.5) and contain carbonates and salts. The salts are generally added with the precipitation as **air-borne salinization** and are translocated into the subsoil at the most, differentiated according to the solubility of the salts formed: carbonates near the surface, followed by sulfates, chlorides and finally nitrates (Fig. 7.29). The reverse sequence is only found due to groundwater salinization in dried-out lakes and oases. ***"Phytogenetic" Solonchaks*** represent a special case, where thousands of years-old acacias followed the decreasing groundwater with their roots and led to the development of hard NaCl crusts of groundwater salts.

The surface of a typical desert soil is normally covered with stones and gravel or with dune sand (Fig. 7.30). On the air-exposed side, the stones and gravel exhibit black to dark brown desert varnish, consisting of iron and manganese oxides. Iron and manganese were liberated from the rocks by microorganisms that survive on the morning dew. At the soil surface or under eolian sand, there is a thin silt layer of dust, which was often fixed by algae and is then called biological crust. It follows a 1–5 cm-thick porous layer with vesicular structure. Their voids were probably created by the pressure of trapped air during strong rainfall. There are cracks between the columns that are usually filled with eolian sand, even in sandy soils. Cracks are formed due to strong temperature fluctuations between day and night as well as between winter and summer. The soil particles are fixed by salts, so that the columns shrink a little as a whole under cold weather and the sand that fell in prevents expansion at higher temperatures (Blume et al. 1984; Alaily 2008, p. 101ff). There are

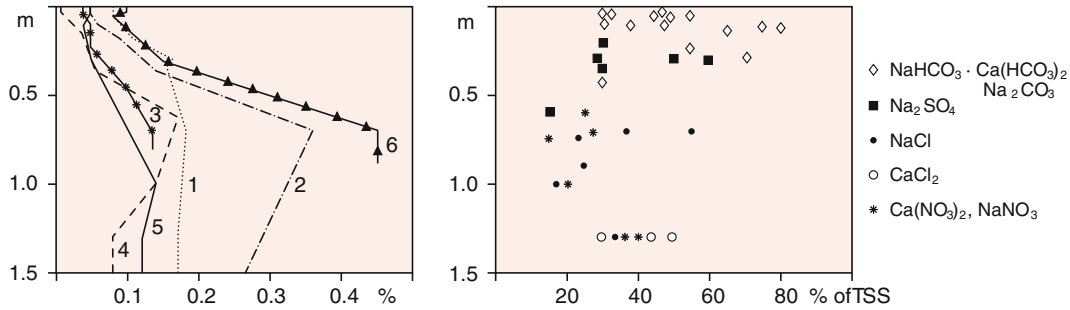

Fig. 7.29 Salt contents (*left*) and dominating salt minerals (*right*) in sandy desert soils of SW Egypt. *1* and *2* "Rainwater" Solonchaks, *3* Yermi-Arenic Calcisol, *4* Yermi-Brunic Arenosol, *5* Yermi-Calcaric Regosol and *6* Yermi-"Arenic" Leptosol (TSS = Total soil solution) (Smettan and Blume 1987)

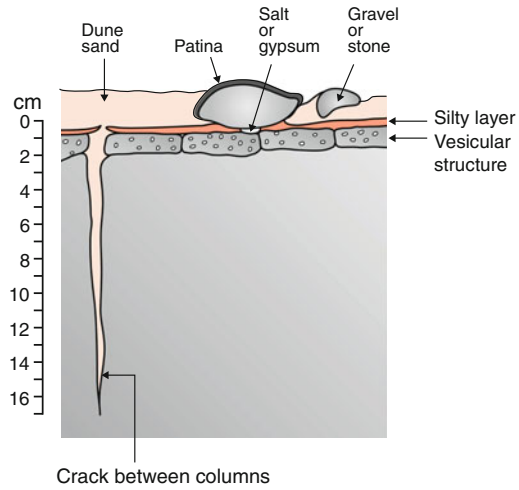

Fig. 7.30 Morphology of a *Yermic* horizon; extremely dry deserts of Central Libya and SW Egypt; cracks filled with eolian sand reach depths from 10 cm to more than 2 m (Blume et al. 1984)

wide-meshed crack networks filled with eolian sand to a depth of 2 m, particularly in SW Egypt, the world's most arid region with less than 10 mm annual precipitation.

Figure 7.31 shows a typical example for *Arenosols* in deserts, which exhibit a *Yermic* horizon and are therefore called ***Yermosols*** on the World Soil Map. The soil surface is covered with gravel, which is colored black by desert varnish. The upper 20 cm exhibit a cracked structure that is filled with eolian sand. The color of the upper 70 cm is dark brown, followed by reddish-brown with mottles and small black concretions. This indicates slight water retention in the subsoil during storm rainfall. There has been weak brunification of the profile, which is also indicated by the increasing contents of Fe going up in the profile. The soil contains a little humus, which may have been formed by the short-term growth of grasses after rare storm rainfalls (hundred-year rain). The salt maximum is not at the surface, which also suggests the effect of storm rainfall. The pH in the upper horizon is almost 10, which can be explained by the highest HCO_3 fraction of almost 0.04 compared to 0.2 further down.

Desert soils are classified as *Aridisols* in the US Soil Taxonomy. Especially because of their extreme aridity and their low humus contents, they are also classified as an individual unit in corresponding national classifications. In the international WRB system, until 1990 they belonged to the ***Aridic Soils*** unit, which have a characteristic *Yermic* horizon or *Aridic* properties or *Takyric* horizon. Subunits included the *Aridisols* in semideserts and *Yermosols* in deserts, as well as *Calcisols* and *Gypsisols*. Today, only the latter represent individual units, while the former are *Aridic* or *Yermic* or *Takyric* subunits of the *Arenosols, Calcisols*, *Fluvisols*, *Gypsisols*, *Leptosols*, *Solonchaks* in hot deserts (Breckle et al. 2008, p. 65ff, 225ff), while even extremely arid, humus-free soils of continental Antarctica without cryoturbation symptoms and

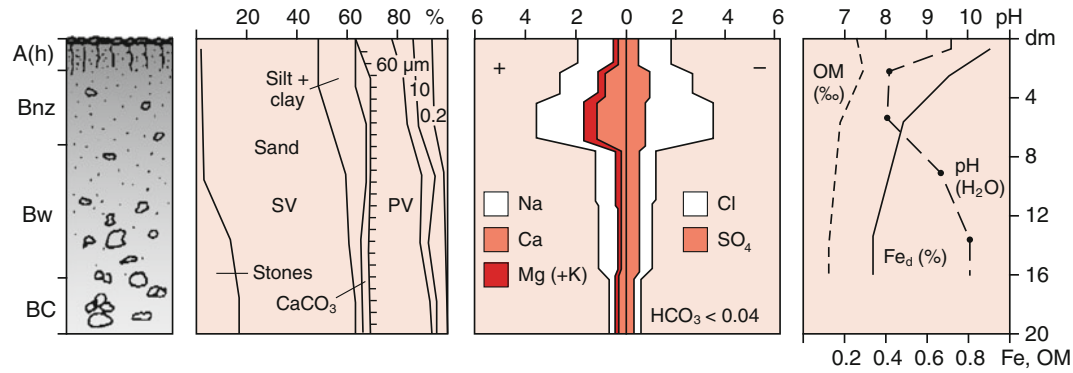

Fig. 7.31 Properties of a *Yermi-Sali-Calcaric Arenosol* developed from weathered sandstone in the desert; Wadi Irawan, Fezzan. (According to analyses by H.-P. Blume and Th. Petermann) (Abbreviations see Appendix, salts in the soil solution in $cmol_c\ kg^{-1}$)

without frozen water in the winter, but sometimes with atmogenic nitrate and chloride accumulation (Campbell and Claridge 1987) as well as accumulation of eolian sand in cracks (Sect. 7.2.6.4; after Tedrow 1966), are called *Cryosol*s (WRB) or *Gelisols* (US Soil Taxonomy) of the cold deserts, only because they are subject to negative soil temperatures almost all year round (Kimble 2004: p. 637ff).

The *Yermic Arenosols* are typical soils of stable dunes and often have silty biological crusts at their surface (Breckle et al. 2008: p. 68, 149ff, 228f, 285ff, 337ff). Young *Yermic Fluvisols* are the result of rare heavy rainfall events, during which the water creates deeply cut wadis and transports fine-grained sediments, and as *Playas,* they form fine silty sebchas. These sometimes led to the development of loamy *Solonchaks* with *Takyric* horizons. On extensive silty-sandy serir areas created by water erosion, mainly *Yermic Regosols* with weak salt accumulation and slightly brunified B horizons were formed, associated with *Yermic Gypsisols* and *Solonchaks* of dried-up lakes. On the hamadas or sandstone mountains, *Yermic Leptosols* as well as *Yermi-Leptic Regosols* and *Yermic-"Leptic" Solonchaks* were observed (Petermann 1987).

Historical arable farming is only possible today in the few still existing oases, while otherwise, some of the serer areas have been used for modern irrigated agriculture since the 1970s.

7.5.18 Gleysols (GL)

References: Blume and Schwertmann (1969), Schlichting and Schwertmann (1973), Blume and Schlichting (1984), Fanning and Fanning (1989), Wittmann et al. (1997) and Duchaufour (1998).

Gleysols are soils that are affected by groundwater with pronounced *Gleyic* properties (Table 7.5). In Germany, they are called *Gleys* (derived from [Low German] *klei* = mud). In the US system, they are grouped together with the *Stagnosols* as *Aquic* subgroups of different main units in the form of *Aquepts*, *Aqualfs*, and *Aquods.*

Profile. The *Haplic Gleysol* has a groundwater-affected horizon sequence Ah/Bl/Cr (Fig. 7.16). The rusty Bl horizon (**oxidation horizon**) follows beneath the groundwater-unaffected Ah horizon, and below this, the permanently wet, grayish to grayish-green or also bluish-black Cr horizon (**reduction horizon**). The mean groundwater level is higher than 80–100 cm, and the closed capillary fringe (of the high groundwater level) is rarely higher than 20–40 cm below the ground surface.

Stronly water-saturated *GL* ([German] *Nassgley*) and *Humic GL* ([German] *Anmoorgley*) are lacking Bl horizons, because their groundwater level intermittently reaches the soil surface. The Ah horizon of *GL* often has rusty root channels, while that of *Humic GL* have an elevated humus content.

Development. *Gleysols* develop under the influence of oxygen-poor groundwater. Reduced conditions prevail in the constantly wet **Cr horizon** of *Haplic GL*, because the groundwater in endorheic depressions or loamy-clayey floodplains only travels slowly, so that microorganisms have consumed the oxygen dissolved in the rainwater. This leads to microbial mobilization of Fe^{2+} and Mn^{2+} ions, which rise with the capillary groundwater and are precipitated as oxides in the **Bl horizon** where they come into contact with atmospheric oxygen. This mainly takes place on the walls of coarse pores such as root channels or aggregate surfaces (Sect. 7.2.5). However, part of the Fe and Mn remains in the form of grayish-blue Fe(II) and Mn(II) compounds as well as black Fe(II) sulfides in the groundwater zone.

The highly variable development of *Gleysols* depends on the catchment basin, the rocks, the rhythm and extent of groundwater fluctuations, the groundwater flow velocity and its oxygen, organic compound, and salt contents. The properties of terrestrial soils located higher up in the groundwater catchment basin also play an important role, because this is where the substance loads come from. Persistent influence of stable groundwater levels and additional Fe inputs from the surrounding terrestrial soils can lead to the development of strongly cemented, hard, Fe-rich (up to 40 % Fe) Blom horizons, which are called *bog iron* or *meadow ore* ([German] *Raseneisenstein*) and result in *Petrogleyic GL*. Despite the often shallow thickness of only 10–20 cm, they have been mined as ore and smelted in Northern Germany from beginning of the Iron Age 500 years before Christ until the 19th Century.

In *Fluvic GL* ([German] *Auengley*), in contrast, due to stronger groundwater fluctuations, the translocated Fe is distributed in a thick Bl horizon. In lowlands of Fe- and Mn-poor rocks, the Bl and Cr horizons are sometimes hardly developed, so that an *Albic GL* ([German] *Bleichgley*) is observed. With fast-flowing, O_2-rich groundwater, which is found in lower slope locations or in gravelly subsoils, as well as in the absence of reducing substances, a Cr horizon can also be completely lacking. In such *Gleysols* ([German] *Oxigleye*), the Bl horizon often reaches great depths and there is no Br horizon. In clay-rich GL, *Stagnic* dynamics occur simultaneously in the dense topsoil, which is then strongly mottled and typical for "*Stagnic*" *GL* and "*Vertic*" *GL*.

In glacial till landscapes, the groundwater is often rich in $Ca(HCO_3)_2$; instead of the Bl, a *Calcic GL* ([German] *Kalkgley*) develops here with a carbonate-rich Blk horizon, which is called *meadow chalk* ([German] *Wiesenkalk* or *Alm(kalk)*). A *Humic GL* ([German] *Humusgley*) has an Ah horizon with a thickness >4 dm.

Groundwater reaching up near the surface all year round only allows for Fe accumulation in the Ah horizon or not at all, so that *wet GL* ([German] *Nassgley*) develop with the horizon sequence Ah/Cr. If, at the same time, the decomposition of organic matter is inhibited by O_2 deficiency, *Histic GL* ([German] *Moorgley*) develop. *Histic GL* differ from *Histosols* in the limited thickness of their peat layer.

Spodic GL often developed from nutrient-poor sands, where a Bh horizon developed in the winter groundwater zone and their profile often contains virtually no iron oxides. If the mean groundwater level is only found at a depth of 8–13 dm in the soil, terrestrial development takes place in the topsoil and "*Cambic*" *GL*, *Spodic GL* or *Luvic GL* are formed.

On slopes, springs can cause wet areas, and depending on the intensity and seasonal change in the spring discharge, they lead to the development of a multitude of different soils, which are classified in Germany with the qualifier *Quell* = spring.

In high-precipitation areas (low mountain ranges, Alps), year-round water saturation can also occur without change of soil layers: In Germany, soils in these locations with >9 % slope inclination are called ***Hanggley*** (*slope GL*) (Sect. 7.2.7.3). Slope *Oxiaquatic GL* are often found below *Albic Planosols* or *Albic Stagnosols*, where iron was transported laterally by slope water from the *Planosols* or *Stagnosols* and then accumulated (Sect. 7.2.7.3 and Fig. 8.2).

With groundwater lowering, the Cr horizon usually rapidly moves down to greater depths,

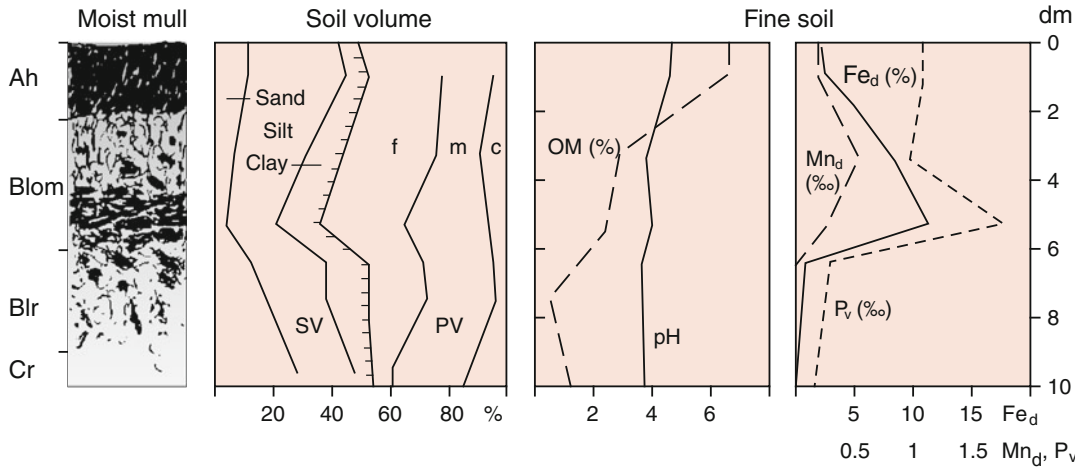

Fig. 7.32 Properties of a *Petrogleyic Gleysol* developed from fluvial loam under grassland; North Rhine; draft by H.-P. Blume according to analyses by R. Sunkel and H.-P. Blume (Abbreviations see Appendix)

while the morph of the Bl horizon can remain for a long time. Therefore, the rust is *relictic* in these *Drainic GL*, which can only be determined by investigating the current water dynamics.

Properties. Depending on the composition and groundwater fluctuation range, the *Haplic Gleysols* exhibit various humus forms. Moist mull is formed when there is intermittent O_2 deficiency. Moist mor can also develop in *Dystric GL*. With strong O_2 deficiency over longer periods of time, a peat layer is formed in nutrient-poor *GL*, and in contrast, a *Molli-Folic GL* is formed in nutrient-rich soils (as a result of bioturbation).

While the **structure** of the only intermittently wet horizons is usually crumbly, subangular blocky or prismatic, the constantly wet horizons in the subsoil of typical *Gleysols* and in the topsoil of *Humic Gleysols* is usually single-grained to coherent. In *Gleysols*, the **pore size distribution** can vary greatly, sometimes the Bl horizon is relatively pore-rich (Fig. 7.32), similar to the Bhs of *Podzols*. *Gleysols* always provide the vegetation with sufficient water, while there is a lack of oxygen in the subsoil. The reaction of most *Gleysols*, except for *Gleysols* containing $CaCO_3$, is weakly to moderately acidic. After groundwater lowering and the associated aeration of the Cr horizon, there may be strong acidification due to the formation of sulfuric acid (Sect. 7.2.5).

By nature, *Gleysols* are often more nutrient-rich than neighboring terrestrial soils, because they receive these dissolved substances through the groundwater. However, the availability of the delivered nutrients is often low. For example, despite high P contents, *Gleysols* with bog iron ore usually have low P availability, and in contrast, strong P fixation. According to investigations by E. Schlichting, molybdenum exhibits similar behavior.

Distribution and land use. *Gleysols* are characterized by a broad distribution, but usually only on small areas on highly variable rocks. They are found in all areas with high groundwater levels, whereby their properties are significantly determined by the associated terrestrial soils. *Gleysols* are natural sites for moisture-loving plant communities such as swamp forests etc. Their suitability for forestry is often very good, especially with the cultivation of tree species with high water consumption such as poplar, ash, alder etc. When the groundwater levels are not too high, *Gleysols* can also be used as grassland and pasture. *Gleysols* without groundwater lowering are not suitable for arable farming.

7.5.19 Fluvisols (FL)

References: Ehrenberg (1838/1854), Post von (1862), Kubiena (1953), Blume (2003a) and Fischer et al. (2014).

Fluvisols are mainly young soils of fluvial, lacustrine or marine deposits. Their name from the Latin ***fluvius*** means river soils. They are clearly stratified. At the bottom of lakes, they form *Limnic Fluvisols,* and at the periodically flooded banks, *Arenic, Gleyic* or *Haplic Fluvisols.* On mudflat coasts, *Tidalic Fluvisols* are subject to the influence of the tides, and are therefore water-free for at least a few hours every day. Many *Tidalic Fluvisols* on the North Sea coast of Belgium, Holland, Germany and Denmark, have been protected from rising sea levels, sometimes since 1000 years, through the construction of dikes that are meanwhile almost 9 m high, and were deeply drained and used for agriculture. Episodical storm floods sometimes destroyed the dikes and covered the soils with young sediments, in Germany for the last time extensively in 1962. *Yermic Fluvisols* of the deserts are only flooded and therefore wet for a few days after rare storm rainfall, otherwise they are dry.

7.5.19.1 Subhydric Soils—Limnic Fluvisols

Limnic Fluvisols are soils at the bottom of watercourses. They exhibit a humic horizon at the bottom of a **water body**, consisting of humified plankton and containing >1 % humus, which is then called *Lh horizon* (WRB 2006/7 and Jahn et al. 2006). This horizon is followed by other *L* layers or water-saturated mineral layers. Peat soils, which sometimes also form under subhydric conditions (e.g. under reeds), belong to the *Histosols.*

In geology, *Limnic Fluvisols* are considered as sediments and are called **muds**. Similar to the peats in moors, there can also be very thick different humic layers underneath each other at the bottom of watercourses, where the lower layers hardly have any biological activity, and are therefore fossil. On the other hand, subhydric soils exhibit pronounced dynamics in the upper, intensely biologically active zone. This results in the following development:

The sediments of inland waters and coasts are the parent material for soil formation. There are also constant additions of organic matter at the bottom of the watercourse from dead organisms. As a matter of principle, the decomposition of organic matter is inhibited because of the slow gas exchange with the atmosphere.

As an alternative source of oxygen for the oxidation of organic matter, microorganisms use the nitrates and sulfates dissolved in the water that are often added by rain, which are then reduced, and depending on the prevalent conditions (Sect. 5.7), lead to the formation of N_2, NH_4, CH_4, metal sulfides and/or sulfur. However, the plankton is relatively easily decomposed, because it hardly contains any poorly digestible structural substances. For this reason, the humus body of subhydric soils is usually very finely grained and more strongly humified. Shallow forest lakes represent an exception, where the poorly decomposable leaf litter that is added to the water by the wind impedes humification.

In Germany, the *Limnic Fluvisols* are called *Unterwasserböden* (subhydric soils), and are classified as follows according to Kubiena (1953). The *Unterwasser-Rohboden* (subhydric immature soil) or the ***protopedon*** ([Greek] = virgin soil, WRB: "*Proto*"-*Limni-Subaquatic Fluvisol*) generally contains O_2 at least in the upper 40 cm (rH > 19) and is therefore free of *Gleyic* properties. It develops from sands, silts, clays, carbonate-rich deposits (limnic marl and chalk), coquina, lake ore formations (limonite) and diatom shells (diatomaceous earth), which are populated with aquatic animals and plants at the bottom of the watercourse. The humus content is <1 %, because they develop preferentially in area of stronger water movement (due the current or wave movement) of fast-flowing streams, where relatively little litter is sedimented or it erodes again and **O_2-rich water** promotes the decomposition of organic matter.

In simultaneously oxygen- and nutrient-poor or dystric lakes, *Dystric*, biologically sluggish soils develop, which are called ***dy*** ([Swedish] =

mud) or '*Braunschlammboden*' (brown mud soils) according to Post von (1862). Their Lh horizon is acidic (pH < 6) and consists of a dark brown mass of predominantly flocculated humified organic matter, which is low in plant and animal organisms. In addition, there are remains from dead organisms, and in small forest lakes e.g. partly decomposed leaves. As a sediment, dy is comparable to *Limnohumite*. In the WRB, they are called *Humi-Limni-Subaquatic Fluvisols.*

Anoxic conditions, but at the same time nutrient-rich watercourses, lead to the development of ***Sapropel*** ([Old Greek] σαπρός *sapros* = putrid. The *Lr* horizon of *sapropels* is black, its rH value is generally below 13 (at pH 7 corresponds to a redox potential of −30 mV), often contains metal sulfides and H_2S, CH_4 and H_2 formed by anaerobic microorganisms. In the WRB, they are called *Thioni-Limni-Subaquatic Fluvisols*. According to Kubiena (1953), marine *Schlickwatt* (mudflats) (see Sect. 7.5.19.3) is also a marine *sapropel*.

In contrast, according to Post von (1862), ***gyttja*** ([Swedish] = mud) or *Grauschlammboden* (grey mud soil) develop in well aerated, nutrient-rich watercourses. The *Lo* horizon of typical *gyttja* consists of mineral particles and coprogenic aggregates that are grayish-green (olive) to reddish-brown in color and have an elastic, liver-like consistence, which corresponds to the sediment type ***Lebermudde*** (liver-mud). Green colors are caused by FeII/FeIII mixed oxides (blue-green rust), which is formed at rH values between 13 and 18 (Blume 2003a). Calcareous forms are called **calcareous *gyttja***, or "*Fluvic*" *Calcisols* in the WRB, and those that have lower contents of secondary carbonate are called *Calci-Limni-Subaquatic FL.* They have a strong colonization by animals and microorganisms in common, as well as rH values > 13, which does not allow for H_2S formation.

Gyttjas are also classified according to the degree of fragmentation of the organic matter (coarse, medium, fine detritus *gyttja*), the predominant parent material (algae, diatoms, leaf *gyttja* etc.) or the origins (tidal flat *gyttja*, *Limnic gyttja*). Today, anthropogenic eutrophication in many lakes has often lead to a transformation (or superimposition) of *gyttjas* into *sapropels*. These *sapropels* exhibit high nutrient and heavy metal contents.

In **flowing waters**, *Unterwasserrohböden* (subhydric immature soils) are more commonly found because there is more erosion. Transitional forms between *gyttjas* and *sapropels* are characterized here by brown Lo topsoils and black Lr subsoil horizons, provided that oxygen is still being added to the topsoil from the flowing water. Strongly contaminated watercourses are also characterized by *sapropels* with continuous black Lr horizons.

In contrast to *sapropels*, *Protopeda* and *gyttjas* provide animals with enough oxygen to live. All sub-hydric soils adsorb dissolved substances from the lake or river water and therefore often protect the groundwater from pollution.

After being drained, *gyttjas* represent nutrient-rich substrates for agricultural use, with a high water holding capacity and pore volume, but often with considerable swelling and shrinking. Their pH lies between 4 and 5, and that of calcareous *gyttjas* is naturally higher. In the Baltic Sea area (Sweden, Finland, Poland), drained *gyttjas* are significant in some areas for agricultural use. *Sapropels* and *dys*, in contrast, can hardly be used after having been drained: The former are then often strongly acidified by the formation of H_2SO_4, and the latter then shrink intensively, whereby they sometimes break down into hard fragments, and sometimes —mainly with frost—into a fine powder.

Thioni-Limni-Subaquatic Fluvisols mainly consist of sulfur, e.g. in the *Grunewaldsee* of Berlin. They are then formed by microorganisms, if there are no dissolved Fe ions to form iron sulfides.

7.5.19.2 Valley Soils—Haplic Fluvisols

Haplic Fluvisols are soils in river valleys. With unregulated flowing waters, they are periodically flooded, otherwise, behind high tide dikes, they are flooded by water under pressure (or upward seepage). In contrast to the *Gleysols*, however,

they hardly exhibit redoximorphic characteristics, at least not in the upper 4 dm of the profile, which constantly have rH values > 33. At greater depths, although there is often a mottled horizon, there are no pronounced reduction horizons because the rH values there are >13.

Haplic Fluvisols are defined as soils from Holocene valley floors (floodplains) of rivers and streams, and are also called floodplain soils or alluvial soils. Floodplains are the parts of the landscape that are still flooded at high water levels today, or are flooded by water under pressure behind dikes.

According to Kubiena (1953), floodplain immature soils in Germany are called ***Rambla*** ([Arabic] *ramla* = coarse sand), the Si-rich A/C soils are called ***Paternia*** (after the Río Paternia in Spain), the calcareous soils are called ***Kalkpaternia***, and the brunified riparian floodplain soils are called ***Vega*** ([Spanish] = fertile plain). Deeply humic, grayish-black, calcareous A/C soils are called ***Tschernitza*** ([Czech] *tscherni* = black). In the US system, the poorly developed forms represent suborders of the *Entisols* (*Fluvents, Fluvic Psamments*); the *Tschernitza* is called *Fuventic Haplustoll*, and the *Vega* is classified as *Fuventic Eutrochrept*.

Development. *Haplic Fluvisols* develop from the sediments of river and stream floodplains. They are characterized by strong groundwater fluctuations, which can reach up to 6 m within the course of a year. The influence of the river water level on the neighboring groundwater level decreases with increasing distance from the river, but its effects can reach distances of 4–5 km in the case of permeable subsoils (e.g. gravel). Furthermore, they are periodically flooded, whereby solid and dissolved substances are added, but sometimes also removed. Soil development is also interrupted by sedimentation and/or erosion. As a result, there is an (alluvial), stratified parent rock and the humic topsoil consists of several layers with changing humus contents.

During transport and sedimentation in the river, the particles are sorted according to their size depending on the flow velocity. The generally smaller gradient in the lower reaches causes finer-grained sediments to be deposited there. The same is true the areas of the floodplain that are further away from the river, because the velocity of the water is more strongly decelerated when it flows over the banks. This also often leads to the formation of a bank wall. The character of the fluvial sediment is also strongly determined by the properties of the rocks and soils in the river catchment basin. For example, the North German sand landscapes are dominated by sandy floodplains, while fluvial loam was deposited in loess landscapes (as well as loess-covered low mountain ranges).

On deposits of unweathered rock material, like in many South German river valleys in the Alps catchment basin, usually coarse-grained ***Rambla*** (WRB: "*Protic*" *Fluvisol*) develops first with an A(h)C profile. The litter from their sparse pioneer vegetation is often eroded by the next flood. When the extent of sedimentation decreases, a stronger accumulation of organic matter in the topsoil leads to the development of sandy-loamy young riparian floodplain soils that often contain $CaCO_3$, the ***Paternies*** with the horizon sequence Ah/C (WRB: *Eutric FL*). They often have a characteristic grey color. Deep-reaching weathering at the deposition site finally leads to the development of ***Vega*** (WRB: *Mollic Fluvisol*; Fig. 7.16) with the horizon sequence Ah/Bw/C. Here, the liberation of larger amounts of Fe oxides, like in the *Cambisols*, led to a brunification of the soil (autochthonous *Vega*). Such *Vegas* must not be genetically confused with soils developed from brown sediments, the allochthonous *Vegas* (WRB: *Colluvi-Fluvic Cambisol*) eroded soils. These sediments can be recognized by their often deep brown coloration with layered alternating (Munsell) chroma; they are often also calcareous. ***Tschernitzes*** have a thick mull A that was formed by intense bioturbation (German = Axh).

Haplic Fluvisols hardly exhibit any redoximorphic characteristics, because strong fluctuations, only short standstill phases and high flow velocities, makes the groundwater accompanying the river relatively oxygen-rich (the rH values are therefore always >13).

In a floodplain landscape, however, *Gleyic* subunits, *Gleysols* and even *Histosols* can be

found, especially with low flow velocity of the groundwater. This is caused by lower hydraulic conductivity in loamy-clayey sediments or by lower flow velocity due to a low gradient or a river that is spreading out towards a lake.

Today, the deposition of fluvial sediments is often largely inhibited due to the building of dikes and river regulation. Still, the dynamics of these soils differs from that of terrestrial soils, because they are periodically flooded by upward seepage, and the dissolved transported substance loads counteract acidification and weathering. Although *Haplic Fluvisols* are only rarely flooded for short periods of time, which does not have a very strong influence on pedogenesis, their subsoil and often also their topsoil are subject to the influence of upward seepage or bank infiltrate every year during spring floods. In contrast, if the floodplain is drained, e.g. due to deepening of the river bed after straightening the course of a river, so that there is no intermittent upward seepage up to 4 dm below the ground surface, the development of the floodplain soil to a terrestrial soil is complete. In the process, transitional forms between terrestrial and riparian floodplain soils can be observed (e.g. *Fluvic Cambisols*).

Properties. *Haplic Fluvisols* are generally oxygen-rich, because their high hydraulic conductivity enables a rapid exchange with O_2-rich groundwater. Especially the coarse-grained *Ramblas* and debris-rich ***Kalkpaternies*** have pronounced alternate drying and moistening conditions with strong water deficits during summer low water levels. In contrast, because of their loamy soil texture, many ***Vegas*** have a high plant-available water capacity, and therefore more balanced water conditions. The same is true for the humus-rich *Eutri-Humic FL* ([German] *Tschernitza*). The $CaCO_3$ content varies across wide ranges. *Vegas* developed from older sediments usually do not contain any more $CaCO_3$, provided that they were not infiltrated again by groundwater containing $Ca(HCO_3)_2$. Many floodplain soils are nutrient-rich, have a high Ca saturation and high biological activity. Some floodplain soils located near contaminated rivers today are strongly polluted with salts and heavy metals. In all floodplain soils, deep-rooting plants are more successful than annual shallow-rooting plants.

Distribution and land use. *Haplic Fluvisols* with an A/C profile are mainly restricted to rivers in mountains, but *Rambles* and *Paternies* are also found on frequently flooded beach walls of lowland rivers. The *Vegas* dominate otherwise here. *Tschernitzes* are mostly found in *Chernozem* landscapes, but are also found outside of loess soils. The natural vegetation of floodplains is alluvial forest, which is very diverse when the groundwater is rich in nutrients and oxygen and with medium clay contents; in Central Europe, they often contain a high fraction of elm, common oak and ash. *Paternies* are often used for forestry (e.g. poplar stands). *Tschernitzas* can be used for arable farming, while *Vegas* are often used as grassland.

7.5.19.3 Tidalic Fluvisols, "Tidalic" Arenosols and Fluvic Gleysols

References: Brümmer (1968), Kittrick et al. (1982), Müller (1994), Verwaltung Naturparks Wattenmeer (1998/9), Bohn et al. (2000) and Janetzko and Fleige (2010).

(a) ***Tidalic Fluvisols*** are semi-subhydric soils on flat tidal coasts of the oceans. Under the influence of low and high tides, depending on the elevation and height of the daily tide amplitude, they are periodically to episodically covered with water and therefore wet, but at low water levels, depending on the soil texture, they are intermittently dry to moist. Depending on the texture of the soils, this causes a constant exchange of the soil solution by oxygen-saturated seawater reaching various depths. In temperate climates, *Tidalic Fluvisols* that are only episodically flooded are found under natural salt meadow vegetation such as the Everglades in Florida/USA; in the tropics, they are then covered with mangrove forests. More than 8000 years ago at today's North Sea coast of Denmark, Germany, and the Netherlands, there were natural salt meadows only

northwest of the Helgoland Island. Further to the east meltwater sands covered with moors dominated. Later on, due to the rising sea level, they were covered with mudflat sediments of highly variable thickness.

In front of the salt meadows towards the ocean, there are the saline and (usually increasing from Denmark to Belgium) calcareous, stratified, fine sandy to loamy **tidal flats**. As stratified *Fluvisols*, soils of tidal flats represent **semi-subhydric soils**. Light grey to black Wr horizons, depending on the texture, follow below a pale yellow (due to sulfur) to reddish-brown (due to ferrihydrite) Wl horizon of a few mm to cm thickness. Depending on the prevalent flow conditions, a distinction is made between the *Schlickwatt* (**G**erman classification, mudflats) with >50 % silty clay, the *Sandwatt* (**G**, sand flats) with >90 % fine sand in addition to silt and clay, and the *Mischwatt* (**G**, loamy tidal flats).

The ***Schlickwatt*** (WRB: *Clayi-Tidali-Subaquatic Fluvisol*) is very loose (PV > 70 %, Fig. 7.33) and therefore cannot be walked on; it is colored black by iron sulfides and humus and is constantly wet; the surface is only slightly lowered at low tide. It is O_2-free (rH < 13). There is hardly any exchange between the soil solution and seawater. It is populated by many microorganisms, but hardly by any higher plants or animals.

The ***Sandwatt*** (WRB: *Areni-Tidalic Fluvisol*) can be walked on and is relatively dense (PV < 40 %). It is somewhat populated by microorganisms, mussels and crabs as well as submersed aquatic plants (*Fucus vesiculosus*, *Ulva lactuca*). The water holding capacity is low. For this reason, there is an almost complete exchange between the soil solution and O_2-saturated seawater twice a day, depending on the tidal range, to a depth between 0.5 and 1 m. There are almost no reductomorphic characteristics (rH > 19).

The ***Mischwatt*** (WRB: *Silti-Tidalic Fluvisol*) is moderately dense to loose (PV 40–70 %); feet sink in by 1–2 cm when walking on it. Depending on the elevation, it is populated by submersed aquatic plants (*Zostera nana*, *Enteromorpha linza*) as well as saltwort (*Salicornia herbacea*) or cordgrass (*Spartina townseni*), whereby the latter was sometimes planted by man as a coastal defense measure. The soils are often strongly populated both by

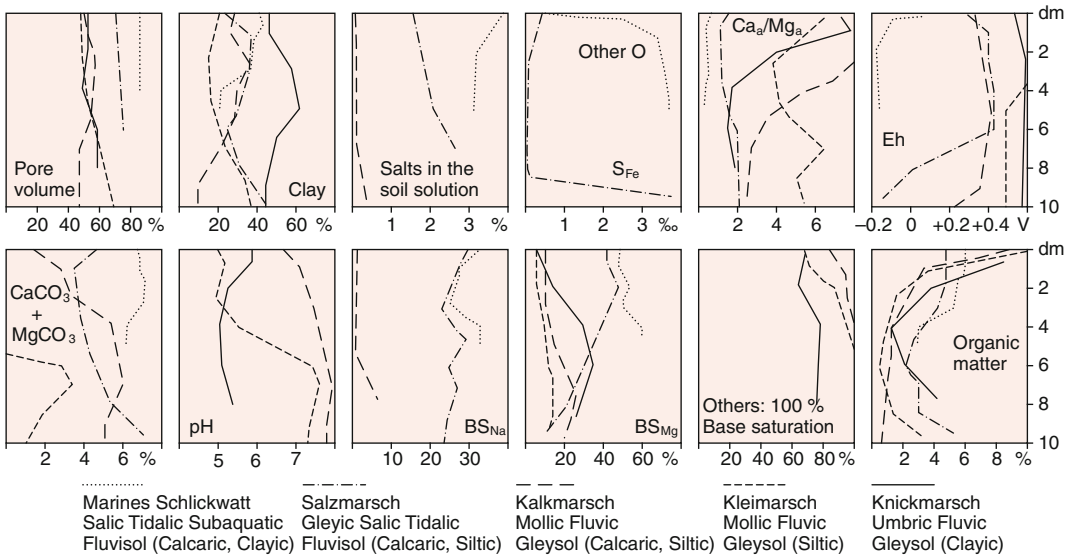

Fig. 7.33 Properties of characteristic soils of tidal flats, salt meadows and arable land behind dikes. West coast of North sea Schleswig-Holstein, Germany (according to data from Brümmer 1968, Abbreviations see Appendix)

microorganisms and animals (mussels, crabs). Especially lugworms (*Arenicola marina*) intensely mix the upper 15–25 cm of the soils (Sect. 7.2.6.1): They form a loose soil without redoximorphic properties above a layer of coarser sand and mussel shells (Blume 2011). Furthermore, depending on the salt content, a distinction can be made between *Salzwatt* (saline flats) (EC_{SE}. in dS/m > 15), *Brackwatt* (brackish tidal flats) (EC_{SE} 0.75–15) and *Flusswatt* (river tidal flats) as well as tidal flats of the eastern Baltic Sea (EC_{SE} < 0.75).

(b) **Beach wall coasts** also developed in mudflat coastal areas that are characterized by stronger currents. Because of their medium to coarse gravelly texture and very high hydraulic conductivity, they desiccate so rapidly especially at low tide that they are also strongly eroded by wind. As "*Tidalic*" *Arenosols* (in German, depending on the flooding frequency, they are called *Strandböden* (beach soils) and *Naßstrandböden* (wet beach soils)), they are used to a large extent as **bathing beaches**. Landwards, they change into medium sand **coastal dunes**, which are prevented from becoming wandering dunes mainly by planting. They have developed into *Protic* or *Rubic* and sometimes even *Dystri-Albic Arenosols* with very low humus contents. Dunes and therefore *Endo-Salic Arenosols*, which are only briefly flooded in the winter during storm floods, also developed on extensive **sand plates** of the North Sea with *Areni-Tidalic Fluvisols*. They are often set aside as bird sanctuaries (e.g. Texel Island) and cannot be accessed, especially in the summer.

(c) **Salt meadows** are slightly flooded on a daily basis with normal tides (Bohn et al. 2000) and overflooded during storm tides. When they have a sandy texture, they are populated mainly with *Pucinellia maritima* and *Statice limonium*, with a fine sandy to silty texture with *Ameria maritima* and *Artimisia vulgaris*, and with a loamy texture with *Juncus gerrardi* and *Festuca rubra.* In Germany, their soils are classified as *Rohmarschen* (crude marsh), which hardly have any *Gleyic* properties when they have a sandy texture, while with a loamy texture, *Gleyic* properties develop all the way up to the surface. According to the WRB, the sandy textures would be classified as *Areni-Tidalic FL*, the fine sandy-silty textures as *Silti-Tidalic FL*, and the clayey textures as *Clayi-Tidalic Fl*.

(d) **Land protected by dikes**. Landwards, the salt meadow landscape turns into a **marsh landscape** that is protected from flooding by almost 9 m-high **dikes**. These young marsh soils gained in the last ca. 100 years, as predominantly strongly stratified, fine sandy-silty, calcareous soils (German: *Kalkmarschen*), are classified in the WRB as *Calcari-Gleyic Fluvisol* or *Calcari-Fluvic Gleysol*, depending on the redoximorphic characteristics. Thanks to a moderate, but continuously existing layer of organic matter consisting of readily decomposable oceanic plankton, they have a high earthworm population, especially under grassland use. These soils with high plant-available water capacities and high nutrient reserves are specifically drained (depending on the texture, land use and season, the groundwater level is kept between 0.6 and 1.2 m under the ground surface using ditch drainage at low tide through a sluice system into the ocean) and used intensively for horticulture or agriculture. With yields of e.g. more than 15 t/ha of wheat, they count among the most fertile soils in the world (some characteristics of these soils are shown in Fig. 7.33).

Landwards, behind an older, less high dike line, the artificially drained soils are followed by soils developed from sediments that were naturally deposited by seawater over the course of centuries, which often lie above peats. They are more clay-rich and exhibit strong *Gleyic* properties, and sometimes also *Stagnic* properties in the topsoil. In Germany, they also belong to the marsh landscape and are classified along with salt meadow soils and human-regulated sedimentation as *marshland soils*. According to the WRB, they are mainly

defined as *Eutri-* to *Dystri-Fluvic Gleysols*, "*Stagni*"-*Clayi-Fluvic Gleysols* or *Humi-Fluvic Gleysols*. Today, they are sometimes located up to 4 m below sea level because of the subsidence of underlying peats due to drainage or the cutting of peat in the Middle Ages, practiced especially for the harvesting of table salt. As marine sediments, they still have a higher fraction of adsorbed Mg and Na ions today, which accounts for their low aggregate stability and therefore poor workability at high clay contents, so that they are often used as permanent grassland. Some of these clay-rich soils exhibited relatively high iron sulfide contents at the time of their sedimentation. Any carbonates they may have originally contained have long been leached out. As a result of drainage, their sulfides have been microbially oxidized to sulfuric acid, so that **acid sulfate subsoils** were formed with pH values sometimes reaching below 3. In the presence of K ions, yellow **jarosite** is formed on aggregate surfaces, otherwise the orange **schwertmannite** (see Sect. 7.2.5; Kittrick et al. 1982). According to the WRB, they are called *Hyperthioni-Fluvic Gleysols*.

7.5.20 Peat Soils—Histosols (HS)

References: Bakker (1979), Sauerbrey and Zeitz (1999), Zeitz (2003) and Wittmann et al. (1997).

Profile. **Histosols** are hydromorphic soils with a peat horizon and strong reduction characteristics in the mineral body. A distinction is made between **fens** with subhydric development (topogenic moors) and **bogs** that developed independent of the groundwater (ombrogenic moors, rainwater moors). Moors differ from mineral soils in that the accumulation of organic matter constantly creates new peat layers and the older layers become fossilized, which are then considered as organic sediments in geology. For this reason, 'peat soils' are often defined as only the upper rooted zone of a peat body.

Name. At the same time, the landscape term 'moor' is also used for the soils of these landscapes in Germany. In the WRB and US system, moors are grouped together with thick humus layers (>60 cm with mostly peat moss and/or d_B < 0.1 g cm^{-3}, >10 cm over hard rock, otherwise >40 cm) of terrestrial soils (e.g. *Tangelrendzinas*) as *Histosols*.

Development. Moors develop when high groundwater (or surface water) or perhumid climates induce air deficiency, which inhibits the decomposition of litter, so that large amounts of organic matter accumulate as peat. Low temperatures, nutrient-poor groundwater or rocks and/or high salt or organic toxin concentrations also promote peat formation.

Fens (WRB: *Floatic, Rheic* and *Limnic Histosols*) often develop (as siltation peats) at the banks of standing waters on subhydric soils, whereby common reed (*Phragmites*), cattail (*Typha)* and/or several sedges (*Carex*) supply the organic parent material. If the peat reaches the average water line, the peat type changes along with the litter under alder (*Alnus*) or willow (*Salix*) swamp forest, while at the same time, the reed bed belt and therefore the fen formation is shifted towards the ocean, until finally the watercourse is silted up (Fig. 7.34).

Topogenic fens also develop in depressions under the influence of rising groundwater (ponding peats) and then do not have underlying **fossil subhydric soils**. As **meadow-moors** (*Histosols* of floodplains), they develop at the banks of many rivers, preferentially behind beach walls or in the shallow inner curve of a river bend

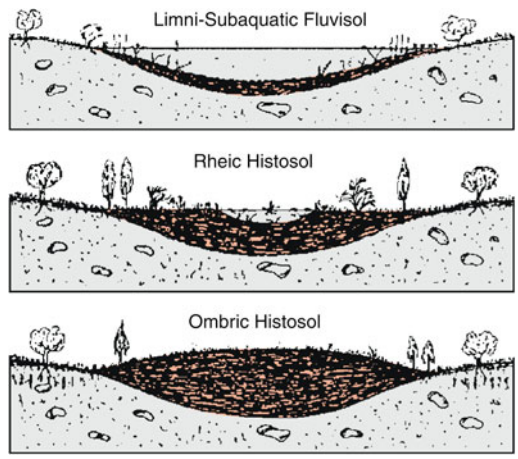

Fig. 7.34 Development of a landscape with Peats in Northern Germany

where the current of water is slow. **Meadow peats** are often interspersed by thin mineral layers due to periodic flooding. Finally, strata water discharge leads to the development of **spring** or **slope fens**.

In landscapes with nutrient-poor rocks (e.g. quartz-rich sands), in contrast, undemanding tree species such as downy birch and pine then populate the acidic fen (formerly: transitional moor). Nutrient deficiencies increase when the peat body grows out of the area of influence of groundwater (and lake water), because there are only small nutrient inputs through precipitation, and a few bog plants appear.

With further growth, the swamp forest disappears under oceanic climate conditions (e.g. Northwest Germany). Pod grass or cotton grass dominate at first and finally different peat mosses (=sphagnum), the residues of which form the often watchglass-shaped bulging **bog** (WRB: *Ombric Histosol*) (Fig. 7.34, bottom). Under more continental climate conditions with more frequent desiccation of the topsoil, in contrast, isolated trees remain on the bog (e.g. dwarf pine in Southern Germany). A complete moor profile developed from the siltation of a lake can therefore consist of layered fen, transitional moor and bog peat, and have an underlying fossil subhydric soil (e.g. *gyttja*).

Bogs also develop directly on organic layers of nutrient-poor *Histic Podzols* (Northwest Germany) and *Stagnosols* (in low mountain ranges), and are then called rooted bogs.

The development of many moors in the North German lowlands began in the Late glacial and Preboreal (Table A.2 in the Appendix) with subhydric soils, which grew up to 20 m in thickness in dead ice lakes and meltwater channels of the moraine and sandur landscapes. In the warmer Boreal (~after 9000 BP), these shallow lakes silted up because of the now stronger established plant growth, leading to the formation of fens. Since the Atlantic (about 7500 BP), they grew under more humid climate conditions to form bogs, whereby initially more strongly humified **older peat** and later (especially under the cooler climate conditions of the Subatlantic) also less humified **fibric peat**. In Northern Germany, moor development was promoted by a strong rise in the groundwater level during the Holocene, which was associated with a rise in the sea level. Since the Middle Ages, dams upstream of water mills and later increasing watercourse eutrophication also promoted the growth of moors.

Properties. Fen peats are usually strongly humified and are then black in color. A sufficient nutrient supply, especially with low water levels in the summer (and therefore good aeration), enables the decomposition and humification of the shoot litter, so that often only the root litter (e.g. reed rhizomes) remains. In contrast, bog peats are usually only moderately (older peat) or weakly (fibric peat) humified, so that plant residues can be recognized. Peats are classified in Germany according to v. Post in terms of their **degree of humification** (H 1 = not humified, H 10 = fully humified; fibric peat H 1–H 5, older peat H 6–H 9, fen peat usually H 8–H 10). In this context, it is wrong to speak of the degree of decomposition, because even at low degrees of humification, a high fraction of litter can be fully decomposed (e.g. at least 40 % with fibric peat, mostly cell contents like proteins). Similarly, in the US and the WRB systems, a distinction is made between *Fibric* (fibrous), *Hemic* (half-fibrous) and *Sapric* (amorphic) *Histosols* (US as *Fibrist*, *Hemist*, *Saprist*). The WRB system also distinguishes the *Gelic Histosols* with underlying permafrost, and the *Folic Histosols* that are briefly wet at the most (as terrestrial, O/C and other soils with thick humus layers).

Moors exhibit a high pore volume: >97 % vol. is considered as almost floating, 95–97 % as loose and <88 % already as dense. They have a high water holding capacity and also for available water, which is naturally only of ecological significance after they have been drained. In contrast, because of their water saturation, moors are air-deficient sites. For the same reasons, they also warm up more slowly in the spring.

Bogs exhibit very low pH values (pH[$CaCl_2$] < 3–4) and as pure rainwater bogs, they are very nutrient-poor (due to air pollution today, however, there are higher salt inputs, esp. of NH^{4+}, NO_3) and are therefore called **dystrophic moors**.

In fens, the pH (4–7.5; also lower if they contain FeS) and nutrient content depend on that of the groundwater or watercourse, which is ultimately determined by the mineral composition of the landscape. Thus, fens of North German sand or South German sandstone landscapes only exhibit moderate nutrient contents, and are therefore **dystrophic** or **mesotrophic**, while fens of younger calcareous glacial till or loess landscapes are nutrient-rich, i.e. **eutrophic**. The pH does not necessarily correlate with the nutrient content, because fens containing $CaCO_3$ with a pH of 7.5 can be **calcitrophic**, but are otherwise nutrient-poor (e.g. lime gravel plains in Southern Germany).

When comparing the nutrient conditions, the nutrient reserves must be related to the rooting zone or the soil volume, because there are large differences in density (*fibric peat* around 0.09, *older peat* around 0.12, *fen peat* 0.2–0.4, and mineral soils usually >1.2 g cm^{-3} of the dry matter) and otherwise, especially in the pore-rich bogs, they would be evaluated too favorably.

Drainage promotes subsidence and aeration promotes decomposition and humification. This is associated with **earthification** (structure formation), in which the soil fauna is strongly involved. In terms of German soil classification, a distinction is made between *natural peat soils* and *earthy peat soils* ([German] *Norm-Nieder (Hoch)moor* and *Erd-Nieder(Hoch)moor*). Agricultural use of moors always causes subsidence and peat decomposition (=resource consumption). Under unfavorable conditions, the changes taking place with earthification can also lead to stronger peat shrinking, which in turn can cause hydrophobia and stagnant water (segregation horizon). Such moors that are strongly degraded by tillage are also called **mulm fens**. Peat subsidence and decomposition can reach up to 1 cm annually with drainage and land use. Therefore, land use also leads to a loss of moor areas. In the area of influence of sea water, moors are often saline.

Distribution. Corresponding to their development, the distribution of moors in Central Europe is closely related to the climate conditions as well as the surface terrain after the retreat of the continental ice sheet. For example, most bogs are found in the high-precipitation, coastal areas of the North Sea. Also in the northern foothills of the Alps, extensive moors are found in the area of influence of the Alp glaciation. Outside of the former glaciation zone, smaller bogs are found in almost all low mountain ranges (mountain moors), where high precipitation, high air humidity and terrain with inhibited water outflow enable the formation of ridge, arched and slope fens (e.g. Ore Mountains, Harz, Black Forest, Vosges). Large fen areas mainly formed in ice marginal valleys (e.g. Oderbruch) and flood plains (e.g. Danube moss).

In global terms, moors have their greatest distribution in cool climates. This is associated with the fact that the activity of litter decomposers is more strongly inhibited by low temperatures than plant growth. For this reason, even in continental Antarctica with −9 °C mean annual temperature, shallow moors are still found. On the other hand, fens also developed in wet depressions of the humid tropics and alternate wetting and drying climates.

Cultivation and land use. In the past century, bogs were often used for more or less haphazard peat cutting to extract combustible peat or for extensive peat fire cultivation. Since the 19th Century in Central Europe, there has been systematic cultivation of moors. In Germany, ca. 85 % were affected. Cultivation is generally associated with an improvement of the climate near the soil surface and a more balanced water regime (increased storage capacity, more uniform discharge) and therefore with higher productivity and broader cropping options. On the other hand, moor cultivation has led to the loss of ecologically valuable wetlands. For this reason, an attempt is being made to preserve the remaining areas in a nature-oriented state through nature conservation legislation. There also are projects aiming to restore moors that have been drained and where the peat was harvested by raising the groundwater level.

Following the Dutch example, in the ***Fehnkultur*** (fen cultivation) coming from the 17th Century, the moor was cut down to the mineral soil. The extracted fibric peat is used as

litter and packaging material, for compost processing and as an additive for gardening soils. Humified peat was mainly used as fuel. After the peat cutting, about 5 cm of the *Bunkerde* (dry, strongly humified peat) is spread back on the harvested areas and mixed with the upper 10–15 cm of the underlying sand, which sometimes contains a hardpan horizon. Soils formed in this way are suitable for agriculture.

With **German fen cultivation**, the bog was cultivated directly after drainage and fertilization. In shallow bogs (<1.2 m) with suitable mineral subsoil up to a depth of 2 m, **sand mixed cultivation** (deep ploughing cultivation) was mostly used. Here, the soil was ploughed to a depth of 1.8 m. The produced profile consists of slanted layers of sand and peat at an angle of about 135°, which has good rootability, sufficient natural drainage, and favorable physical properties. The cultivated areas can be used for field agriculture. Drainage of the Northwest German bogs was accomplished by building more ditch networks and drainage pipes or mole drains.

In Germany, the usual methods for fen cultivation were *Schwarzkultur* (black cultivation) and the *Sanddeckkultur* (sand cover cultivation). In the case of **fen black cultivation**, the pure moor soil was cultivated. Because of the high risk of 'becoming puffy' or 'peat rotting' (loss of rewettability after strong desiccation), this method is less suitable for arable land. The **sand cover method** is suitable for arable land use, where a 15 cm-thick sand layer was spread on the moor surface, but in contrast to the **mixed cultivation** of bogs, it was not mixed much with the organic matter of the subsoil.

Fen soils generally do not require liming and also not N fertilization in the first years after cultivation. The *sand mixed cultivation* method was also used on fens.

7.5.21 Cryosols (CR) and Other Soils with Permafrost

References: Tedrow (1966), Campbel and Claridge (1987), Beyer and Bölter (2002) and Kimble (2004).

Cryosols (Fig. 7.20) are soils affected by frost. At least the subsoil is constantly frozen; it is called **cryon** and is designated with an I (ice horizon) or Cf (frozen subsoil). Above this, there is the active layer that thaws in the summer ([Swedish] *Tjäle* = frost). It is often characterized by **cryoturbation** with frost creep, geli- and solifluction (Sect. 7.2.6.2). In the US Soil Taxonomy, they are called *Gelisols*.

In the WRB soil classification, in contrast to the USA, it is only classified with the independent unit of the *Cryosols* if, in addition to permafrost, there are also traces of active cryoturbation in the topsoil. In this case, a distinction is made according to diagnostic horizons, properties and materials (Tables 7.4 and 7.5) between *Glacic*, *Turbic*, *Histic*, *Leptic*, *Salic* and *Umbric* CR etc.

In Siberia, the permafrost reaches depths of up to 1500 m. The summer thaw horizon is 0.1–2 m deep: it depends on the climate, terrain, vegetation and soil properties. Short summer or long snow cover, closed vegetation and thick humus layers (=lower thermal conductivity) as well as water-saturated loamy-clayey soils (=high heat capacity) lead to smaller thawing depths, and sunny slopes and coarse-grained soils have a greater thawing depth.

In the summer, the *Tjäle* is subject to soil development. Low temperatures and daily fluctuations promote cryoclastic weathering as well as cryoturbation, and therefore (despite low temperatures) also chemical weathering and the new formation of minerals (Sects. 2.4.1 and 7.2.1.1). Because the meltwater cannot seep into the frozen subsoil, the soils are often wet and exhibit redoximorphic characteristics (*Reductaquic* and *Oxiaquic CR*). Air and heat deficiency inhibit soil organisms and therefore litter decomposition, so that thick humus layers and therefore *Histosols* also develop. In contrast, slope locations and sandy soil textures prevent water retention: Under such conditions, depending on the substrate, *Gelic Regosols* or *Leptosols* develop and also *Gelic Cambisols* through brunification.

Cryosols are the dominant soils of the Antarctic Islands and are even found on Continental Antarctica. In a semiarid, ice-free coastal

strip, they are found as silty to loamy soils that are strongly mixed by cryoturbation up to ca. 40 cm above the permafrost, while neighboring *Lithic Leptosols* and sandy *Podzols* do not exhibit permafrost and are covered with lichens.

In the extremely **dry valleys** of Continental Antarctica, there are soils with deep cracks filled with eolian sand, just like those that are typical for the driest areas of the Sahara (Sect. 7.5.17). They develop in the same way through crack formation caused by deep-reaching temperatures fluctuations below 0 °C (Tedrow 1966: 61–108), just like those that are typical for many *Albeluvisols* in Northern Germany (Sect. 7.5.6.1). In dry valleys, "*Nitratisol*" are observed in addition to *Gypsisols* (Campbel and Claridge 1987: p. 249ff): These soils probably originate from atmogenic salts, whereby NO_3 was probably formed from N_2 and O_2 as a result of electrical discharge in the atmosphere.

Cryosols and *Gelic* subunits can only be used extensively, in the tundra e.g. as reindeer pasture, and also for forestry in the taiga.

7.5.22 Anthrosols (AT)

Literature: Bakker (1979), Blume and Leinweber (2004) and Wittmann et al. (1997).

Section 7.1.6 described the different ways in which the majority of soils used for agriculture, forestry or horticulture were modified by human interventions. As long as the essential characteristics of the former soils can still be recognized, the formed cultivated soils, which usually have an Ap horizon created by ploughing, are given the name of the original soil type.

In contrast, cultivated soils where the original soil type was completely altered or the entire profile is man-made are called anthropogenic soils or ***Anthrosols*** (WRB; in Germany *Kultosols*). Similar to the naturally developed soils, in Germany a distinction is made between terrestrial, semi-terrestrial and moor *Kultosols*. However, the water balance of hydromorphic and organic *Kultosols* were generally significantly changed with cultivation, so that they often have dynamics similar to the terrestrial soils.

Soils where colluvium accumulated over longer periods due to erosion (also caused by humans) or where plaggen were applied and mixed with the underlying soil by ploughing also belong to the *Kultosols* in Germany.

7.5.22.1 Hortic Anthrosols

Hortic Anthrosols ([German] *Hortisols*) mainly formed in settlements after decades to centuries of cultivation. The strongly humic and crumbly horizon is a result of the strong organic fertilization (sometimes with fecal matter and waste), the deep tillage, the intense irrigation, and the promoted activity of mixing soil fauna (earthworms). In *Hortisols*, the water and nutrient binding capacity was improved compared to the original soil; furthermore, they exhibit high nutrient reserves (especially N and P). Today, they are found in all horticultural regions (e.g. Rheinaue wetlands, old monastery gardens, etc.).

In Germany, ***Rigosols*** are defined as soils that developed through repeated deep soil restructuration. This is the case in vineyard soils, some of which are more than 1000 years old and were formerly trenched manually every 30–80 years, and today mechanically every 20–40 years. Their trenched horizon (R) is 50–80 cm thick, in rare cases up to 120 cm, and contains various amounts of foreign material (rock debris, marl, loess, slags, waste etc.). Deep-reaching trenching was also performed in floodplain soils and marshes, aiming to improve the properties of the topsoil.

In Germany, ***Treposols*** are defined as soils that were deeply trenched once to a depth of 0.7–1.2 m to improve the water and air balance. Morphologic characteristic traits of these soils are oblique layers of the former horizons. The same is true for soils formed by moor cultivation (see also Sect. 7.5.20), which are called sand mixed moors, as well as for soils that were formed after the ripping of *Podzols* to break up the hardpan (e.g. NW Germany, the Netherlands).

7.5.22.2 Colluvic Subunits

In Germany, ***Colluvic* subunits** as ***Colluvisols*** belong to the *Kultosols* in Germany. They consist

of humic soil sediments that were transported by water or wind (then also **eolian colluvial soil**) with a thickness >40 cm, and due to their large distribution in the cultivated landscape, they are treated as an individual soil unit on soil maps. The upper part of the diagnostic, deeply *Humic* topsoil consists mainly of sedimented material, while the lower part mainly consists of native material, because the plough mixes the layers after every sedimentation event. By nature, *colluvium* can cover many different soils, terrestrial soils just as groundwater-affected soils and moors. As relocated arable soils, they are often enriched with nutrients. In the **WRB system**, *Colluvic* subunits are formed depending on the properties of the native soil (e.g. *Colluvic Gleysol*). *Colluvic material* is defined with a thickness >20 cm.

7.5.22.3 Plaggic Anthrosols

References: Blume and Leinweber (2004) and Schnepel et al. (2014).

Plaggic Anthrosols ([German] *Plaggenesch*; [US] *Plagganthrept*) (Fig. 7.16) are mainly found in Northwest Germany, in the Netherlands and in Belgium. ***Plaggen*** or sods are defined as the shallow excavated pieces dug out with a spade or hoe from the strongly humic and rooted topsoil of mineral soils that are vegetated with heath or grass. These sods are used in barns as litter, and then spread along with the contained animal feces and urine on a somewhat more elevated arable field of the village, called the ***Esch***. The original soils on these fields (mainly *Podzols* and *Cambisols*, more rarely also *Luvisols*, *Gleysols*, *(Tidalic) Fluvisols* and *Histosols*) were sometimes previously trenched, dug over or leveled. During the course of the centuries, this artificially raised, grey to brown humic horizon can reach a thickness of 30–120 cm. *Plaggic AT* have a higher plant-available water and nutrient binding capacity than their parent soils. This is particularly true for the **brown** *Plaggic Anthrosols*, where silt-rich grass sods from loess or mud flats were used, and less so for the **grey** *Plaggic AT* of sandy heath sods. Generally speaking, however, the nutrient reserves (esp. N and P) are increased. In contrast, soils where the sod was harvested are depleted.

7.5.22.4 Paddy Soils—Hydragric and Irragric Anthrosols

Paddy soils are often strongly altered by human activities, so that they are also classified as ***Hydragic*** and ***Irragric Anthrosols*** in the WRB among the *Anthrosols*. ***Hydragric AT*** (from [Greek] *hydor* = water, and [Latin] *ager* = field) have a B horizon that is associated with wet cultivation. *Irragric AT* ([Latin] *irrigare* = to irrigate) have an A horizon that builds up gradually through continuous applications of irrigation water containing substantial amounts of sediments. Both are generally soils characterized by redoximorphosis; NN (1985).

Paddy soils are flooded, often for several months, by (a) rainwater, (b) artificial irrigation, (c) artificial raising of the groundwater level or (d) directed flooding by rivers that flow over the banks during the rainy season. The water is generally kept on the fields by dams and infiltration is often impeded by puddling (manual tillage of the water-saturated soil). Already a few days after the soil has been saturated, anoxic conditions lead to the microbial formation of CO_2, H_2S, N_2O and CH_4, especially in the topsoil, which then escape in bubbles. At the same time, the SO_4 and NO_3 ions are reduced, as well as Mn^{4+} and Fe^{3+} ions. Furthermore, the NH_4^+, PO_4 and H_4SiO_4 concentrations in the soil solution strongly increase, while the redox potential strongly decreases (<300 mV at pH 6), which is associated with a rise in pH in acidic soils. During the dry periods, the above-mentioned processes then take place in the inverse direction: The Eh values increase, and the pH decreases. In the process, microbially oxidized Fe and Mn are preferentially precipitated on the surface of desiccation cracks. Therefore, periodic flooding causes strong redoximorphic characteristics.

In the more weakly biologically active subsoil, the redox potential hardly decreases, so that Mn and Fe oxides accumulate at the boundary to the topsoil.

Because puddling destroys the soil structure and soil material is extensively relocated with the building of level plots or terraces, many paddy soils count among soils that were particularly

strongly altered by humans and are still constantly being altered.

Many paddy soils in Southeast Asia are therefore characterized by a more than 50 cm-thick sequence of wet cultivation: at the very top, there is an intensely mixed horizon (puddled layer) with grey reduction colors and rusty aggregate surfaces as well as low bulk density ($d_B < 0.8$ g cm^{-3}), and below this, a compact ($d_B > 1.2$ g cm^{-3}) plough sole with platy structure and rusty aggregate surfaces, followed by an illuviation horizon with strong redoximorphic characteristics, clay humus skins on aggregate surfaces, and secondary accumulation of pedogenic Fe oxides.

7.5.23 "Zoosols" (ZO)

References: Blume (2011), Smith and Smith (2001) and Tatur (2002).

Zoosols are neither part of the WRB nor of the German Classification System.

Zoosols ([Greek] *zõon* = organism) are soils that are either produced by animals, or soils where the morphology has been deeply altered by bioturbation. A distinction can be made between soils that (a) are produced by brush-tailed penguins, or deeply characterized by the activities of other penguin species as well as *weaverbirds*, (b) are deeply altered by bioturbation by earthworms and soil-dwelling mammals, (c) are deeply altered by bioturbation by termites of the alternate drying and moistening tropics or ants in temperate climates, and (d) are deeply altered by bioturbation by lugworms as *Tidalic Fluvisols* (Sect. 7.5.19.3).

7.5.23.1 Soils Produced by Penguins or Influenced by Weaverbirds

Brush-tailed penguins (*Adelie, Chinstrap* and *Gentoo P., Pygoscelis adeliae, antarctica* and *papua*) have produced soils of a depth of ½ to more than 2 m on continental Antarctica and the Antarctic Islands. The birds are 50–90 cm in size and build nests with 15–25 cm Ø made of cobbles near the coast. They eat krill and small fish that they catch in the ocean and feed to their offspring in the nests. Soils developed from excrements and dead young penguins in active rookeries, with a pH($CaCl_2$) of 6.5, around 30 % org. matter with C/N ratios below 2, and BS values above 90 %, should be classified as *Humi-Skeleti-Gelic Zoosols* (permafrost was never found beneath recent or former rookeries: they should therefore not be classified as subunits of the *Cryosols*. Protein-rich feces and dead juveniles are mineralized (thanks to the elevated temperature of the soil warmed by the animals). H_2SO_4 and NO_3 are formed, which increasingly acidify the (initially neutral) soil, while mainly phosphates accumulate. In *Skeleti-Gelic Podzols* of former penguin rookeries in Casey, Continental Antarctic, up to 80 % apatite $Ca(Cl,OH)(PO_4)_3$ was found beside strengite $Fe(PO_4)\cdot 2H_2O$ and vivianite $(Fe[II]_{3-x}Fe[III]_x)(PO_4)_2(OH)_x\cdot(8-x)H_2O$; in *Humi-Gelic Umbrisols* of Arctowski/King George Island, mainly vivianite was found beside variscite $Al(PO_4)\cdot 2H_2O$, apatite, arctowskite $(Al_{8.4}Fe_{0.6})(OH)_3(PO_4)_8$, taranakite $(K, NH_4)_3Al_5H_6(PO_4)_8$, and some amorphous Al-phosphates (Beyer and Bölter 2002, p. 117ff, 128f, 161ff). In addition to the nest-building cobbles and the marine compounds, the soils also contain natural silicate minerals, which were probably carried in by the penguins when they walk around from the coast to the nests. Active colonies are often located at an elevation of several decameters, and former colonies sometimes lie at elevations of more than 50 m, however, this is attributed to uplifting of the islands and of the continent because of the melting of their ice caps during the last centuries and millennia.

Brush-tailed penguins mainly live in colonies of 100 to more than half a million birds around the coast of Continental Antarctic (*Adelie P.*), as well as the Antarctic Peninsula, South Shetland and Orkney Islands, South Georgia, Falkland Islands, Heard Islands and Macquarie Island (*Chinstrap* and *Gentoo P.*).

In hot deserts, e.g. the Namib or the Sahara, there are trees growing in the *dry wadis* with huge nests from ***weaverbird*** colonies, which transform the *Yermic Fluvisols* under their nests into *Humic* subunits with their feces.

7.5.23.2 Soils Formed by Earthworms and Mammals

Deep and strong influence of ***earthworms*** and ***steppe mammals*** such as hamsters, ground squirrels or gophers is a characteristic of many *Chernozems*, *Phaeozems* and *Kastanozems* (Sect. 7.5.5) in the form of *Vermic* properties, i.e. numerous wormhole casts, and/or filled animal burrows in the A and B horizon, together with a stone line beneath the B of soils from gravelly to stony parent materials. Until now, they were classified as ***Vermic*** subunits instead of *Haplic* subunits of ***Chernozems***, ***Phaeozems*** and ***Kastanozems***: degradation to subunits in the WRB 2014 is not considered.

7.5.23.3 Soils Formed by Termites and Ants

In African and Australian savannas and deserts, mainly **termites** as *mouth diggers* burrow several meters deep to bring up moist fine soil material for building mounds on the soil surface as well as for subsurface galleries and chambers. They often formed thick, loose, gravel- and stone-free soils above a buried gravelly and stony layer. In the dry highlands of Namibia, the termites *Macrothermes michaelseni* gather moist soil for building mounds and chambers at depths of several meters, and water from depths of more than 4 m (Blume 2011). Altogether, soils were altered so strongly by termites that they should no longer be classified as varieties of the former soil, but rather according to their Latin name as ***Isoptera-Zoosols***.

Ants of large colonies in European forests can work like termites.

7.5.23.4 Soils Formed by Lugworms

In *Silti-Tidalic Fluvisols* of the North Sea coasts of the Wadden Sea, mainly the **lugworms** (*Arenicola marina*) as geophages constantly mix (Table 7.8) the upper 15–25 cm of the soils with high intensity. They form loose A horizons, which alternate twice a day between moist and dry at low tide, above a layer of coarse sand and mussel shells, similar to the gravel layer of soils formed by termites. The layering of the former *Fluvisol* is completely destroyed by the animals.

Table 7.8 Bioturbation (in kg m^{-2} a^{-1}) in different soils around the world (Blume 2011)

Animals	Ecotope	Quantity
Earthworms	Meadows (UK)[a]	1.8–4.5
Earthworms	Gardens (Centr. Europe)	1.0–2.5
Earthworms	Meadows (Centr. Europe)	0.5–12
Earthworms	Forests (USA)	1.8
Earthworms	Tropics	3.6–27
Ants	Forests, steppes (Europe)	3.1
Ants	Steppes	3.1
Ants	Ants moist area (USA)	2.0
Ground squirrels, susliks	Steppes (Russia)	1.8
Ground squirrels, susliks	Semi-deserts	0.15
Prairie dogs	Prairies	7.0
Moles	Forests (Europe)	0.7–12
Termites	Savanna	1.2–6
Termites	Deserts	0.002–0.5
Lugworms	Mud flats (Europe)	60–300

[a]After Darwin (1881)

7.6 Paleosols on Earth, and Soils on Mars and Titan

Fossil soils ([Latin] *fossilis* = buried) are generally defined as soils that are no longer biologically active and/or are covered with a layer of younger sediment of variable thickness. The soil development therefore came to a halt. If this is not the case, then it is called a relict soil. Fossil soils that were formed in the soil development phases before the Holocene are also called ***Paleosols***. Similar soils were found on the planet *Mars* and moon *Titan*, but until now it is unclear, whether they are *Paleosols* or active soils with life.

7.6.1 Paleosols on Earth

Literature: Bronger (1982) and Felix-Henningsen (2011).

In addition to **recent soils**, which developed under the current constellation of pedogenic factors, there are soils that were formed in earlier geological periods under different conditions. If they are without life and/or were covered by new sediments and interrupted in their further development, these ***Paleosols*** either remained unchanged as **fossil soils** (Bronger 1982), or are found at the surface as **relict soils** and are now subject to soil development under the present conditions (**polygenetic soils**). This either largely eliminated the formerly developed soil characteristics (in Central Europe, e.g. often because of strong clay migration), or preserved them due to their stability to such an extent that the former soil type can still be clearly identified.

Old land surfaces, some of which were already present in the Tertiary or in earlier epochs, are still found today e.g. at higher elevations in tropical regions, or also in temperate humid climate regions, e.g. in large parts of the Rhenish Slate Mountains and other German low mountain ranges. On such land surfaces, the constellation of pedogenic factors changed several times over the course of time, sometimes dramatically. In this way, some of the soils found at these sites were formed by different climate and/or relief conditions. As a product of such **polycyclic** development, the genesis of many soils in the tropics and subtropics is very difficult to identify. Also in Central Europe, there are still remains of soils that were formed during the tropical and subtropical climate periods of the Cretaceous and Early Tertiary (e.g. *Ferralsol* relicts). However, provided that they were not covered, they were subject to renewed pedogenesis under different conditions in the Pleistocene and the Holocene.

During the warm interglacial periods and the shorter interstadial periods of the **Pleistocene** (Table A.1 in the Appendix), soils were formed again in Central Europe, where in many cases, they were covered again during the subsequent glacial period by glacial till deposits, eolian loess deposits or solifluction deposits and were thus fossilized. These ***Paleosols*** are often buried under thick loess deposits, and serve today for research on the geological course of the Pleistocene.

Also on geologically very young deposits, the course of soil development was not undisturbed, as can be seen on the examples of dune sand and calcareous glacial till (see Fig. 7.10). The climate only reached two weak warm maximums during the **late glacials** in the *Bölling* and *Allerød* (Table A.2 in the Appendix), which can be identified in the soils of several parts of Central Europe. In the warmest and simultaneously driest period of the *Holocene*, the *Boreal* (8800–7500 BP), *Chernozems* and *Phaeozems* were formed on some sites instead of *Luvisols* on loess and calcareous glacial till. The development of these soils has stopped since the beginning of the more humid Atlantic and was replaced by pedogenic processes of more humid climates.

Fossil soils always exhibit a profile with horizons, as they are also known from recent soils. Especially the *Paleosols* are usually lacking an Ah horizon, because microorganisms decomposed the soil humus before their fossilization by covering sediments. Figure 7.35 shows the upper horizons of a relict *Petric Plinthosol*, the properties of which can be seen in Fig. 7.26. The Ah and the topmost B horizon

Fig. 7.35 *Petric Plinthosol* from partly eroded "*Stagnic*" *Ferralsol* developed from granite-gneiss as an *Inselberg* (Island Mountain) near Oskote/NE-Bangalore, India. See Fig. 7.26 for properties; photo by H.-P. Blume

were eroded; in the upper dm of the exposed mottled *Stagnic* B, the rust zones with Fe oxides are hardened to plinthite, while the bleached zones consisting of kaolinite are washed out by water and wind. The soil that developed as a "*Stagnic*" *Ferralsol* under humid tropical conditions of the Tertiary with depths of more than 35 m of weathered granite was strongly eroded under the semiarid conditions of the Quaternary and transformed into a *Petric Plinthosol*.

When the age of fossil soils is known, they represent important records of the landscape and Earth history. For example, the investigation of an arable soil under a hedgerow in northwest Germany, Schleswig-Holstein ([German] *Knick* = hedge banks built in the second half of the 18th Century) can reveal the depth of ploughing at the time and whether lime or marl were applied.

Paleosols generally provide evidence for the climate, vegetation and terrain conditions in former times. Thick loess covers both in Central Europe and in Central China have been fruitful research subjects in this respect: They often consist of layers of different ages, where *Paleosols* from different interglacial periods are lying over each other.

7.6.2 Soils on Mars and Titan

References: Jakosky and Phillips (2001), Lexikonredaktion (2006), Schulze-Makuch and Irwin (2008) and Yen et al. (2000).

The exploration of space in the past decades has shown that it is highly probably that two celestial bodies in the solar system were or are biologically active, and therefore exhibit *Paleosols* or even recent soils. This has been known for some time for the planet **Mars**, and recently also for the moon **Titan** of the planet Saturn.

Soils on Mars. Under the influence of solar radiation, Mars has a mean temperature of –55 °C, with a minimum temperature of –133 °C and a maximum of +27 °C, which, compared to the Earth, makes the presence of life forms seem to be basically possible. Its surface exhibits erosion channels from flowing water and craters of extinct volcanoes. Mars has two permanent polar ice caps consisting mainly of CO_2 ice, but also with frozen water. Figure 7.36 shows a part of a channel on Mars with a depth of several decameters, which was probably cut by water erosion, whereby deeply weathered soils were exposed. The red colors of hematite dominate at the top (a). Some white colors follow below (b), followed by black colors (c). Recent investigations on the upper ca. 10 cm of the Mars surface at other sites have revealed high salt concentrations. The color and habitus of (a) apparently correspond to the topsoil, (b) to the subsoil and (c) to the decomposition zone (or saprolite) as well as the basaltic parent rock of a deeply weathered *Plinthosol* or *Ferralsol*, like they were formed on Earth over the course of millions of years under humid tropical climate conditions (see e.g. Figs. 7.26 and 7.35).

In the same way as the listed soils on Earth, the described Mars soils could have developed through the weathering and mobilization of Fe^{2+} ions from silicates containing ferrous silicates, capillary rise (and therefore bleaching of the subsoil) and oxidative precipitation in the topsoil. Weathering through chemical dissolution and capillary rise (as well as the later exposure of the soils by erosion) require water. The oxidation of Fe^{2+} ions in the topsoil requires oxygen. The exceptionally thin atmosphere on Mars today (0.6 % of the pressure on Earth) consists in the bottom area of 95 % vol. CO_2, 2.7 % N_2 and 1.6 % argon, but only traces of water vapor (<0.002 %) and O_2 (0.01 torr). There is a relatively high amount of H_2

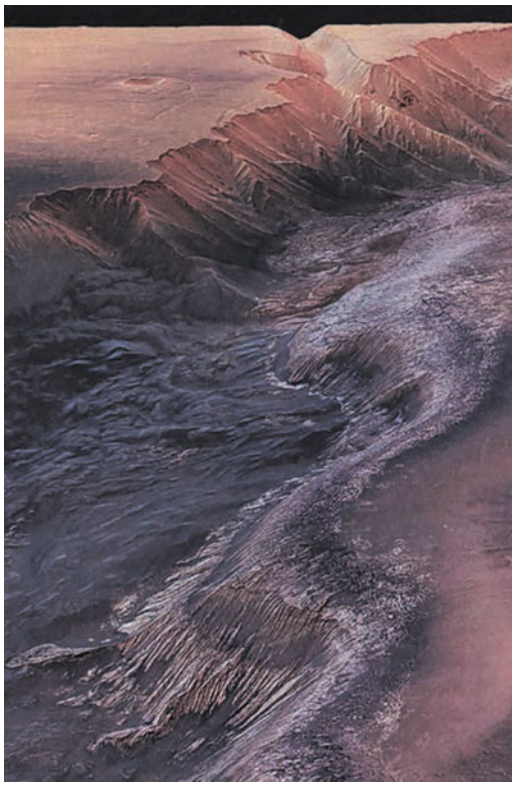

Fig. 7.36 Section of a deep erosion channel on the planet Mars with exposed soil (image taken by *Mars Express* from ESA on 15.01.2004 in the Hellas Basin area)

in the upper atmosphere. This leads to the conclusion that the atmosphere on Mars used to contain more water vapor, and that energy-rich photons from the sun split the water molecules and the fragments escaped into space. The slow desiccation of soils on Mars from the top would also explain the high salt concentrations measured near the soil surface. The former atmosphere on Earth also contained hardly any O_2. It was only really formed ca. 2.7×10^9 years ago through the assimilation by organisms and released into the atmosphere. Since then, iron oxides have formed on Earth. The overall mean temperature of the soil-near air layer on Mars today is below zero. Under former higher temperatures, organisms could have formed oxygen like on Earth, which may have accumulated in the Mars atmosphere and enabled the formation of Fe oxides in the soils on Mars. However, no traces of organic matter have been found in Mars soils until now. The occurrence of superoxide radicals in analyzed soil samples from Mars suggests that there may have been humus in the past (Yen et al. 2000). Abiotic oxidation of dissolved weathering products from ferrous silicates (Lexikonredaktion 2006) is thought to be an alternative to biotic oxidation, but does not offer a plausible explanation for the great thickness of the upper oxidation zone overlying bleached horizons of similar thickness.

In the Central Sahara of SW Egypt, erosion has also exposed deeply weathered *Plinthosols* similar to those in Fig. 7.36, which must have developed under humid climate conditions of the Tertiary. They are also to be considered as *Paleosols* today, because with currently <1 mm annual precipitation, there are hardly any organisms living on or in the soil, except for a few microorganisms that survive on a little dew water at the soil surface on occasional winter mornings. This corresponds to the conditions found on Mars today.

Possible Soils on Titan. Titan is a moon of the planet Saturn. The annual mean temperature at its surface is −180 °C (due to its great distance from the sun). However, similar to Earth, the interior of Titan exhibits higher temperatures, caused by the release of energy with the decay of radioactive elements. At a pressure of 1.47 bar, the atmosphere of Titan consists of 98.4 % nitrogen, 1.6 % methane + argon and traces of organic compounds. Its solid surface exhibits dunes, cry volcanoes and black 'lakes' of liquid hydrocarbons, similar to *Pitch Lake* on Trinidad Island (Schulze-Makuch 2010). Methane in Titan's atmosphere could have also been released by microorganisms, like in the *Asphalt Reductosols* of Pitch Lake (Schulze-Makuch and Irwin 2008).

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Soil Geography

8

8.1 The Pedosphere

Soils are **natural bodies** and as such four-dimensional sections of the Earth's crust, in which the media rock, water, air and organisms are interacting. In doing so, it is important that the soils are populated by organisms. Soils may not be considered as a living organism, but rather as a complex system of pores and solids. Soils consist of four phases: the gaseous, liquid, solid mineral and solid organic phases.

The **pedosphere** comprises all soils as a whole. It is a continuous zone in the upper Earth's crust, the soil cover. It covers the continents and the ground of water bodies. Soil or the pedosphere is found wherever the **lithosphere**, the **atmosphere**, the **biosphere** and the **hydrosphere** pervade. From this perspective, the pedosphere covers the entire globe. Nevertheless, the question should be asked: where is no soil? This is the case where one of the spheres that are required for the pedosphere is not present. In other words, if organisms, water or the atmosphere are lacking on the Earth's surface or in the Earth's crust, there is no soil. These sites are very rare. They are found for example on lava streams that are just cooling down, on the break surfaces of a rockslide, on the surface of glaciers or on a fresh concrete or asphalt road cover. All of these exceptions will sooner or later turn into soil. In other words, development into soil is the normal case on the surface of the earth. This is not the case on the Moon. Here, there is no water, no organisms, and no atmosphere. Because there is only rock and debris, soils cannot develop.

The thickness of the pedosphere can vary. It is often already found on the surface of hard rocks due to the growth of lichens, fungi and mosses; here, the soil cover is limited to a range of a few millimeters. The situation is different on old tropical land surfaces, where weathering and colonization of soils reach depths of up to 30, 40 or 50 m, before unweathered rock is found. Also in many karst landscapes, the influence of soil organisms and the meteorological cycle of water reaches depths of 50 or even 100 m. Compared to the Earth's crust with a thickness of 5–30 km, or compared to the radius of the Earth of 6.370 km, the pedosphere is only a thin skin. Precisely this property, being the skin of the **Earth**, makes the pedosphere so important. All of the substances wanting to reach the Earth's surface or the atmosphere from the interior of the Earth must first cross through the soils and produce interactions. Inversely, the soil also acts as the skin of the Earth by buffering the effects from the universe through energy input, radiation and particle additions. As an important regulator of all processes, the soil cover can therefore have an effect on the Earth's surface and in the Earth's crust. The image of the skin of the Earth can also be transferred to major disasters. If the Earth's skin is destroyed or ripped apart, it can no longer fulfill its function as a filter, buffer and as a habitat. With increasing interference in the soil cover, Man should ask himself, if he wants to and can

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preserve this protective function of the skin of the Earth (cf. Sects. 1.1, 7.1 and Chap. 11).

8.2 Paradigms of Soil Landscapes and Soil Genesis

During the evolution of pedology or soil science, specific basic principles have emerged for the classification of the soil cover. Only developed in the 19th Century, one of the basic principles today is the **profile principle**. Every soil has a profile, i.e., it consists of different soil horizons following each other according to certain principles. For example, a Cambisol exhibits the following horizons: an Ah horizon as a humus accumulation horizon in the topsoil; a Bw horizon that is not affected by humus accumulation, but shows properties caused by other processes such as weathering by hydrolysis, the new formation of clay minerals and iron oxides; and finally the Cw horizon in the subsoil, which mainly consists of only physically weathered rock.

The individual soil horizons are divided into aggregates. Every aggregate of a soil horizon still has all of the properties of a soil. It can be considered as the smallest unit of the soil cover, since it contains a solid, liquid and gaseous phase, it generally contains life, and is naturally also four-dimensional, because it involves the coordinates of space and time. Although the soil constituents include further subdivisions such as soil particles or even molecules and atoms, but these no longer have properties like a soil in the strict sense.

The next significant progress made in soil science was the conclusion that soil distribution depends on the relief within a landscape (**catena principle**). This sequential distribution of soils in the landscape was first discovered by Milne (1935) in East Africa, where he recognized significant differences between plateau soils, soils on slopes and soils in depressions. Today, this would be described as an Acrisol-Luvisol-Vertisol-Catena.

Regarding the need for a higher scale of abstraction in the soil cover, Dokučajev already developed the idea of **soil zones** very early. This idea emerged as Dokučajev was traveling from St. Petersburg via Moscow to the Crimean Peninsular and recognized the different soil developments. From the taiga across the forest steppe, the grassland steppe (prairie), the semi-deserts and finally to the Mediterranean, a zonal pattern was established for the soil pattern based on different factors and also corresponding to the interaction between factor, process, and property. Today, soil zones are belts that stretch around the Earth parallel to the equator, in which the soil factors, especially the climate, vegetation, but also the rock and relief, act in the same direction (Fig. 8.1 Soil zones on Earth).

8.2.1 Basic Principles of Soil Associations

Soils are natural bodies and therefore landscape segments. Within a landscape, soils with different properties that are classified as different soil units are found side by side, and form together a specific soil pattern or a specific soil landscape. The various soils are arranged in specific and often regular patterns in the landscape. The soil cover therefore exhibits a structure that is characteristic for the landscape.

In Central Europe, the structure of many soil landscapes is very heterogeneous, because there are great differences in the soil properties, which is the result of a change in at least one of the pedogenic factors often within a small area (e.g. relief, rock).

The smallest spatial unit of a soil cover is the soil or the **pedon**; it has a base area of about 1–100 m^2 (Fig. 8.2). Neighboring pedons of the same soil form represent a **polypedon** (also called soil body). In soil classification, the polypedons will generally be classified into one soil unit according to the small variation of the properties of their horizons (all pedons of a polypedon should have the same parent material) (Sect. 7.4). As **pedotopes**, however, they also differ spatially in terms of their position in the

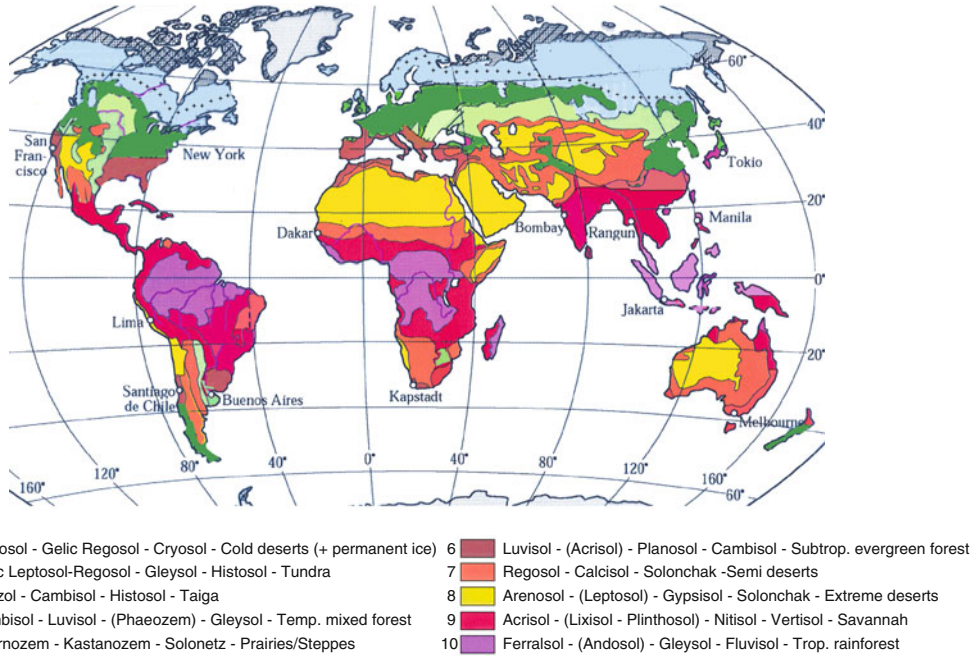

Fig. 8.1 Soil zones of the world (according to Schultz 2008, modified). The permafrost boundary in the northern hemisphere in Zone 3 is marked with ++++

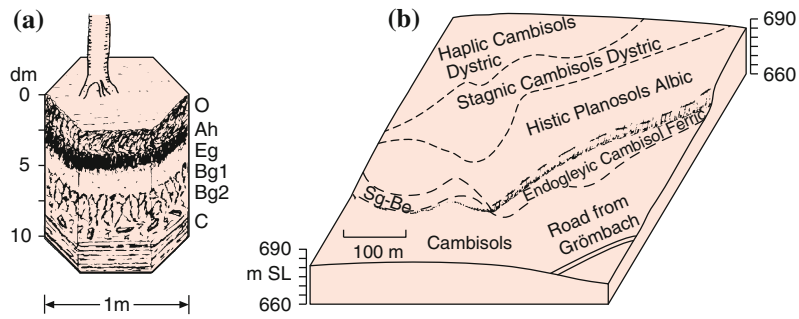

Fig. 8.2 **a** Pedon (Planosol) and **b** section from a soilscape (or microchore) with six pedocomplexes under spruce in a heather (German: Missen) landscape of the sandstone Black Forest; Grömbach, Württemberg (draft by H.-P. Blume according to investigations by V. Schweikle)

relief, surface area and pattern, as well as their association with neighboring pedotopes.

The properties of the pedons in a polypedon only vary within a narrow range (e.g. horizon thickness) due to small terrain irregularities or differences in the parent rock or land use. A polypedon or a **pedotope** is therefore generally the smallest unit of a soil map. Different polypedons alternating over a small area are grouped together in **pedocomplexes**. For example, Fig. 8.2 shows a Planosol unit (German: Stagnogley) as a pedocomplex, with Histic Planosols in small depressions and Endogleyic Cambisols Ferric (ochre) and Dystric Cambisols on more exposed sites with coarser grained rock.

Several polypedons or pedocomplexes form a basic **soil landscape**, or simply soilscape, which, taking account of the spatial conditions (see above), corresponds to the **pedochore** (Fig. 8.3). The different soils (including parent material)

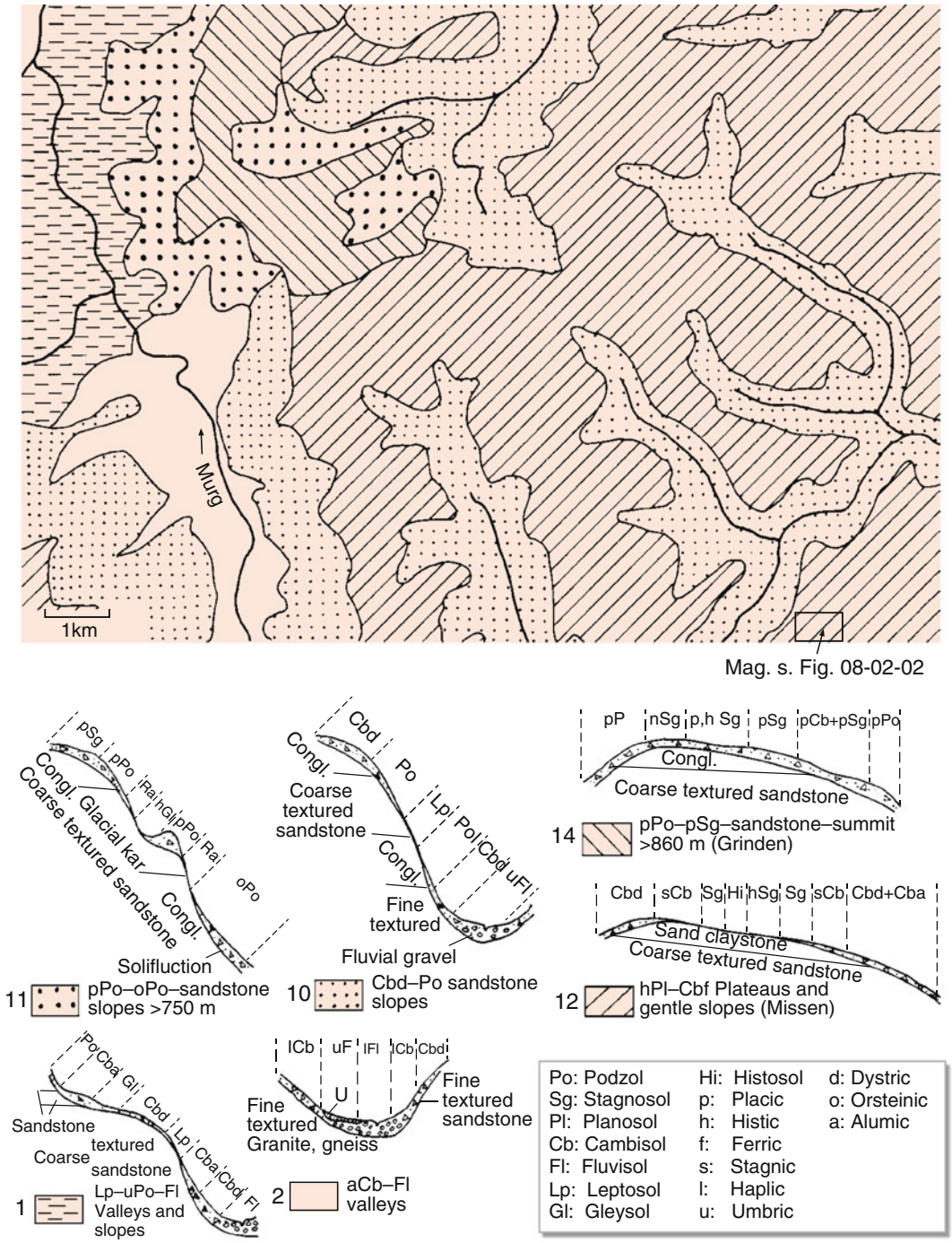

Fig. 8.3 Section from a soil region (or macrochore) of the Black Forest north of Freudenstadt and catenas to identify the spatial structure of their soilscapes (or microchores) (according to H.-P. Blume)

of a soilscape represent a **soil association**. The spatial structure of a soilscape can be best characterized by a **catena**, which reflects the relationships with relief and rock.

The designation of a soilscape may consist of the **index soils** (often the dominant terrestrial and the most common groundwater-affected soil) in combination with the landscape form (geomorphic unit) (e.g. Chernozem—Mollic Gleysol—hills on loess soilscape). Neighboring pedochores have different soil associations. In the simplest case, the difference may only be in variable area proportions of the polypedons, but totally different polypedons can also be observed (e.g. with a change from carbonate rock to sandstone).

Several identical and different soilscapes together represent a **soil region** or a **pedomacrochore** (Fig. 8.4), several regions form a **soil province**, and several provinces form a **soil zone** (Fig. 8.1), which is filled with more and more complex and large-scale soilscapes. These are also characterized by generalized catenas.

The soils of a landscape are often connected with each other through **matter translocations** (mass transfers on slopes, erosion, and translocation of and by slope water, see Sects. 7.2 and 7.3). Therefore, they interact in their genesis. In the soilscape shown in Fig. 8.2, the flow of water from the Fragic Cambisol area leads to increased waterlogging and thus to the formation of Stagnosols and Planosols, while the Fe that was also transported by slope water caused ferrous ochre formation and thus the development of "slope" Gleysols.

The soils of a landscape often share a set of interactions. The **depression structure**, which is affected from alternating sides, is distinguished from the **slope structure**, where the substance transport only takes place in one direction as shown in the example above (Fig. 8.2), and therefore creates a unidirectional coupling. The former is observed e.g. when floodplain soils are covered with erosion material from slopes, and also dissolved substances are transported into the slope soils from the valley with high groundwater levels.

The basic principles of **soilscape systematics** state that the association is characterized by the type of structure, the substrate (rock), and the soil development (soil inventory). At the topmost classification level, a distinction according to the type of structure (see above) is suggested: If there is a **plateau structure** (with a level to slight undulating topography), a mutual influence between the pedotopes of a landscape is largely lacking, or is restricted to short distances. In soilscapes with a **slope structure**, in contrast, there is coupling of the pedotopes going down the slope. The plateau and slope associations should then be subdivided according to rock-specific, geomorphic units, and finally according to specific combinations of different pedotopes. As a matter of principle, associations in depressions (**depression structure**) are characterized by mutual couplings between the pedotopes (see above), however, one direction generally dominates. In doing so, a distinction is made between floodplain, valley, bog and fen, and tidal plain soil associations. **Floodplain associations** include active fluvial flats or dammed plains along rivers; **valley associations** are defined as those of endorheic depressions with lacking or only minimal outflow (e.g. the Podzol-Gleysol-Bog iron Gleysol (German: Raseneisengley) associations in North German lowland sand plains). A **bog and fen association** is typical for large-scale associations characterized by bogs and fens in humid and/or cold regions, while **tidal plain associations** are subject to the influence of the ocean tides with strong translocation of sediments and dissolved substances. Associations that are strongly characterized by surface sealing through human activities (>30 % sealed area and buildings) in urban industrial areas, with an inherent **urban climate** and a high proportion of **Anthrosols**, as well as soils developed on technogenic substrates (Technosols) with a random distribution pattern, are grouped in a special reference group (see Sect. 8.3.2).

Even on plains or plateaus, soils may be coupled with each other. For example, on a forested, completely level ground moraine plate in Southern Germany with Alic Stagnosols, the soils in small clearings were wetted so strongly by throughfall that Fe was reduced and laterally translocated, and led to the formation of

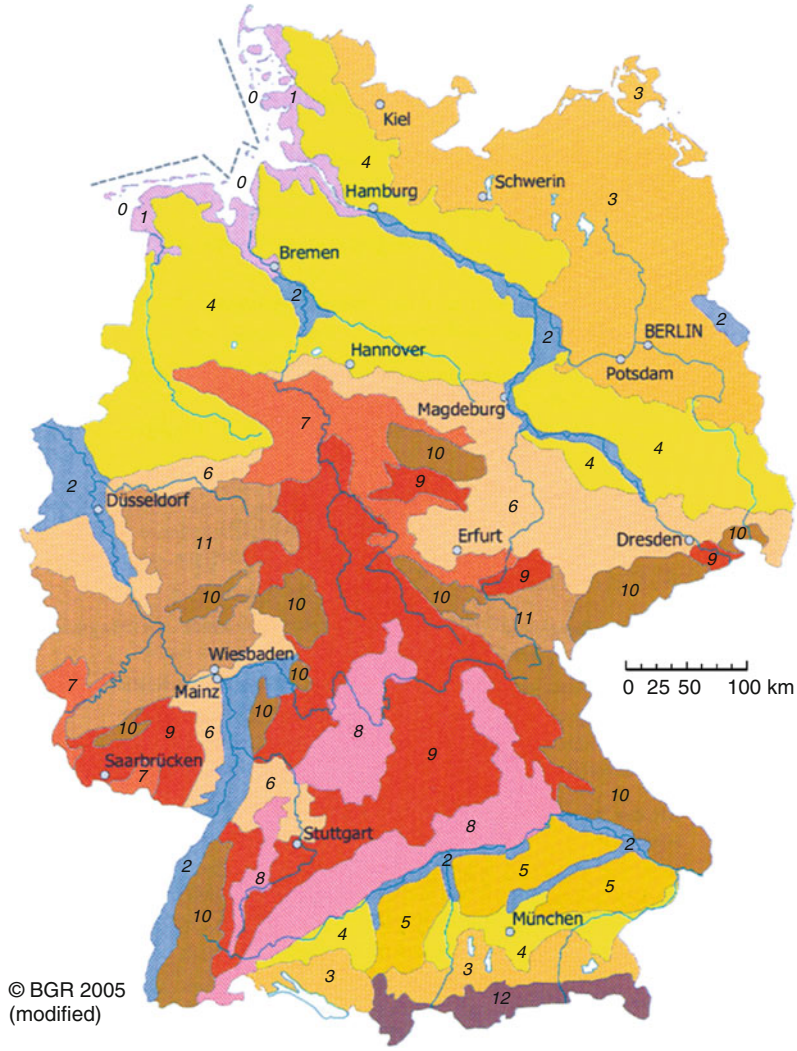

Fig. 8.4 Soil associations in German soil regions (based on: Map of the German soil regions, Ad-hoc Soils Working Group: Bodenkundliche Kartieranleitung, 5th Ed., 2005). *0* Mudflats and beaches—the Coastal Holocene soil region. *1* Marshlands and peatlands—Coastal Holocene soil region. *2* Riparian floodplain soils, Gleysol and Fluvisol—soil regions in the (supra regional) fluvial landscapes. *3* Luvisol, Gleysol and Histosol—soil regions of young (Weichselian) moraine landscapes. *4* Luvisol, Stagnosol (Southern Germany), Albeluvisol Podzol Histosol (Northern Germany)—soil regions of old (Saalenian) moraine landscapes. *5* Luvisol, Pararendzina, Stagnosol—soil regions in the older fluvioglacial terraces and tertiary hilly landscapes in the foothills of the Alps. *6* Luvisol, Calcaric Regosol, Anthrosol and Chernozem—soil regions in loess and sandy loess landscapes. *7* Cambisol, Stagnosol, Podzol—soil regions of loess-influenced mountain and hilly landscapes developed from sedimentary rock. *8* Rendzic Leptosol and Lixisol (Terra fusca)—soil regions in mountain and hilly landscapes developed from limestone. *9* Cambisol, Vertic Cambisol, Luvisol, Stagnosol—soil regions in mountain and hilly landscapes developed from Mesozoic sand-, silt-, claystones and marls. *10* Cambisol, Podzol, Gleysol—soil regions in mountain and hilly landscapes developed from igneous and metamorphic rocks. *11* Cambisol, Stagnosol, Planosol, Gleysol—soil regions in mountain and hilly landscapes developed from quartzite, silty and clayey schists. *12* Rendzic Leptosol, Cambisol, Dystric Leptosol, Gleysol—soil regions of the Alps

Fe-depleted Stagnosols Albic beside concretion-rich Stagnosols Ferric.

The explanation of such correlations is not only important for the understanding of soil and landscape genesis, but also especially for land use and landscape planning. For example, in the case of forest clearing, the slope location of a forested area must be considered, since deforestation causes reduced evaporation and increased surface runoff and leads to water surplus in the depression sites. Thus, in South and West Australia, salts that were previously uniformly (in ecologically insignificant quantities) distributed in all soils of the landscape after clear-cut were concentrated in the lowlands by slope water, resulting in strong salt damage in the vegetation on these sites. This also led to additional erosion damage.

8.3 Soil Association Systematics and Soil Regions of Central Europe

8.3.1 Soil Regions of Central Europe (Fig. 8.4)

The majority of soils are younger than 12,000–15,000 a, because during the last glacial, large areas were covered by glacial sediments and loess deposits, and some older soils were removed by solifluction. The strong differentiation results mainly from petrographic (Fig. 2.2) and geomorphological differences.

The climatic conditions are relatively homogeneous in the temperate humid, oceanic macroclimate. This led to strong acidification and leaching of bases, and in contrast, moderate silicate weathering and clay formation on silicate rocks. Only the elevation zonal pattern and latitude-related trends are also reflected in the soil cover.

In soils on free draining sandy substrates, it often leads to podzolization, and to peat formation in corresponding, slow-draining groundwater-affected soils, while loamy and clay-rich terrestrial soils were subject to lessivage and sometimes stagnation, and Gleysols and Fluvisols developed in the lowlands. **Basin landscapes** in the wind shadow of mountains (e.g. Magdeburg Börde, Thuringian Basin) are drier, so that Chernozem—Mollic Gleysol associations intercalated with Luvisols were formed as a result of strong bioturbation and only slight weathering.

In the **lowlands** (e.g. North German Plain), the climate led to the development of moderately developed Podzol—Cambisol intergrades, Histic Gleysols and Histosols on sandy areas and piled-up dunes in the big Urstrom (glacial outwash) valleys in the drier and continental East, while the more humid and Atlantic climate in the West produced Podzol-Arenosol-Histosol associations, which also include anthropogenic plaggen soils/Plaggenesche. The Luvisols in the Ionian and Calabrian terraces and loess hills exhibit decalcification and lessivage to great depths, and are more strongly intercalated with Stagnosols than those of Tarantian landscapes (soil regions 4 + 5 compared to 3, Fig. 8.4).

The coast of the North Sea is dominated by marsh soils, where those that are close to the ocean as silty Calcaric Gleysols (Kalkmarsch) and Haplic Gleysols (Kleimarsch) are used for intensive agriculture, and those further away from the ocean as older and more clayey Histic Gleysols and Gleyic Stagnosols (Knickmarsch) are used for grassland.

The **low mountain ranges** are dominated by soilscapes from Tarantian mudflows, which also largely cover old terrestrial surfaces. Despite solifluidal mixing, the different magmatic rocks as well as Paleozoic, Mesozoic and Tertiary sedimentary rocks, further differentiated by various added quantities of loess and great differences in relief, created a broad spectrum of different soilscapes. Their diversity can only be shown on large-scale maps.

Especially karstified plateaus of Mesozoic limestones also exhibit older soils, e.g. Luvisols, Lixisols and Acrisols (Terrae fuscae and Terra rossa). The **high altitudes** of the Alps are dominated by immature Leptosols and Regosols, Cambisols and Gleysols. Histosols and Histic

and/or Rendzic Leptosols (Tangelrendzina) or Podzols are often found in pass road locations and near the forest line.

Most Central European soils have been changed to varying extents by human land use.

8.3.2 Soil Regions in Urban Industrial Areas

In urban industrial areas, the environmental conditions as well as the pedogenic factors, i.e. relief, parent rock, climate as well as fauna and flora are intensively altered by human activities (Sect. 7.1.6). As a result, many properties of these soils differ greatly from those of soils in the surrounding area and have an effect on their functions as a site for plant growth, habitat for organisms, contaminant filter and regulator of the landscape's water balance (Chaps. 1 and 11).

For example, the relief was repeatedly strongly changed by removal and addition, cutting and filling. This also led to a removal of soils and refilling of anthropogenic soil substrates and rocks. Landfills from lignite-mining are often rich in coal or pyrite. Technogenic substrates such as building rubble, ashes, slags, sludges, urban waste and thermally cleaned soil substrates (Sect. 2.3.4) were often also landfilled and mixed with each other and with the above-mentioned substrates. Some of these anthropogenic parent materials are already considered as soils and e.g. are designated in the WRB classification as Technosols.

The annual mean temperatures in urban climates are 1–3 °C warmer than in the surrounding area, because domestic fuel, industry and traffic liberate energy, there is less cooling by evaporation, and because large areas are developed and therefore sealed. Here, the differences are less pronounced and less pronounced in lower latitudes than in the middle or higher latitudes. (Arable agriculture is possible at the outskirts of the megacity of Vakuta in N-E Russia, while in the surrounding area, an annual mean temperature of −6 °C due to permafrost make farming impossible.) Contaminants are added to the soils through the polluted atmosphere. It rains a little more, because the air contains more cloud condensation nuclei for raindrops due to the dust. Still, the soils are generally drier, because more water runs off and less evaporates, and groundwater levels are lowered due to groundwater extraction, drainage and substrate infilling. Finally, special uses lead to specific contaminations.

The soils are distinguished according to sealed soils, modified soils with natural development, as well as soils from anthropogenic filling of natural substrates, technogenic substrates and mixtures thereof.

Sealed soils are defined as those that are overbuilt or covered by any kind of pavement. Sealed soils were often previously excavated or compacted to varying degrees. Urban centers and industrial areas are often >75 % sealed. Areas that are covered by buildings or asphalt or concrete are completely sealed, and their soils are therefore fossilized. Areas sealed with paving stones or gravel are porous, so that a certain gas, water and substance exchange with the atmosphere remains possible. These soils often serve as a rooting space for wild plants and urban trees. The sealing substrate provides a habitat (similar to rock outcrops in mountains) for pioneer plants, and can develop into **immature soils** (Sect. 7.5.1.1) Lithic or Histic Leptosols O/C soils (Sect. 7.5.1.3). On some flat roofs, decades of dust accumulation and/or intentional substrate application sometimes even enable the development of A horizons (Mollic Leptosols) under an almost closed plant cover.

As a matter of principle, the same **natural soils** can be expected as in the surrounding area; and therefore in coastal regions and floodplains, different soils compared to elevated lowlands or mountains. City-specific changes then sometimes took place through groundwater lowering, partial excavations, relocation, compaction and surface crusting, incorporation of wastes, dust and contaminant inputs from polluted air, pipeline and tank leaking. Many soils in urban agglomerations are therefore drier and yet have lower air contents (because they are more dense), more alkaline, more eutrophic and polluted and more frequently have disturbed horizons than those in the surrounding area. Oil (e.g. under petrol stations) or gas contaminations (e.g. in case of pipeline leaks

or near organic waste deposits) can cause oxygen deficiency at least intermittently, and can therefore create conditions that are typical for soil with complete reduction (German: **Reductosols**) (Sect. 7.5.1.16). On the other hand, under old parks or gardens, long-term loosening, compost fertilization and irrigation can lead to the development of deeply humic, productive soils: Hortic Anthrosols (Sect. 7.5.5).

As a matter of principle, soils developing from **artificial filling** with **natural substrates** develop similarly to those from natural sediments. Relocated (non-compacted) loess can develop into a Calcaric Regosol within a few decades just like from loess itself. However, landfills from lignite mines can develop into acid sulfate soils (Thionic Fluvisols) with pH-values reaching <3 due to the formation of sulfuric acid (Sect. 7.2.5).

Naturally, the development of soils on **technogenic substrates** strongly depends on the properties of the substrate itself. For example, building rubble (a mixture of bricks and calcareous mortar, which is found over large areas in bombed cities of Central Europe), developed within a few decades into a skeleton-rich Calcaric Regosol or an Urbic Technosol), and with high groundwater tables, into a Gleysol, which is also true for natural glacial till. The porosity of bricks increases the binding of water (however, only part of it can be used by plants), similar to corresponding natural substrates such as freshwater limestone. The same is true for immature soils developed from slags (Spolic Technosol).

Regosols (Technosols) developed from fly ash and fully oxidized sludges have high porosity, air and plant available water. However, similar to those from industrial slags and waste, they are often strongly contaminated with heavy metals and organic pollutants (Garbic Technosol Toxic). Young substrates with higher contents of readily decomposable Organic matter, such as urban waste, sewage, industrial or harbor sludge, exhibit methane fermentation especially in high-density landfills, and lead to the formation of (German) Reductosols (see above) (Sect. 7.5.1.16; Garbic Technosol Reductic), i.e. nutrient and pollutant-rich, but extremely poorly aerated sites.

Soils from sludges and slags are often extremely alkaline (sometimes pH > 10, mainly caused by soda). Long-term wastewater irrigation can also lead to the development of Reductosols; however, it more frequently leads to **irragric** soils strongly contaminated with heavy metals.

Soils developed from anthropogenic deposits can therefore sometimes be extremely acidic, sometimes extremely alkaline, and sometimes extremely low-aerated. These properties are of a transient nature: For example, with the decomposition of organic matter, Reductosols in landfills are transformed into better aerated, deeply humic soils within 40–60 years. In alkaline slags, a lowering of the pH takes place even more rapidly, while the pH-values of acid sulfate soils rise. With increasing age, soils formed on anthropogenic substrates therefore develop more favorable conditions for plant growth and soil organisms.

8.4 Soil Zones of the World

The following describes the most important soils (Table. 8.1 and 8.2) of the individual soil zones (Fig. 8.1) in terms of their relationship with the landscape and their potential land uses. The soils are named according to the international WRB system; any deviating names from the World Soil Map according to the FAO are given in brackets.

The soil regions (some of which still have outdated soil names) can be taken from the World Soil Map published in 1974, which is available on 17 sheets at a scale of 1:5 million, along with the descriptive booklets.

8.4.1 Ferralsols-Gleysols-Fluvisols Soil Zones in the Inner (Humid) Tropics (Rain Forest)

The zones in the humid tropics can be divided into three major landscapes. The old remains of the big southern supercontinent of Gondwana in Brazil, Central Africa and Southern India, which have been weathering since the Jurassic. The large river

Table 8.1 Soil-forming processes in the soil zones (soil zones arranged like in Fig. 8.1)

	Soil zone									
	1	2	3	4	5	6	7	8	9	10
Humus accumulation	−	+	+++	++	+++	+	(+)	−	+	+
Depletion										
Dealkalization	−	+	+++	++	+	++	−	−	++	+++
Decalcification	−	+	+++	++	(+)	++	(+)	−	+++	+++
Desilification	−	−	−	−	−	+	−	−	++	+++
Transformation										
Clay new formation	−	(+)	+	+	+	++	(+)	−	++	+++
Browning/iron oxide form	−	−	++	+++	+	+++	(+)	−	+++	+++
Rubefication	−	−	−	(+)	(+)	++	+	−	+++	+++
Carbonatisation	−	−	−	−	(+)	+	+++	(+)	++	−
Alkalinization	+	−	−	−	++	−	+++	++	−	−
Translocation										
Clay illuviation	−	−	+	+++	+	++	+	(+)	+++	+
Podzolization	−	(+)	+++	++	−	−	−	−	−	++
Wet bleaching	−	++	+++	++	−	−	−	−	++	+++
Gleying	−	−	++	++	++	++	(+)	(+)	+	++
Salinization	(+)	−	−	−	(+)	(+)	+++	++	(+)	−
Turbation										
Cryoturbation	++	++++	++	(+)	(+)	−	−	−	−	−
Hydroturbation	−	−	−	+	+	++	+	−	+++	+
Bioturbation	−	−	−	+	+++	+	−	−	++	+

The number of crosses indicates the intensity of the process − not observed, (+) very weak, +++ very strong

floodplains of the Amazon and the Congo and the young volcanic regions of Central Africa, Indonesia, the Philippines and South America.

The remains of the old continent are dominated by deeply weathered **ferralitic laterite** profiles (Fig. 7.2). The river systems generally cut into the saprolite or even into the unweathered rock. The plateaus are covered with extremely strongly and deeply weathered Ferralsols. At the edge of slopes, they can turn into Acrisols. The upper slope often forms a morphologically emerging stage of plinthite horizons. Plinthosols are found here. Underneath, in the range of the weathering zone, bleached zone and the mottled zone, Ferralsols are found again, which as opposed to the Rhodic Ferralsols on the plateaus, often are Xanthic or Geric. Gleysols are found where streams flow in narrow floodplains. Ferralic Arenosols or even Podzols are found today in regions where the parent material for pedogenesis is Palaeozoic sandstone rather than granite and gneiss.

In the big floodplains, the so-called white water rivers like the Congo and Amazon, where fresh, but usually previously strongly weathered sediments are regularly deposited, young riverbanks with Fluvisols are found, and behind that, low-lying depressions with clayey Gleysols and sometimes Histosols. Rivers that have a very gentle gradient and are retained to some extent by the white water rivers, form black water systems with peaty floodplains (Histosols). The river deltas have fine sulfur-rich sediments from the tropical marsh regions, which are naturally populated by mangrove forests. Here, Thionic Fluvisols and sometimes even Solonchaks are developed.

Younger landscapes in volcanic areas with active volcanism are characterized by Vitric Andosols. These turn into Umbric or Haplic Andosols, and with persistent weathering,

Table 8.2 Index soils (according to the WRB) of the world with fractions of potential arable land (pot. rainfed arable)

Soils	Total		Pot. rainfed arable	
	Mill. ha	(%)	Mill. ha	(%)
Acrisols, Nitisols, Lixisols	1530	11.5	500	15
Andosols	110	0.8	80	2
Cambisols, Umbrisols	1195	9.0	500	15
Chernozems, Phaeozems	415	3.1	200	6
Cryosols	608	4.6	0	0
Ferralsols, Plinthosols	750	5.6	300	9
Fluvisols	335	2.5	250	8
Gleysols	715	5.4	250	8
Histosols	280	2.1	10	0
Leptosols	1660	12.4	0	0
Luvisols, Alisols	744	5.6	600	15
Planosols	125	0.9	20	1
Podzols	490	3.7	130	4
Albeluvisols (Retisols)	315	2.4	100	3
Regosols, Arenosols	1150	8.6	30	1
Solonchaks, Solonetz	430	3.2	50	2
Vertisols	320	2.4	150	5
Kastanozems	470	3.5	100	3
Calcisols, Gypsisols, soils with yermic phase	1280	9.6	0	0
Strongly alternating soil conditions	420	3.1	0	0
Sum	13,342	100	3270	100

Nitisols with deep weathering and lessivage are found, until they also turn into Ferralsols in this soil zone.

Land use: All terrestrial soils exhibit strong potassium and phosphorus deficiency as well as phosphorus fixation. Arenosols seldom carry a fully developed rainforest, because the nutrient deficiency is very severe. Fluvisols and Gleysols, in contrast, are very favored; settlements are traditionally found on Fluvisols, because the rivers also represent the transport arteries. Sustainable horticulture and fruit cultivation can be practiced here. Gleysols and Histosols are less favorable for arable farming, except for crops like paddy rice and sugar cane, because they grow well in marshy areas. The volcanic ash regions are naturally the most fertile, because the soils not only have a high nutrient supply, but also a very favorable structure. Nonetheless, here also, phosphorus fixation and unbalanced mineral composition often lead to specific nutrient deficiencies.

8.4.2 Acrisols-(Luvisols-Plinthosols)-Nitisols-Vertisols Soil Zones in the Outer (Seasonal) Tropics (Savannah)

The characteristic threefold landscape division from the rainforest also continues in the savannah (cf. Fig. 8.1; Table 8.1).

The subhumid and alternate seasonal tropics exhibit a broad range of different soils depending on the rock, relief and especially the age of the stable land surfaces. Strongly weathered and kaolinite-rich Ferric Acrisols and Lixisols are found on the older land surfaces in West Africa, Eastern Brazil or Northern Borneo. Plinthosols are also observed. Younger land surfaces with a more active morphodynamic (SE Asia), as well as landscapes with longer dry periods, are covered with Nitisols and Ferric Planosols, whereby depressions exhibit Gleyic and Stagnic forms.

Vertisols dominate in regions with strong alternate wetting and drying until the arid parts of the savannah, in landscapes with clay-rich weathering, e.g. in Venezuela and India as well as in Sudan and Ethiopia. On substrates with lower clay contents, they are mainly associated with Lixisols under drier climatic conditions, and with Nitisols under more humid conditions; on younger land surfaces also Vertic Cambisols and Chromic Luvisols, and on very old surfaces, Plinthosols are widespread. Here, Vertisols dominate on plains and depressions, while other soils are mainly found on the neighboring ridges. Especially in Asia, the coastal regions are characterized by Gleysols and Fluvisols that are modified by long-term rice cultivation (Anthrosols).

Land use: Plinthosols and Acrisols have very low nutrient reserves and are therefore used for shifting cultivation in South America and West Africa. Under permanent farming, they are more likely to be suitable for Al-tolerant crops such as tea, rubber or oil palm. Lixisols and especially Nitisols are highly productive. Water erosion represents a special problem with arable land use. Despite poor workability, Vertisols are particularly nutrient-rich, fertile sites, which are used for agriculture in the humid savannah and in drier areas with additional irrigation, and otherwise for pasture. The same is true for deeply developed Nitisols and Lixisols.

8.4.3 Regosols-Calcisol-Solonchak Soil Zones in Semi-deserts

The semi-deserts account for about 20 % of the land surface on Earth, and are divided into three different climate areas, which exhibit convergence in terms of their soils. Hot semi-deserts that are dry in the winter are found in the tropics, the most strongly developed being in the northern Sahel zone from Senegal through Sudan towards Somalia. Summer-dry semi-deserts are found in the subtropics, in a belt from the Canary Islands through Morocco, Tunisia, Israel, Iraq and all the way to Pakistan, as well as in large parts of Australia, Mexico and New-Mexico. The third group of semi-deserts is found in temperate climates, from Southern Russia towards the east through Central Asia and up into Mongolia. Such semi-deserts are also found in Patagonia or within the Rocky Mountains, in the northwest USA and in adjacent Canada.

It is important for pedogenesis in semi-deserts that soil development in situ and transport of sediments with wind and water take place regularly at the same times. There is no "undisturbed soil development" like in the humid zones. Despite pronounced carbonate translocation, there are no carbonate-free soils. Clay mineral development tends towards swelling clay minerals like smectite and vermiculite, as well as fibrous palygorskite and sepiolite (German: Meerschaum, Sect. 2.2). Because all semi-deserts were affected by climate change during the Pleistocene, most of the soils are quite young. For this reason, Calcaric Regosols, Cambisols and Arenosols dominate. Calcic Luvisols represent the maximum level of development reached in semi-deserts. Especially in subtropical semi-deserts, a characteristic catena is observed with Calcisols on the plateaus, Petric Calcisols on the upper slopes and Solonetz and Solonchaks in the depressions. Due to the long dry periods in semi-deserts, natural and particularly the anthropogenic salinization reach their maximum.

Land use: Semi-deserts are traditionally used as pasture because their shrub, herbaceous and grass vegetation is diffuse and has a low productivity. About 20 % of the area can be used for dryland agriculture with barley, wheat or legumes. About 3 % of the surface is covered with natural river or spring oases. Because they have been overused since prehistorical times, many semi-deserts are more strongly desertified than would be their natural predisposition. Wind and water erosion as well as salinization are the most important soil degradation processes. Due to the generally high carbonate contents, the phosphorus and potassium availability is low. Trace element deficiencies (Fe, Mn) are widespread.

8.4.4 Arenosol-(Leptosol)-Gypsisol-Solonchak Soil Zones in (Extreme) Deserts (Fig. 8.1)

In the (hot) deserts of the world, a distinction is made between three different broad groups of landscape types, characterized by their parent rock and with their own soil associations (Fig. 7.2):

1. The dune fields or **ergs**,
2. The hard rock plateaus and mountains of the **Hamada** or rocky deserts and
3. The wide plains of the **Serir**, unconsolidated sediments of aquatic and eolian origin, which are cut by wadis and are found in most oases.

By nature, due to their active sand translocation, **ergs** only exhibit incipient soil development. In deserts, sporadic rainfall helped the Protic Arenosols to develop low salinity levels and minimal organic matter contents through temporarily growing algae. Brown or red soils are relicts from more humid climate epochs. Dune valleys often exhibit clayey soils, such as Calcic Cambisols or Gypsic Solonchaks.

Due to their lack of vegetation, **hamadas** are strongly eroded by episodical storm rainfall and wind. For this reason, the surface is generally covered with rocks as **deflation pavement**, under which the bedrock is found in the case of Leptosols, and in contrast, in the case of Leptic Regosols, a 20–50 cm-thick solum is found, which is extremely low in humus and generally contains salts. Only traces of soil formation are found in Lithic Leptosols with Fe/Mn/Si crusts (**desert varnish**) on the rocks, while many Regosols exhibit a typical columnar structure with salt effluorescences and sand-filled desiccation cracks, as well as weak brunification. The bed of the wadis has deeply developed Calcaric Cambisols and Calcisols: Here, the terminal lakes are often rich in clay and silt, and sabkhas (saline clayey plains) in deserts accumulated gypsum (Gypsisols) or salts (Solonchaks), while Playas of extreme deserts developed a columnar structure (Takyr) (Calcaric Sodic Cambisols).

Serirs in deserts are characterized by an association with saline Calcaric Cambisols, Arenosols and Regosols, Calcisols and Haplic Solonchaks, where the salt maximum is found in the subsoil. Gravelly deflation pavements cover the surface of plains, and a shifting sand cover is found in shallow depressions. Former lakes in this landscape are often characterized by extensive sabkhas with extremely salt-rich and/or gypsum-rich Solonchaks or Gypsisols, e.g. in the Salt Lake in Utah and especially in the desert of Gobi. Oasis soils are caused by groundwater, spring water or river water. In addition to Anthrosols, Calcaric Fluvisols and Calcaric Cambisols, they also have Gleyic Solonchaks with a pronounced salt maximum in the topsoil and often also a takyric structure.

Land use: In the desert, only irrigation agriculture is possible, for which only the sandy to loamy-sandy Calcaric Cambisols, Arenosols and Regosols in the Serir landscape can be used, because clay-rich soils are particularly at risk of secondary salinization.

8.4.5 Planosol-Luvisol-(Acrisol)-Cambisol Zones in the Mediterranean Region

The climate in the summer-dry subtropics of the Mediterranean region, as well as coastal areas of Central Chile, California, the Cape Province and Southwestern Australia, are characterized by relatively mild, humid winters and hot, dry summers. Under hardwood deciduous forests, the latter led to the formation of humus-poor, primarily reddish soils with moderate acidification (as Cambisols Chromic) or secondary carbonate accumulation (as Luvic Calcisols) and often strong clay migration (then Luvisols Chromic). Clay-rich, bright red colored Luvisols Chromic on limestone as "**Terrae rossae**" are characteristic for the Mediterranean area. Calcaric Fluvisols are found in floodplains, and also Gleysols and Gleyic Solonchaks near the ocean.

In addition to the Mediterranean regions on the west side of the continents, there are subtropical

areas on the east side of Asia, North America and Australia, which are characterized by summer rain and therefore do not have a drought period. In these areas, mainly leaching, decalcification and acidification are much more advanced, and for this reason, the Luvisols are replaced by Acrisols and Alisols. Andosols are also found in the South of Japan and on the South Island of New Zealand, as well as in parts of the Mediterranean countries.

Land use: The limiting site factor here is the soil water retention capacity: if it is high, good harvests can be obtained and rice cultivation is possible on irrigated valley soils. In contrast, permeable, dry soils only allow for the cultivation of deep-rooting permanent crops (olive, almond, fig, carob, or grapevine). The Mediterranean area was deforested at an early stage, and as a result, the soils eroded and shallow, dry Leptosols only allow for extensive pasture.

8.4.6 Chernozem-Kastanozem-Solonetz Zones of the Grasslands (Steppe, Prairie, Pampa, Veld) (Fig. 8.2)

In soils of the inner-continental basins in temperate climatic zones, humus accumulation through bioturbation plays an important, profile-forming role. Depending on the moisture penetration in the soils, there is another clear soil zonation with Phaeozem, Chernozem and Kastanozem as index types, which is observed in Russia from the north to the south, in North and South America from east to west, and is accompanied by a pronounced vegetation zonation (Fig. 7.3).

Phaeozem-Mollic Gleysol sub-zones In regions with winter-cold forested steppe and 500–700 mm annual precipitation, typical prairie soils dominate the mid-west of the USA and in the Argentinean Pampa with strongly humic, decalcified and brunified Phaeozems, which often exhibit lessivage (=Luvic Phaeozem) and are associated with thick humic groundwater-affected soils (Mollic Gleysols). In the Ukraine and Siberia as well as in Argentina, there are associations with sandy-loamy/clayey Luvisols and waterlogged Stagnic Albeluvisols (Retisol), Ah-bleached Greyic Phaeozems and loamy-clayey, Luvic Chernozems, while the humid depressions are often covered with humus-rich Mollic Gleysols, and with high clay contents, also Mollic Vertisols and alkaline soils (=Mollic Solonetz).

Chernozem-Mollic Gleysol sub-zones In the long grass steppes, the very deeply developed, humic, worm-bioturbated (=Vermic) and often Calcic Chernozems dominate over a broad range of texture from sandy loam to loamy clay. Groundwater-affected soils are also characterized by deeply humic, often calcareous A horizons (=Mollic Gleysols), where the high Na-fraction on the sorption complex leads to weak alkalinization: Mollic Solonetz dominates at higher clay contents.

Kastanozem-Solonetz sub-zone Short grass steppes are dominated by Calcic Kastanozems, which are rich in carbonate or gypsum, depending on the parent material. Vertisols develop on clayey substrates, and calcareous Regosols on sandy substrates, while the depressions are covered with Solonetzes and also Solonchaks. Increasing aridity under herbaceous and desert steppes results in low-humus Calcisols or Gypsisols with carbonate or gypsum accumulation. The rims of the deserts in Australia, South Africa and western China are also characterized by such soils.

Land use: Chernozem zones exhibit the most fertile arable soils in the world. However, drought years suffer from low yields. In terms of the soil properties, many soils both in forest steppes and in short grass and desert steppes are less favorable. Both are dominated by lower humus contents, where the Phaeozems are more nutrient-poor than the Chernozems, while the Kastanozems and especially the Calcisols are too dry and often have Calcic—Horizons (parkland) that impede rooting. However, the Phaeozem zone delivers higher yields than the Chernozems when they are fertilized, because there is enough precipitation even in

dry years. Kastanozem zones are mainly found under pasture: Arable farming is only possible using crops with low water requirements or additional irrigation, however, there is a great risk of secondary salinization.

8.4.7 Cambisol-Luvisol-Gleysol Zone of Temperate Zones (Mixed Forest and Forest Steppe)

Soils in humid-temperate regions were already described in detail in Sect. 7.5, and the soil distribution in Central Europe in Sect. 8.3. The soil zone is found on all continents except in Africa. In Europe, it stretches from Northern Spain up to Russia, and then reaches all the way to Western Siberia in a continuation in the forest steppe with the index soil group **Albeluvisol** (**Retisols**; **WRB 2014**). In Asia, it is found in the North Chinese lowland plain, Korea and Northern Japan, in North America in the North-Eastern US and South-Eastern Canada, in the North-Western US, in Southern Chile, South-East Australia, the Southern Island of New Zealand and Tasmania. The soils are generally young. They have a very close relationship with the parent material. Marls develop into Luvisols, limestones into Rendzic Leptosols and Lixisols, acidic coarse-grained rocks into Dystric Cambisols and Podzols, floodplains develop Fluvisols, Cambisols and Gleysols, in loess landscapes Phaeozems, Luvisols and Alisols, in higher mountains Dystric Cambisols and Umbrisols, in strongly volcanic regions Andosols, and finally in the continuation of the continental forest steppes Albeluvisols (Retisols) and Phaeozems. Stagnosols can develop on flat lands on plateaus of all landscapes.

Land use: Because of the favorable climate and the often quite fertile soils in this zone, the original mixed deciduous forest has been transformed into various forms of agricultural land. Based on the high fertility, and with increasing intensification, maximum yields in plant and animal production are achieved today. However, this form of production has led to strong anthropogenic changes in these soils, so that the fraction of soils eutrophicated by human activities and transformed into Anthrosols and even Technosols is higher than in other soil zones. There is strong erosion in gently rolling loess regions, and in contrast, significant sedimentation on young river terraces and also in deforested floodplains. Special land use problems here are associated with low-lying clayey-peaty sites, such as Vertic Gleysols and perimarine Marshlands. Acid sulfuric acid and sulfidic marshes or riparian floodplain soils with “Maibolt” (jarosite) cannot be used without performing extensive land reclamation measures (Thionic Fluvisol and Thionic Gleysol).

8.4.8 Podzol-Cambisol-Histosol Zone of Boreal Forests (Taiga)

The zones in the boreal forests (taiga) can be divided into soil regions with and without permafrost. In the southern hemisphere, permafrost is only found in the Andes, continental and maritime Antarctica, and on the Falkland Islands.

Regions with permafrost: The continental region of Siberia and the interior of Canada are dominated by Umbrisols and Humic Cambisols, which are associated with Gleysols and Histosols (peatland) in the depressions. In oceanic and perhumid Northern Europe, Eastern Canada and Alaska, in contrast, Podzols and Stagnosols and Planosols are more common. Even though frozen soils dominate in Eastern Siberia, the permafrost is no longer continuous. At least in the upper meters, there is no more permafrost on slopes exposed to the sun and in coarse-grained sandy soils, so that Skeletic and Histic Podzols are also found in addition to Leptosols, Skeletic or Humic Umbrisols or Cambisols, and otherwise Gelic sub-units are found where there is more shallow permafrost. Further in the south, the latter are limited to shaded lower slopes and especially Histosols and Histic Gleysols, while permeable, loamy substrates already developed into Albeluvisols. These soils also exhibit significant signs

of cryoturbation and solifluction as a witness of former permafrost.

Regions without permafrost: In Western Siberia and North-Eastern Europe, loamy Umbric and Stagnic Albeluvisols (Retisols) are associated with sandy Haplic and Gleyic Podzols and Histosols in the depressions. In Canada, depending on the rock, Leptosols, Podzols, Umbrisols or Albic Luvisols dominate; especially regions with dense calcareous glacial till in the Inner Basin (e.g. NW of Great Slave Lake) are covered with Gleysols, Stagnic Luvisols and Histosols.

Land use: The boreal zones are mainly used for forestry: the wood harvest covers about 90 % of the worldwide demand for paper and timber. Particularly outside of the permafrost regions, a cool humid climate enables the cultivation of spring cereals and forage plants in addition to grassland management. To do so, the frequently waterlogged and/or acidic sites require suitable drainage and/or liming.

8.4.9 Leptosol-Regosol-Gleysol-Histosol Zone of the Tundra (Polar Steppe)

The soils of cold steppes (tundra) exhibit a closed vegetation cover (as a result of several months without snow cover and then mean temperatures above +2 °C). Strong cryoturbation, frost blasting and solifluction lead to the formation of Cryosols as frost pattern soils with different characteristics. On hilly terrain, frost debris layers often develop into Leptosols and Regosols with thin Ah topsoils or mor Oh layers, and on favorable sites also Gelic Cambisols. Waterlogging over the permafrost often leads to the formation of redoximorphic Stagnic and Gleyic Cryosols in addition to Gelic Gleysols and particularly Gelic Histosols. Because of ice lens formation, Cryic Histosols are often raised to form palsas, while in broad river plains (e.g. Mackenzie Delta), pingos were formed for the same reason with a height of up to 50 m. There is less cryoturbation in sandy-gravelly parent materials, so that Gelic Podzols develop with a generally thin E and a spodic B horizon rich in humic substances.

Soils formed on recent and old penguin colonies represent a special feature of the south polar latitudes. As 'Ornithosols', the former are rich in nutrients and contain large amounts of apatite, and the latter are often strongly acidic, sometimes podzolized and exhibit strong Al and Fe phosphate accumulation. A high percentage of the area (>20–30 %) can be attributed to the fact that almost only narrow coastal strips are free of ice, and these surfaces were strongly uplifted during the last millennia (>50 m).

Land use: Only small surfaces of the tundra are currently being used extensively as deer or sheep pasture. However, animal grazing and treading on slopes promotes soil erosion, which can be counteracted by N fertilization and thus stabilization of the turf (e.g. in Iceland). In rare cases, small amounts of barley, potato and some forage plants are cultivated for domestic use. However, the unfavorable climate (short vegetation period and low heat) does not allow for intensive plant cultivation and permafrost impedes deeper root systems.

8.4.10 Leptosol-Gelic-Regosol-Cryosol Zone of Cold Deserts

Permafrost is found in the extreme north of America and Eurasia, as well as in Antarctica. Particularly the climatic differences cause various sub-zones with different soil patterns: the polar ice deserts, the Solonchak-Cryosol-frost debris regions, and the Cryosol-Leptosol frost debris regions.

The **ice deserts** dominate in continental Antarctica and in the mountainous regions of the Antarctic islands, but are also commonly found in the Arctic, especially in Greenland. Because snowfall often exceeds snowmelt, they are covered with ice all year round, so that no mineral soils can develop.

The **Solonchak-Cryosol regions** are characterized by an arid cold climate. Low precipitation

(<50 mm, practically only as snow), annual mean temperatures lower than −15 °C, mean temperatures in the warmest month below 0 °C, but the fall winds from neighboring glaciers cause relatively strong evaporation and enable intermittent snow-free conditions. Here, over longer periods of time without vegetation, some areas in the Antarctic cold deserts (Victoria Land, Transantarctic Mountains) developed humus-free, neutral to alkaline Gelic Solonchaks with strong accumulations of atmogenic salts (chlorides near the coast, and nitrates at a distance from the coast). Salic Cryosols are also found. Recent cryoturbation is low, because the water in the relatively dry soils only rarely melts. Sand wedge polygon networks are partially developed (Sect. 7.2.6.4). Cryosols with salt accumulation are also found in small areas in Northern Greenland and N-E Siberia.

Cryosol-Gelic-Leptosol regions exhibit a humid cold climate. With lacking or sparse vegetation (mainly lichen, moss, and algae), intense cryoturbation and strong frost blasting predominantly led to the formation of Cryosols. Frost pattern soils with ice wedges, stone rings and/or nets are commonly found, or garland and stone stripe soils on slopes. Lithigelic Leptosols developed on shallow hard rock. Compared to the soils in the Arctic, the soils of Antarctica are more strongly acidified, because carbonate rocks are largely lacking. Sandy-gravelly soils with more vegetation are partly podzolized, while wet depressions and slope steps may exhibit thin peat (Histosols).

Land use: Biomass harvest is not possible in cold deserts.

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9 Soil-Plant Relations

Soils are the natural sites for all terrestrial plants, which they take up water, oxygen and nutrients from the soil through their root system. This requires good rootability and distance to bedrock (Sect. 9.1). Hence, soils must be able to store sufficient plant available water (Sect. 9.2), provide enough gas exchange (Sects. 6.5 and 9.3) and thermal fluxes (Sects. 6.6 and 9.4), and also contain large enough quantities of available plant nutrients (Sect. 9.5). These properties are significantly determined by the thickness of the rootable soil zone. Because fertile soils are the basis for supplying a growing human population with food and because arable soils are a limited good, they must be protected from damage and destruction, in order to preservetheir fertility and to prevent famine among the population. Their capacity to produce any kind of yield is called **soil fertility** or **productivity** (Chap. 11).

9.1 Rootability and Rooting Zone

Higher terrestrial plants consist of the aerial shoot system and the subsurface root system, whereby the root system usually accounts for 10–20 % of the total plant material in forest trees, 10–50 % in crop plants, and 50–80 % in grassland vegetation. It therefore supplies the main material for organic matter transformation processes taking place in soils (Sect. 3.1), and represents the basis for the development of diverse underground biocoenoses in the rooting zone of soils (Chap. 4). Through photosynthesis, the shoot system builds organic substances, which also supply the root system. The root system is responsible for anchoring the plants, and supplies the shoot system with water and nutrients from the rooted soil zone. In doing so, the roots also absorb oxygen to produce the energy required for metabolic processes from photosynthesis products through respiration. Therefore, **root respiration**, in addition to the mainly oxygen-breathing microorganisms and soil fauna, significantly contributes to the total **soil respiration** and CO_2 release into the pore space (Sects. 6.5 and 9.3).

9.1.1 Root System of Plants and Rootability

The root system of plants is divided into coarse roots (Rc; diameter >2 mm) and fine roots (Rf; <2 mm). Behind the tips of fine roots, there is also a large number of root hairs with a thickness of 5–20 μm and a length of up to 1000 μm, which only remain functional for a few days and then die off. While the coarse and fine roots penetrate into the coarse pores of the soil (diameter >10 μm), depending on their size, the numerous root hairs penetrate into a large portion of the mesopores (2–10 μm). This enables the uptake of water and nutrients especially from the wide mesopores. In the fine pore range (<0.2 μm), these substances only reach the plant roots through slow diffusion processes along

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concentration gradients in the soil solution. In contrast, oxygen is mainly supplied to the roots through the large coarse pores in the soil (>50 µm) and their gas exchange with the atmosphere (Sects. 6.5 and 9.3). Root length density frequently reaches several m per dm^{-3}. Nevertheless, usually less than 1 % of the total accessible soil volume is rooted by plants, up to a maximum of 10–20 % even in the A horizons.

Through longitudinal and radial growth, roots penetrate into the accessible pore space in the soil and absorb the required quantities of water and nutrients. This stabilizes the soil against mechanical influences such as erosion and compaction, whereby the immediate surroundings of radially growing roots are also compressed, and then also act as a support for soil loosening (see Sect. 6.3). For profile descriptions in the field, the horizontal and vertical rooting observed at each plant site is described in terms of the rooting intensity and depth (number of roots per dm^2) for each horizon in the soil profile.

On the one hand, rooting intensity and depth depend on the genetic properties of the respectively cultivated crops or natural vegetation. On the other, they are also affected by a series of other site factors, such as the water and nutrient distribution and the soil space accessibility. In this way, the plant-typical root pattern can be strongly modified e.g. by plow pan compaction and cause sugar beet to develop branched tubers. In Central Europe, deep-rooting crops include e.g. winter wheat, winter rape, sugar beet and especially alfalfa, which can reach available soil water up to a depth of 18–20 dm on loess sites with deep groundwater tables. In contrast, more shallow-rooting crops, especially potato, but also spring barley, maize and field bean only absorb water from a depth of 9–15 dm. Grasses on intensively managed pastures develop their main root mass in the topmost 10–20 cm of the soil, and only few roots reach depths of more than 5 dm. Among forest trees, spruce is a shallow rooter that usually develops its main root mass in the topmost 5 dm of the forest soil, while oak is a deep rooter, reaching depths of several meters. From overall observations, the potential main rooting zone for the water, oxygen and nutrient supply of plants is estimated at 5 dm for intensive grassland, about 10 dm for field crops, and about 15 dm for forest stands.

9.1.2 Potential Rooting Zone

The potential rooting zone of soils is defined as the depth of the potentially rootable soil zone at the respective site, where vertical root growth is not restricted by mechanical or physiological boundaries. Mechanical boundaries include e.g. compacted layers in the topsoil (e.g. plow pan layers) or compacted or hardened subsoil horizons (e.g. hardpan horizons in Podzols), as well as C horizons consisting of over-compacted calcareous glacial till, hard rock or stone layers. **Physiological boundaries for the potential rooting zone** include e.g. water-saturated subsoil horizons with O_2 deficiency (e.g. in Stagnosols and groundwater-affected soils) or also strongly acidified subsoils with aluminum toxicity (e.g. in forest soils). The mechanical and physiological restrictions of the **potential rooting zone** are determined on the soil profile and according to soil analyses (**effective rooting zone**: see Sect. 9.2.1). The rooting zones in the soil are then classified as shallow, intermediate or deep.

In addition to the significance of the vertical rootability (potential rooting zone) for continuous root growth, the horizontal rootability of soils is decisive for the rooting intensity of soil horizons. Unfavorable structural forms, such as coarse polyhedral and prismatic structures in clay-rich soils, only have low coarse pore fractions and therefore impede horizontal root development. A typical example is the pronounced vertical root growth in shrinkage cracks of Vertisols (Pelosols in the German classification systems) with low horizontal rooting intensity.

9.2 Water Supply to Plants

Plants absorb available water from the rooting zone, where the quantity depends on the respective climate, relief and the soil properties.

Water uptake by roots is essentially a passive process taking place through osmotic forces from the soil solution with lower osmotic pressures towards the outer cells of the plant roots with higher pressures. The water molecules travel from the root surface through the cell membrane (plasmalemma) mainly along small, water-specific channels (aquaporins). These channels can be closed under unfavorable conditions, e.g. drought stress, but also as a result of O_2 deficiency in cases of flooding as well as through the effect of several toxic substances, and when they are closed for a longer period of time, it always results in wilting symptoms, regardless of the cause. The further transport of water from the roots into the shoot system is then mainly triggered by transpiration in the leaves and needles (Sect. 9.2.2). The roots of most crops are only capable of absorbing the fraction of soil water that has a higher potential (= lower pF values; Sect. 6.4.2) than the potential at the *PWP* ($-10^{4,2}$ hPa or pF 4.2, see Sect. 6.4.5.1). In addition to the rainwater stored in the soil, water from the groundwater capillary fringe can also reach the rooting zone (see Table 9.1). Both fractions together represent the plant-available soil water. It is one of the most important soil hydrological parameters for the assessment of water balance components (evapotranspiration, groundwater recharge), irrigation requirements, and productivity of a site.

9.2.1 Plant-Available Water

At sites with low groundwater tables, the quantity of plant-available soil water (W_{pl}) corresponds to the water volume inside the effective rooting zone (RZ_e) within the range between field capacity (*FC*) and the permanent wilting point (*PWP*). Making use of easily determined soil parameters, it can be described using the expression:

$$W_{pl}\,(\mathrm{mm}) = [FC\,(\mathrm{mm\,dm^{-1}}) - PWP\,(\mathrm{mm\,dm^{-1}})] \cdot RZ_e\,(\mathrm{dm})$$

The difference in water content between the *FC* and *PWP* is also called **plant-available water** (*PAW*), and when based on the effective rooting zone, it is called *PAW* * *RZ*. For soils with low groundwater tables, the following applies:

$$W_{\mathrm{pl}}(\mathrm{mm}) = PAW\,(\mathrm{mm\,dm^{-1}}) \cdot RZ_{\mathrm{e}}\,(\mathrm{dm})$$

The water contents determined for *PAW* and *PAW-RZ* represent maximum values for the plant-available soil water, which are generally reached at the beginning of the vegetation period in temperate humid climate regions. Under arid

Table 9.1 Mean effective rooting zone (RZ_e) in Central European arable soils, plant-available water (PAW), plant available water in the effective rooting zone ($PAWRZ_e$) and air capacity (AC) for commonly occurring soil textures (medium bulk density) and for peat horizons/moors (after German Soil Mapping System 2005; Wessolek 2007)

Soil texture and abbreviation	RZ_e (dm)	PAW (% vol.)	PAW * RZ_e (mm)	AC (% vol.)
Coarse sand (cS)	5	5	25	34
Medium sand (mS)	6	9	55	31
Fine sand (fS)	6	11	65	29
Loamy sand, sandy loam (lS, sL)	8	16	125	19
Sandy silt (sU)	11	20	220	13
Silt (U)	12	22	240	11
Silt loam (uL)	11	18	200	12
Loam (L)	10	16	160	12
Silty clay loam (ucL)	10	17	170	11
Clay loam (cL)	10	14	140	12
Clay (C)	10	12	120	5
Peat, moor	2–4	50–60	100–240	10–25

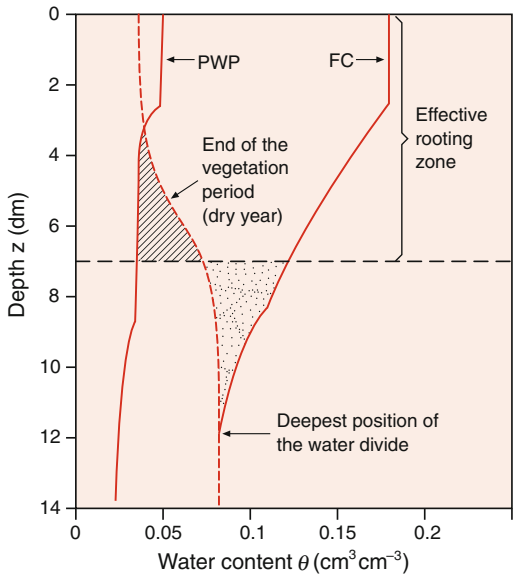

Fig. 9.1 Water contents at FC and PWP for a sandy soil

conditions, in contrast, field capacity is often never reached because of the low amounts of precipitation. The degree of utilization of the available soil water then depends on the rooting intensity and the effective rooting depth at the respective site.

The **effective rooting zone** can be determined by measuring the uptake of water by plant roots during low-precipitation years. Figure 9.1 shows water contents at *FC* and *PWP* for a sandy soil, as well as the water contents reached at the end of the vegetation period. The depth profile of the moisture contents measured at the end of the vegetation period shows that the water content still remaining below a depth of 12 dm corresponds to the field capacity (delta $\psi_H = 0$). This boundary is called horizontal divide. Above this, the still remaining water content is lower than the values for the *FC*, and above a depth of about 3.5 dm, it is also lower than the values for the *PWP*. Plants are only capable of utilizing stored soil water up to the *PWP* in very intensely rooted topsoils (0–3.5 dm), because the flow sections for the water to the root are small, and at the same time, the potential gradient between the root surface and the adjacent soil is high. The lower the unsaturated hydraulic conductivity and therefore also the lower the water content in this water tension range, the steeper the gradient and therefore water uptake is concentrated in a more narrow, root-near area (cf. Fig. 6.30). For this reason, the completeness of water utilization up to the *PWP* depends on the hydraulic conductivity (k_ψ) of the soil horizons and their rooting intensity. Therefore, with increasing depth in the soil, it generally is not the binding strength of water that causes wilting, but rather the lacking accessibility due to insufficient rooting intensity and/or water replenishment.

To enable calculation of the plant-available water volume for all soils based on mappable criteria using the described equation, the boundary for the effective rooting zone (RZ_e) is mathematically defined such that the water volume up to the *PWP* that is still available above this boundary (hatched area) is equal to the lacking water volume up to *FC* beneath this boundary (dotted area). The values given in Table 9.2 for the mean effective rooting zone have been determined for field crops according to this method. The Table shows that the effective rooting zone and the *PAW* strongly depend on the soil texture.

The effective rooting zone also depends on the type of crop. With the same soil texture, it generally increases in temperate climates according to the following sequence: Grassland < arable land < forest (coniferous forest < deciduous forest). For sandy soils, the *PAW* * *RZ* obtained from the values for RZ_e and *PAW* according to

Table 9.2 Depending on the organic matter content and soil texture, humic horizons receive and add-on to their *PAW* (in vol%)

SOM content (%)	mS	sL	uL	U	uL	L	ucL	cL	C
1 to <2	2	1	1	1	1	1	1	1	1
2 to <4	4	3	3	2	3	3	2	3	2
4 to <8	7	6	5	4	6	5	5	4	3
8 to <15	12	9	8	7	8	9	8	7	5

Table 9.1 usually lies between 40 and 135 mm. Due to their high medium pore fraction and large effective rooting zone, loamy and silty soils are characterized by particularly high W_{pl} values (140–240 mm). Clayey soils have average values with about 120 mm. The indicated values are applicable for soil with medium bulk densities. In more dense soils, sands usually have somewhat higher W_{pl} values, whereas silts and clays have lower values; corresponding opposite trends in the *PAW-RZ* are obtained for loose soils.

In addition to the mineral substance, organic matter also binds plant-available water. For example, strongly humified peat horizons in moors have a very high *PAW* (Table 9.1). For this reason, depending on the organic matter content and soil texture, *PAW* may increase by 1–12 % (Table 9.2).

Depending on the respective effective rooting zone, the plant-available water volumes bound by the mineral and organic matter in soils then result in the W_{pl} values shown in Table 9.3 for soils commonly found in Central Europe (field sites).

On soils with very low W_{pl} such as Skeletic Leptosols, Rendzic Leptosols and Podzols, water deficits in drought years lead to yield losses, while deep Cambisols and Luvisols and Phaeozems developed from loess and deep Colluvic Luvisols and Calcaric Fluvisols under temperate humid climate conditions seldom exhibit water deficits.

For the determination of the plant-available soil water in groundwater-affected soils, the **capillary water rise** from the groundwater into the effective rooting zone must be considered in addition to the W_{pl}. It can be calculated for the different soil textures using the Darcy equation (Sect. 6.4.3) under certain assumptions (Sect. 6.4.3.4). Table 9.4 shows the daily rates of capillary rise for common soil textures depending on the distance from the groundwater surface to the lower boundary of the effective rooting zone.

According to Table 9.4, for example, for a medium sand with a distance of 4 dm from the lower boundary of the *RZe* to the groundwater surface, a capillary rise from the groundwater of 1.6 mm d^{-1} can be expected, assuming a matrix potential of −120 hPa (at 70 % *PAW*) at the lower boundary of the rooting zone. For a distance to the groundwater surface of 6 dm, there is only 0.5 mm d^{-1} of capillary rise, which could still be relevant for plants in drought periods. In silt-rich soils, in contrast, there is still significant supply from the groundwater at a distance of 17–25 dm. In loamy soils, a distance of 17–20 dm is still relevant for the water supply, and

Table 9.3 Common values for the plant available water in the effective rooting zone (PAW-RZ_e) of central European soils with different effective rooting zones (RZ_e) as well as different soil textures (gS C) and soil organic matter contents (SOM; Ap horizons, farmland) (after German Soil Mapping System 2005, Wessolek 2007)

Soil type (RZ_e; soil texture; SOM)	PAW-RZ_e (mm)	Evaluation of PAW-RZ_e
(RZ_e 1 to ≤3 dm; sL; SOM 2–8 %) Haplic Leptosols	20–50	(<50 mm) very low
(RZ_e 1 to ≤4 dm; cL; SOM 2–8 %) Rendzic Leptosols	20–70	(50 to <90 mm) low
Podzols (RZ_e 5 to ≤7 dm; gS…lS; SOM 2–8 %)	50–115	(90–140 mm) medium
(RZ_e 10 dm; C; SOM 2–8 %) Vertic Cambisols	125–135	(90–140 mm) medium
(RZ_e 7–9 dm; sL–L; SOM 1–4 %) Cambisols, Luvisols	110–150	(140 to <200 mm) high
(RZ_e 8–11 dm; sL–uL; SOM 1–4 %) Cambisols, Luvisols	150–210	(200 to <270 mm) very high
Phaeozems, Colluvic Luvisols, Calcaric Fluvisols (RZ_e 11–12 dm; uL; SOM 1–8 %)	210–290	(≥270 mm) extremely high

Table 9.4 Rate of the capillary water rise (mm d^{-1}) from the groundwater up to the lower boundary of the effective rooting zone (RZ_e) depending on the soil texture and the distance (dm) to the mean ground water surface (GWS) during the vegetation period (assumed moisture tension at the lower boundary of RZ_e corresponds to that at 70 % *PAW*) (after Renger et al. 1984; German Soil Mapping System 2005; Wessolek 2007)

Soil texture	Rate of capillary rise (mm d^{-1}) at distances (dm) between the GWS and lower boundary of the RZ_e of								
	4	6	8	10	12	14	17	20	25
Coarse sand (gS)	0.5	0.1							
Medium sand (mS)	1.6	0.5	0.2						
Fine sand (fS)	>5	3.3	1.4	0.5	0.2				
Loamy sand, sandy loam (lS, sL)	5	1.6	0.7	0.3	0.1				
Sandy loam, loam (sL, L)	>5	5	2.8	1.7	1.2	0.8	0.5	0.3	0.1
Sandy silt (sU)	>5	>5	4.1	2.7	1.8	1.2	0.7	0.4	0.1
Silt (U)	>5	>5	>5	5	3.3	2.4	1.5	1.0	0.5
Silt loam (sL)	>5	>5	5	2.8	1.8	1.3	0.7	0.4	0.1
Loam (L)	>5	>5	4.2	2.6	1.7	1.1	0.4	0.1	
Silty clay loam, clay loam (ucL, cL)	>5	5	3.1	1.9	1.2	0.8	0.5	0.3	0.1
Clay loam (cL)	>5	3.8	2.2	1.3	0.9	0.5	0.3	0.1	
Clay (C)	1.3	0.5	0.3	0.1					

for clayey soils, only 6–8 dm. With a daily capillary water rise of 2–5 mm, the water supply for plants in temperate humid climate regions with suitably high groundwater tables is also ensured in periods of drought.

For the calculation of the total plant-available soil water volume, the daily rates of capillary rise shown in the Table are multiplied with the duration of the main growth phase (in days) and then added to the *PAW-RZ*. Both together then result in the total quantity of maximum plant-available soil water for groundwater-affected soils. In Central and Western Europe, the main growth period is usually assumed to be of 60–80 days for silage maize, spring and winter cereals, 60 and 90 days for root crops (potato, sugar beet), about 100 days for winter rape, and 120 days for grassland. Therefore, taking account of the plant's water requirements (Sect. 9.2.2), the relevant groundwater levels for the water supply can be calculated for any soil type.

The exploitation of water reserves stored in the soil can be limited in the case of rapid desiccation, because plant roots cannot reach deeper soil zones still holding available water, e.g. if the root system did not develop deeply enough due to plow pan compaction. Many plants on extremely dry sites (xerophytes) increase the accessible water volume by increasing their osmotic pressure. This increases the gradient of the water potential and therefore inflow to the roots. Similarly, halophytes on saline soils have adapted to an osmotic increase in the water potential.

9.2.2 Water Transport in the Soil–Plant–Atmosphere Continuum

In temperate humid climates, the main portion of the solar radiation energy (global radiation) is used for the evaporation and transpiration. Only 2–5 % are used for plant photosynthesis. The flow of transpiration required by plants to maintain their life processes is ensured by the water potential gradient between the atmosphere and the soil, which depends on the irradiated energy. In the absence of plants, this gradient results in water losses caused by evaporation directly at the soil surface. Plants integrate themselves into this system by facilitating the transition of water from greater soil depths into

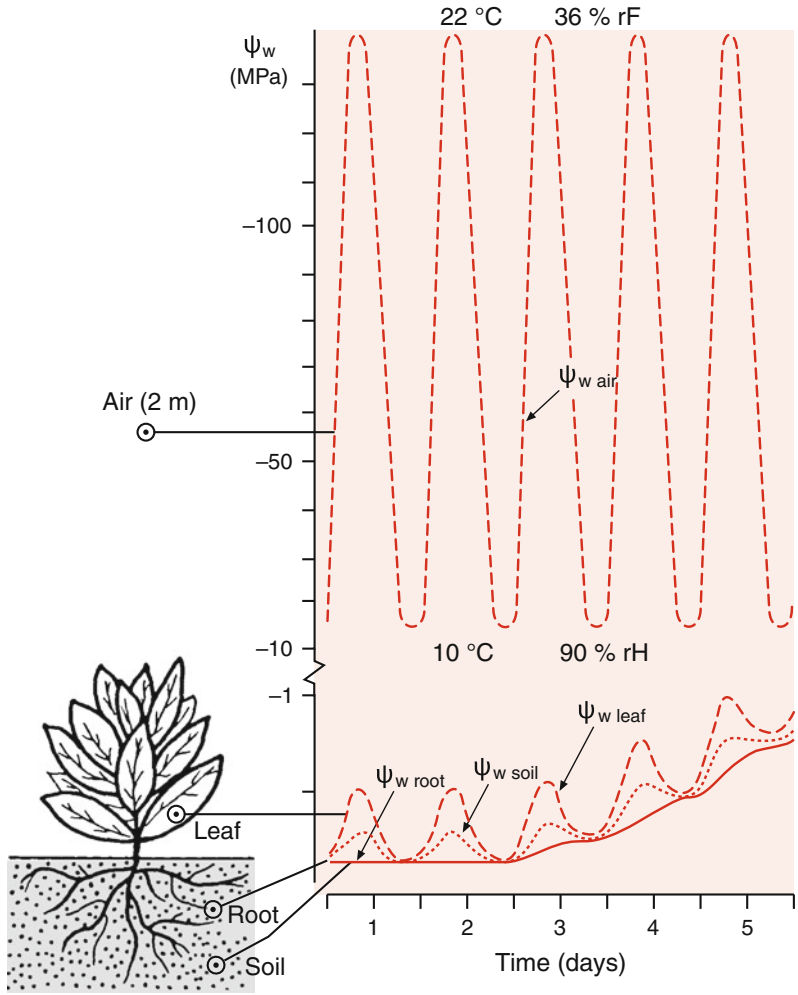

Fig. 9.2 The course of the water potentials (ψ_W) in the soil (ψ_{WS}), roots (ψ_{WR}), leaves (ψ_{WL}) and atmosphere (ψ_{WA})

the soil-near atmosphere through the roots, shoots and leaf surface. They therefore act as a 'bypass', as long as the height of the water potential in the atmosphere, which mainly depends on the irradiated energy, has the character of a depression, and the water potential in the soil has the character of a spring.

The course of the water potentials (ψ_W) in the soil (ψ_{WS}), roots (ψ_{WR}), leaves (ψ_{WL}) and atmosphere (ψ_{WA}) shown in Fig. 9.2 demonstrates that the value in the atmosphere fluctuates much more strongly depending on the time of day than in the soil. The greater the difference between ψ_{WA} and ψ_{WL}, generally the higher the transpiration of the plants standing in between with the water potential ψ_{WR} and ψ_{WL}. In fully developed plant populations, more than 80 % of the global radiation can be used for (evapo-) transpiration.

9.2.2.1 Water Transport to Plant Roots

Water uptake by plants initially causes a decrease in the matrix potential and thus also in the water potential in the immediate surroundings of the roots. The resulting potential gradient towards the root surface causes water to flow back into the less stressed soil volume, like with a drainage pipe (Fig. 6.39). In the main rooting zone, the distance traveled by water until it reaches the root surface is several mm. However, the decrease in the matrix potential in the root surroundings also leads to a corresponding reduction in the

hydraulic conductivity and thus also in the water flow, whereby this reduction is greater the more the hydraulic conductivity decreases with decreasing matrix potential ψ_m. Sandy soils have a particularly unfavorable relationship between the hydraulic conductivity and the water tension. In silt- and clay-rich soils, in contrast, the reduction in the hydraulic conductivity with increasingly negative matrix potentials or lower water tensions is much smaller, especially in the range of higher degrees of desiccation (pF ≈ 3–4; $\psi_m \approx -10^3$ to -10^4 hPa). For this reason, the water supply from the root surroundings to the root surface in silty and clayey soils is less inhibited than in sandy soils at more negative matrix potentials. For plants, a low soil hydraulic conductivity therefore means that the potentially available water is not readily accessible. The lower the unsaturated hydraulic conductivity, the more the roots have to grow towards the water and develop denser roots in order to take up a constant proportion of the plant-available water. In this case, the roots may grow up to 2 cm in depth per day.

9.2.2.2 Water Uptake by Plants

The potential gradient between water in the soil and in the plant resulting from transpiration ensures a constant flow of water from the soil to the plant. With a sufficient supply of water, i.e. with a high matrix potential in the soil, water uptake by plants is mainly determined by the height of the **potential evapotranspiration** (ET_p) (Sect. 6.4.4). With decreasing (more negative) matrix potential in the soil, water uptake by plants is increasingly retarded compared to the potential evapotranspiration, because the hydraulic conductivity is always decreasing and the flow resistance is always increasing. The plant must therefore restrict its transpiration. The remaining lower evaporation is called **effective evapotranspiration** (ET_e).

The correlation shown in Fig. 9.3 between the ratio of the actual to the potential evapotranspiration and the water tension demonstrates that the higher the potential evapotranspiration, the more the effective transpiration decreases with decreasing matrix potential in the soil. With an ET_p value of 6.4 mm d^{-1}, the effective transpiration rate already drops below the potential rate when the matrix potential is −0.015 MPa (−150 hPa). In contrast, if the potential evapotranspiration is 1.4 mm d^{-1}, ET_p and ET_e are equal up to a water tension of about −0.3 MPa (−3000 hPa).

Just like with any other water movement, the extraction of water by the roots of a plant population can be related to the units of the flow cross section and be represented as a flow (see Sect. 6.4.6). The amount (v_R) can then be determined as the difference between the total flow (v_t) and the capillary water flow (v_H) caused by the hydraulic potential gradients delta ψ_H:

$$v_R = v_t - v_H$$

The v_t can be calculated using the continuity equation (Sects. 6.4.4 and 6.7.1) if the water content and water tension in the soil as a function of time and depth are known.

The spatial distribution of water extraction by plant roots changes within the rooting zone. At a comparable matrix potential, water extraction in the upper part of the rooting zone is greater than in the lower part because of the intense root development. With similar rooting intensity, the maximum water extraction is at the depth with the highest water potential (lowest pF value), provided that there are no physiological restrictions due to aeration problems.

If the vegetation only has access to the water volume stored in the soil, it generally means that the zone of maximum extraction is shifted to greater soil depths during the vegetation period. This then leads to an increase in depth of the horizontal divide in the soil as mentioned in Sect. 9.1.2.

In addition to meteorological factors, the height of the effective evapotranspiration depends on the plant-available water in the rooting zone, the supply from the groundwater, and the land use. With the same climate, the effective evapotranspiration in sites with low groundwater tables therefore mainly depends on the plant-available water (PAW) and the land use (Fig. 6.44).

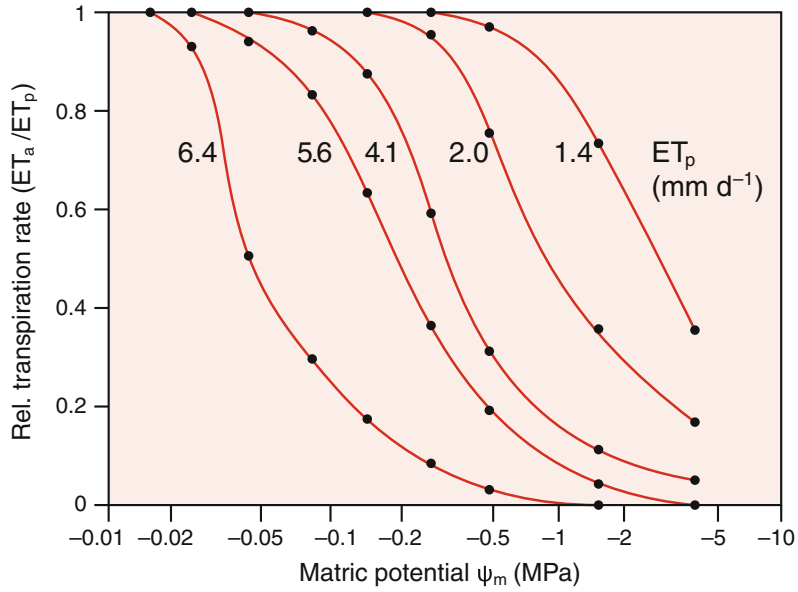

Fig. 9.3 The correlation between the ratio of the actual to the potential evapotranspiration and the matric potential

9.2.3 Water Consumption and Plant Yields

Water consumption by plants during the entire vegetation period and during a single day mainly depends on the irradiated solar energy (global radiation) and other meteorological factors (water vapor saturation deficit in the air, wind influence, advective heat addition), as well as on the type and degree of development of the foliage and the supply of available water in the soil. Especially field trials using large lysimeters deliver realistic values for the water consumption of crops. However, it is difficult to differentiate between evaporation (E) and transpiration (T) in field tests, so that both parameters are usually grouped together as **evapotranspiration** (ET).

Based on the entire vegetation period, most crops in Central Europe have mean ET values of 2–3 mm per day, and forests of about 1 mm d^{-1}. During the main growing period, the evapotranspiration in closed, fully developed crops averages 3.5–4.5 mm d^{-1} and can increase to more than 8 mm on clear summer days, in forests up to 3 mm d^{-1}. By closing the stomata, plants are capable of strongly restricting water evaporation through the stomata on hot summer days. In many temperate humid climate regions like in Central Europe, the average summer precipitation is not enough to cover crop water requirements, so that the water volumes stored in the soil at the beginning of the vegetation period (Table 9.3) and then recharged by subsequent rainy periods have a decisive effect on the water supply for plants and therefore on the soil's productivity.

When all of the other influencing factors are constant, the yields for a specific plant species or variety increase with increasing transpiration, i.e. with increasing water consumption. A comparison of the water consumption by different plants therefore requires a constant, optimal water supply (e.g. through irrigation) for the crops. Table 9.5 shows ET values measured under these conditions of virtually unlimited evapotranspiration ($ET_e \approx ET_p$). These values demonstrate that the height of the ET significantly depends on the length of the growth period.

The evapotranspiration coefficient (ETC) is often used to characterize the efficiency of water consumption by a plant species or variety. It describes the correlation between the effective evapotranspiration (ET_e) and the development of dry mass, and indicates how many kg of water are consumed by the plant to produce 1 kg of dry mass. The evapotranspiration coefficient is specific to each plant species or variety. Especially

Table 9.5 Length of the growth period (germination to harvest), evapotranspiration (ET) and evapotranspiration coefficient (ETC) for different crops in Central Europe under conditions of mainly potential evapotranspiration

Plant species	Growth period (days)	ET (mm)	ETC (kg H_2O kg^{-1} DM)
Welsh ryegrass	349	690	360
Winter rape	321	645	296
Winter wheat	262–300	479–545	330–373
Sugar beet	170–182	396–483	176–311
Spring barley	124–131	334–346	217–225
Silage maize	135	361	191
Potato	104–129	195–380	216–218
Bush bean	68	231	456

Results from the Buttelstedt lysimeter station, Thüringer Basin, Germany; Roth et al. 2005 DM = dry matter

millet and maize, followed by potato and spring barley, have low ET coefficients, whereas winter wheat, winter rape and grasses (Table 9.5), and especially spruce among the forest trees, have considerably higher values and also have an absolute significantly higher water consumption, and thus exhaust the water reserves in the soil more strongly (lower groundwater recharge).

For specific plant species and variety, the water use efficiency also increases with the height of the yield and yield-determining factors, such as the nutrient supply, especially nitrogen fertilization of the crop, and a favorable water supply in the soil. In spring barley, for example, the ETC drops from ca. 350 at 40 dt ha^{-1} to 285 at 70 dt ha^{-1}, and in winter rye without fertilization, from more than 500 to ca. 350 with higher fertilization. The water supply in the soil has a similar effect on the magnitude of the ETC (Fig. 9.4). In maize, the lowest values for (E)TC are measured at matrix potentials in the field capacity range (−100 to −200 hPa; pF 2.0–2.3). With decreasing matrix potentials, the (E)TC then increases; higher water consumption per kg of DM is then required. At matrix potentials > −100 hPa (i.e. in the virtually saturated range), the values for (E)TC then also increase, because with increasing soil moisture, O_2 deficiency causes closing of the water uptake channels (aquaporins) in the roots (Sect. 9.2), and therefore

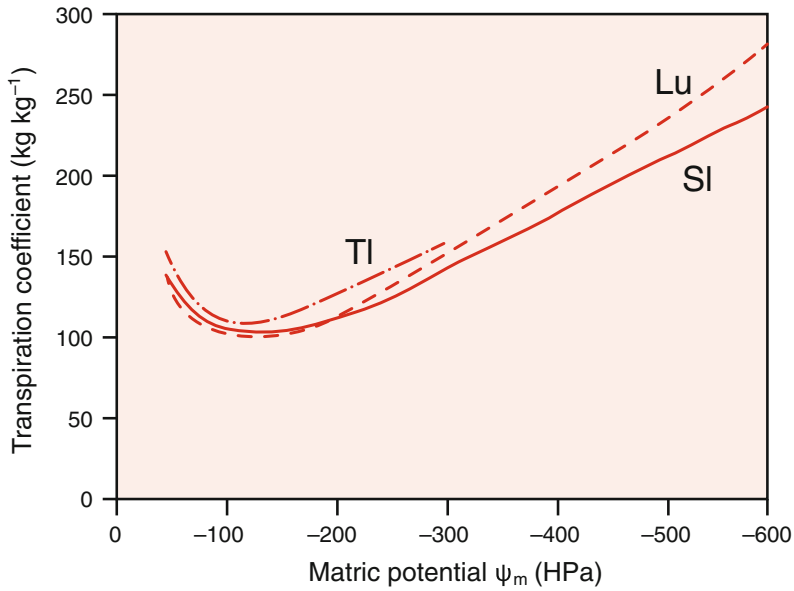

Fig. 9.4 Transpiration as a function of matric potential for different soil textures (Lu = silty loam, Tl 0 loamy clay, Sl = loamy sand

impedes transpiration and substance production. These correlations clearly demonstrate that with a good nutrient supply, favorable water availability and optimal pest control, crop yields increase more strongly than the water consumption, and are therefore overall more water efficient.

In view of the climate change forecasted for Central Europe and other regions, with warmer and drier summers and wetter winters, the water use efficiency during the summer months will probably gain in importance. Optimal transpiration and yield development is possible if the soil moisture in the rooting zone does not drop considerably below 80 % of the *PAW* (Table 9.1). There can be considerable yield losses in the case of longer periods with less than 40–50 % of the *PAW* in the main growth phase, so that irrigation may become increasingly necessary, especially in arid regions of Central Europe. However, it is also not advisable to irrigate too early at the beginning of vegetation, because this may impede root depth development of crops such as winter rape, winter wheat and sugar beet, which are capable of reaching soil water at depths of more than 18 dm.

9.3 Soil Air and Oxygen Supply to Plant Roots

The quantity and composition of the soil air (Sect. 6.5.1) affect both growth and activity of the roots of higher plants, with the exception of swamp plants, as well as the composition and activity of microbial and animal populations in the soil. Most crops require sufficient aeration and oxygen supply for plant roots, to enable root respiration and thus sufficient energy for performing physiological processes, such as water and nutrient uptake by the roots and transport in the shoot system, among others. Root respiration involves the absorption of oxygen entering the soil mainly through diffusion from the atmosphere into the soil air (Sect. 6.5.2), and the release of CO_2 (Fig. 9.5).

9.3.1 Soil Air Budget

Diffusive O_2 and CO_2 gas exchange between the soil and atmospheric air mainly takes place in the large coarse pores (Sects. 6.5.2 and 6.5.3), the volume fraction of which in the total soil volume is called **soil air capacity** (*AC*). Table 9.1 shows that of all soil textures on sites without groundwater, sands exhibit the highest AC (and lowest *PAW*) values. With increasing silt and clay fractions, *AC* decreases strongly; however clays may have very good to completely lacking values. The humus content also influences *AC*, and with medium humus contents of 2 to <4 %, it generally lowers the *AC* in sands by 1 % vol. (and increases *PAW* accordingly), while in loam (Lt, Lu) and silt (Ul, Ut), there is an increase in *AC* by 1–2 % vol., and in clay (Tu, Tl, Tt) by 2–4 %, therefore improving the *AC*. The soil air

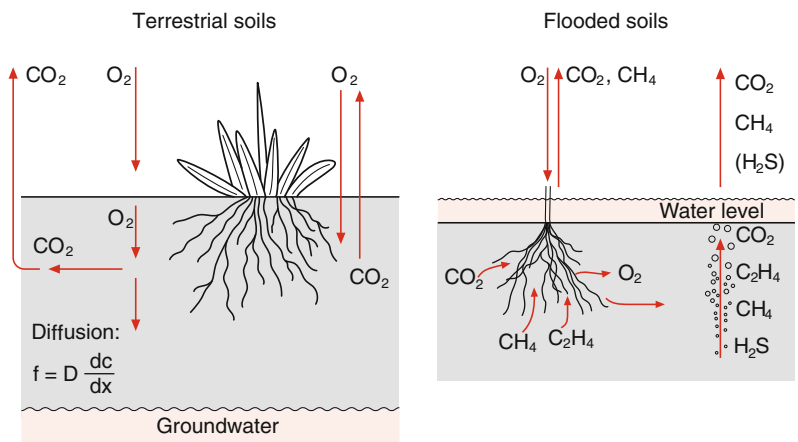

Fig. 9.5 Root respiration involves the uptake of oxygen entering the soil mainly through diffusion from the atmosphere into the soil air, and the release of CO_2

budget is evaluated based on its air capacity from very low (<2 % vol.) to very high (>26 % vol.). In addition to the volume fraction of the soil air, its O_2 content is decisive for the site properties.

9.3.2 Oxygen Supply to Plant Roots

Diffusive gas exchange of O_2 and CO_2 between the soil and atmospheric air increases with increasing air volume in the soil (cf. Fig. 6.50). For this reason, the O_2 supply to the roots can be derived from the respective prevalent air volumes or in approximation from the soil's air capacity (Table 9.1). Furthermore, it can be determined by measuring the **O_2 diffusion rate (ODR**; Table 9.6). An ODR ≥ 0.2 μg cm^{-2} min^{-1} generally ensures sufficient O_2 supply in the rooting zone. Compacted and especially also smeared zones in the soil, such as e.g. plow pans, inhibit diffusion because of their low air contents. In this case, the lower the O_2 concentration above the diffusion obstacle, the more difficult it is to reach the minimum required O_2 supply for the roots of higher plants. Subsoils with stagnating surface water can exhibit ODR values <0.05 (Table 9.6), and Br horizons in Gleysols as well as flooded soils can have values of 0 μg cm^{-2} min^{-1}. The O_2 reduction in the soil air is accompanied by an increase in CO_2, and under anoxic conditions, also ethylene (C_2H_4). As a matter of principle, ethylene can be produced by all plant organs. However, in soils with stagnant water and anoxic conditions, with salt stress or mechanical root damage, the roots of most crops and also anaerobic microorganisms increase their C_2H_4 production (Fig. 9.5). Elevated ethylene contents in the soil and roots can trigger growth inhibitions in crops and a serious change in physiological processes all the way up to the shoot system.

Most agricultural crops will still grow if the O_2 content in the soil air does not drop considerably below the critical value of 10 % vol., and the CO_2 contents are <10 % and the air capacity is ≥5 %. 1–2 % CO_2 in the rooting zone can stimulate root growth; however, significantly higher contents are usually associated with insufficient O_2 supply. The stronger the plant growth, the greater the importance of a high O_2 diffusion rate and thus also a high air volume in the soil for plant development. Waterlogging-sensitive crops, e.g. potato and Brassica roots as well as rye, require sites with a high ODR (Table 9.6) and a corresponding high *AC* (Table 9.1) in the entire rooted zone. Wheat, barley, maize and sugar beet also thrive with medium ODR and *AC*. Pasture grasses generally only require good aeration in the topsoil, so that stagnic clayey soils can also offer good conditions for growth. Several trees suffice with the oxygen dissolved in the flowing groundwater, such as poplars and willows. These trees still exhibit strong growth even when their entire root system is immersed in the groundwater flow.

Flooded and water-saturated soils, in contrast, usually exhibit oxygen deficiency, because the O_2 diffusion from the air into the water-filled pores takes place 10,000 times more slowly than in air-filled pores. Plants adapted to flooding and oxygen deficiency, e.g. rice and other bog and

Table 9.6 Range of O_2 diffusion rates in different soils during the year depending on the soil depth (after Blume et al. 1968)

Parent material	Soil type	O_2 diffusion rate (μg cm^{-2} min^{-1}) at a depth of		
		10 cm	30 cm	80 cm
Loamy till (Glacial period: Riss, Illinoian)	Luvisol	0.2–0.3	0.2–0.3	≈0.05
	Stagnic Luvisol	0.2–0.6	0.05 to 0.1	0.01–0.05
Clayey till (Glacial period: Würm, Wisconsin)	Cambisol	0.2–0.4	0.1–0.3	0.05–0.2
	Stagnic Albeluvisol	0.2–0.4	0.1–0.3	<0.05
	Stagnosol	0–0.2	<0.05	<0.05

aquatic plants, therefore have O_2-conducting tissues (aerenchyma) that conduct atmospheric oxygen through the shoots into the roots and enable their respiration. At the same time, this creates oxidizing conditions in the immediate surroundings of the roots (Fig. 9.5). Under reducing conditions, in addition to CO_2, ethylene (C_2H_4), methane (CH_4) and hydrogen sulfide (H_2S) are formed in the soil (Sect. 5.7) and liberated in the soil-near air. Elevated C_2H_4 contents can stimulate the growth of root hairs in bog and aquatic plants, and accelerate shoot growth, e.g. with rice, so that the assimilation organs remain above water. Already at low concentrations, H_2S has a strong toxic effect on the roots of many higher plants. In contrast, they tolerate larger concentration fluctuations of CO_2 or CH_4. The concentrations of these two gases are therefore important, because they take the place of oxygen in the soil air.

Because oxygen, like all gases, moves fastest in the soil, an increase or decrease in its content can also result in rapid changes of the redox properties and therefore the redox potential of the soil. For example, the processes of nitrification and denitrification closely depend on the oxygen content and the redox conditions in the soil (Sect. 9.6.1).

With drainage, the entry of oxygen in secondary pores at the edges of aggregates results in a rapid rise in the redox potential. However, inside aggregates that are saturated with water for longer periods of time, the redox potential only changes very slowly, because gas exchange is restricted by the low diffusion of oxygen dissolved in the water.

9.4 Soil Thermal Budget, Soil Temperature and Plant Growth

Soil heat as a growth factor for the root system of plants is just as important as the heat of the ambient air for aerial plant parts. The thermal budget also affects growth and activity of the soil biota as well as the rate of chemical processes in the soil. The term "soil heat" represents a complex capacity parameter, while "soil temperature" describes the intensity of the heat and is easy to measure (Sect. 6.6).

According to their thermal budget and soil temperatures, stagnic clayey soils that only warm up slowly in the spring and where the beginning of vegetation is considerably delayed are called "cold plant sites". However, these soils also retain soil heat longer in late autumn. In contrast, dry sandy soils, where the topsoil warms up rapidly in the spring, are called "warm sites". Here, germination and plant growth begin much earlier. However, they also cool down much faster with sinking temperatures (see Sect. 6.6).

Under temperate climate conditions like in Central Europe, the minimum soil temperatures generally affect the site properties more than their maximum temperatures. The boundary of frost resistance during winter dormancy with longer-term soil temperatures is of about −25 °C for rye, −20 °C for winter wheat, and −15 °C for winter barley and winter rape. The resistance boundary for short–term late frosts in the spring is −8 °C for spring cereals, −7 °C for sugar beet, and −3 °C for seed potatoes. In addition to frost damage caused by direct effects on plants, winterkill damage also occurs indirectly through the soil due to frost heaving of the crops, creating a loss of contact between the roots and the soil, tearing of roots and stalks, and desiccation damage as a result of water deficits in frozen soil and higher air temperatures. However, a good crop cover, such as winter rape, reduces penetration depth and impacts of soil frost. Other soil covers also have this effect, such as straw, mulch, foliage, etc. or snow.

Germination and the beginning of plant growth also strongly depend on the soil temperature. The minimum germination temperature is 1–2 °C for rye, 2–4 °C for winter rape, wheat and barley, 6–8 °C for sugar beet, and 8–10 °C for potato and maize. The beginning of plant growth, defined as a net gain in substance, generally takes place at soil temperatures that are 2–3 °C higher. The frost resistance for all crops decreases with the beginning of the growing period; in the case of late frost, the boundary is at soil temperatures

of ca. −4 °C for winter cereals, and +2 to +3 °C for sugar beet. Considerable lowering of temperatures in the rooting zone generally impedes root growth less than shoot growth, which can be inhibited by insufficient nutrient, oxygen and water uptake by plant roots, and then additionally by the synthesis of ethylene precursors in the roots and their transport into the shoot system, resulting in wilting symptoms.

With increasing soil temperature, the water, oxygen and nutrient uptake by the roots increases due to an increase in cell wall permeability with a simultaneous decrease in water viscosity. The optimal soil temperature for root growth is usually lower than the optimal air temperature for shoot growth, e.g. 15–20 °C for potato roots, ca. 25 °C for wheat roots, and 20–25 °C for other central European crops. Root growth is generally considerably reduced at soil temperatures above the optimal value. In Central Europe, heat damage to the aerial plant parts usually occurs at temperatures above 40–45 °C, especially if insufficient water supply to the plants does not provide evaporation cooling to counteract the heat. Altogether, a dense vegetation cover reduces fluctuations in soil temperature, because it reduces heat insulation and heat emission from the soil surface.

9.5 Plant Nutrient Supply

To build organic substances, all plants require carbon and oxygen from the CO_2 and O_2 in the atmosphere and soil air, hydrogen from the soil water, as well as 14–16 other essential elements and a series of beneficial elements from the nutrient reserves in soils. Essential elements, without which plant growth would not be possible, are called essential **nutrient elements** or also **minerals**, because they come from the mineral constituents of soils.

According to the amount of the elements required by the plants, a distinction is usually made between **macro-** and **micronutrient elements** (Table 9.7). **Beneficial elements** promote plant growth and resistance; several can also contribute to the nonspecific functions of essential elements. For some plant species, several elements in this group are also essential, e.g. Si (for rice, horsetail plants) and Na (for C_4 plants, Crassulaceae etc.).

Table 9.7 Macronutrient and micronutrient elements (according to decreasing contents in the plant material) as well as beneficial elements for plant growth

Macronutrient elements	N, K, Ca, Mg, P, S, (Si)Cl, Fe, Mn, B, Zn, Cu, Ni, Mo, (Na)
Micronutrient elements	Si, Na, Al, Co and others
Beneficial elements	

The nutrient elements absorbed by the roots of plants are found in the soil in a specific form (species), e.g. nitrogen as NO_3^- and NH_4^+ ions, phosphorus as $H_2PO_4^-$ and HPO_4^{2-} ions or potassium as K^+ ions (see Sect. 5.1.2). The chemical forms (species) of nutrient elements that can be taken up by the roots are called **nutrients**.

In addition to the elements that are essential and beneficial for plants, animals and human beings also require small amounts of Cr(III), Se, I as well as F, V, Ni, Sn, As and Pb as additional essential micronutrient elements. Several elements such as Br, Sr and Ba are also considered to be beneficial in small amounts. Therefore, a favorable mineral balance in the soil and a corresponding supply to the plants are of great importance for adequate animal and human nutrition. Adequate nutrient supply to the plants can only be achieved if there are balanced nutrient inputs according to "Good Professional Practice" using mineral and organic fertilizer. For this reason, many countries have issued Fertilizer Ordinances defining the legal framework for the use of fertilizers; in Germany e.g. the Fertilizer Ordinance of 2006/2007, which will be referred to in the following examples.

Fertilization adapted to the plant requirements, in addition to a series of other influencing parameters, has contributed significantly to an increase in yields over the past decades. However, it should be kept in mind that not only nutrient deficiencies are detrimental for plant

growth and quality, but an excess of certain nutrients can also have negative effects. Furthermore, nutrient excess may also lead to elevated losses, especially of N and P, from the soils, which can lead to groundwater pollution and the eutrophication of surface waters, as well as to an elevated liberation of environmentally harmful and climate-relevant nitrogen gases (e.g. NH_3, N_2O) into the atmosphere. Precise monitoring of the soil nutrient balance is therefore essential.

9.5.1 Nutrient Contents, Binding Forms and Budgets

The majority of plant nutrients is native to terrestrial soils of Central Europe, i.e. it originates from the soil parent material. The contents of different macronutrient elements for minerals of magmatic and metamorphic origin are shown in Table 2.3, for magmatic rocks in Table 2.8, and for sediments in Table 2.9. The micronutrient element and potentially toxic trace element contents of various rocks are shown in Table 9.16. Another portion of the nutrients enters the soil through fertilization and inputs from the atmosphere and the groundwater when the groundwater surface (GWS) is high.

In soils, nutrient elements are present in the following **binding** forms: (a) dissolved or as soluble salts, (b) adsorbed or exchangeable on the surface of mineral and organic adsorbents, (c) in poorly exchangeable forms, e.g. in the interlayers of clay minerals or in the intraparticulate pore space of Fe, Al and Mn oxides, (d) in the organic matter, e.g. in some heavy metals as complexes/chelates, (e) in the biomass including the microbial biomass, (f) in defined inherent compounds/minerals, and (g) immobile as a lattice component of silicates or Fe, Al and Mn oxides.

The transition of an insoluble or hardly soluble nutrient into a weaker binding form or into the soil solution is called **mobilization** or also **replenishment**, and the inverse process is called **immobilization** or fixation. Dissolved nutrients can be fixed in a readily, poorly or non-plant available form. The terms **desorption** and **adsorption** or sorption are commonly used for exchange processes (Sect. 5.5).

Mineralization refers to the microbial decomposition of organic **matter in soils**, producing simple inorganic substances.

In agricultural soils, the content of plant-available nutrients is of particular significance for achieving sufficient yields. According to the German Fertilizer Ordinance of 2006/07, the nutrient requirements must be determined according to the directives for the respective crops on each field, depending on the soil's nutrient supply. The fertilizer requirements can be determined (a) through soil analyses (Sects. 9.5.2 and 9.5.3), (b) through plant analyses (Sect. 9.5.3), and (c) through legally prescribed nutrient budgets. Compliance with soil and environmental protection regulations requires an almost balanced nutrient budget, resulting from long-term nutrient inputs and outputs. The difference between inputs and outputs characterizes both the nutrient management efficiency and the possible risks for soil fertility (in the case of significantly negative or positive balances), as well as possible pollution of the groundwater, surface waters, and the atmosphere (in the case of significantly positive balances). For example, on a three-year average from 2008 to 2010, a maximum of 70 kg ha^{-1} a^{-1} surplus N may not be exceeded, and for 2009–2011, a maximum of 60 kg ha^{-1} a^{-1}. For phosphorus in soils with an average P supply, the P surplus may not exceed 9 kg P $ha^{-}1$ a^{-1} on a six-year average. Balanced nutrient budgets, calculated from the annual nutrient input and outputs in various forms and related to the total area of a farm (**farm budget**) and to the individual fields (**field budget**), enable ecologically and economically optimized fertilization and land use.

9.5.1.1 Nutrient Inputs

Nutrient inputs in arable soils essentially take place through **mineral fertilization** and **manuring**. On farms with large populations of livestock, considerable amounts of N and P as well as other nutrient elements can be added to the soil with the feed acquired from outside the

Table 9.8 Wet and dry deposition(Mean value and range in kg ha^{-1} a^{-1}) of nutrient elements in the field in different regions of Central Europe (after Gauger et al. 2008, and various other authors)

N[a]	P[b]	S[c]	K
28	0.35	11	5
5–132	0.05–1.2	2–50	0.5–10
Ca	Mg	Na	Cl
6	1	4	8
2–20	0.5–8	1–17	2–25

[a]N as NO_3 + NH_4
[b]P as orthophosphate
[c]S as sulfate

farm through liquid manure, barn manure, compost etc. and through the excrements of grazing animals, and must therefore be accounted for in the nutrient budget. The cultivation of legumes also involves symbiotic N-fixation (Sect. 9.6.1).

Furthermore, sometimes nutrients that are added to the soil through wet and dry deposition (Sect. 10.2.1) from the air must also be considered in budgets (Table 9.8). Higher inputs are mainly observed with nitrogen in regions with high livestock densities and associated high NH_3 emissions, with sulfur near urban agglomerations and industrial areas, and with Na, Mg, Cl, S and B near the sea. Because of the filtering effect of trees, especially with conifers that carry needles year-round, the deposition of substances in forest regions is often 2–3 times higher than inputs on open fields.

For forest trees, the addition of nutrients from the groundwater into the rooting zone can be significant when the GWS is high, and can cover the full spectrum of essential nutrients. Also on arable land, especially in drought years, there can be considerable additions of readily soluble salts from the groundwater. This is particularly significant in lowland plains, flood plains and some coastal regions.

9.5.1.2 Nutrient Losses

Nutrient losses result from (a) the uptake of nutrients by plants when the harvest products are removed, including wood out of forests, (b) washing away with surface runoff, (c) leaching with interflow and groundwater runoff as well as with drainage water, (d) the erosion of topsoil material containing nutrients (Sect. 10.7.1), and (e) in the case of nitrogen and sulfur, also from the dissipation of gaseous compounds (NH_3, N_2, N_2O, NO, H_2S) from soils and from animal excretions into the atmosphere (see Sect. 9.6.1).

The **extraction of nutrients** by plants (Sect. 9.5.3) depends on the plant species, variety and yields as well as the nutrient supply in the soil, in addition to the climatic influences. Vegetation residues (straw, beet leaves, potato leaves etc.) contain considerable amounts of nutrients from the soil, which become available again after mineralization and must therefore be considered in subsequent fertilization. However, a portion of the nutrients is removed through the sale of harvest products from the farm. Also, the portion of nutrients remaining on the farm is sometimes not returned to the same area, and therefore field budgets are also important.

Nutrient leaching takes place under the influence of precipitation with seepage water in the soil. It causes nutrients to be translocated from the topsoil into the subsoil. Nutrient leaching refers to the removal of nutrients from the rooting zone. The amount of leaching depends on the nutrient concentration in the seepage water (Table 5.2) and the seepage water volume. Leaching is not only significant in terms of the loss of readily available nutrients out of the soil, it also affects the quality of surface waters and groundwater. During the transportation of water and substances from the rooting zone to the groundwater surface (GWS), microbial processes (e.g. denitrification), exchange and precipitation reactions as well as dilution or concentration processes (when there is lateral inflow of water from other catchment basins) lead to changes in concentration.

Table 9.9 shows examples for the leached amounts of different nutrient elements and aluminum from a loamy Luvisol and from three adjacent sandy Podzols under different land uses. The arable land was intensively managed and fertilized; the pine site and the hay meadow remained without fertilization. These as well as many other results led to the general conclusion

Table 9.9 Leached quantities of nutrient elements and aluminum (measuring depth 170 cm) out of the rooting zone of a Luvisol developed from loess and out of sandy Podzols in Central Europe (Hannover) on a 3-year average (11.01.1974 to 10.31.1977; average precipitation: 605 mm a^{-1}) (after Strebel and Renger unpubl.)

Soil	Land use	Seepage water (mm)	Leaching (kg ha^{-1} a^{-1})							
			Ca	Mg	K	Na	Al	Cl	SO_4-S	NO_3-N
Luvisol	Rainfed arable/ Arable land	94	262	23	<1	36	–	215	72	31
Podzol 1	Rainfed arable/ Arable land	252	199	16	36	28	–	135	49	9
Podzol 2	Hay meadow	255	45	2	30	6	–	21	36	5
Podzol 3	Pine forest	215	28	5	20	28	39	74	83	9

Luvisol: pH ($CaCl_2$) 7.5; $CaCO_3$ 0.2 %; field capacity 350 mm per 100 cm of depth
Podzols: pH ($CaCl_2$) 5.5–4.5, field capacity 120 mm per 100 cm of depth

that leaching in temperate humid climate regions is greater on arable land than in forest soils, caused by greater reserves of readily mobilized nutrients in the soil and often higher seepage rates. In forest soils, the generally strong acidification and the input of strong acids and acid producers from the atmosphere (especially HNO_3 and NH_4^+) have a dominant effect on leaching (Sect. 10.2.1). It also increases with increasing amounts of seepage water. The soil texture also influences the leaching rate. With the same amount of precipitation and otherwise constant conditions, the higher the field capacity and thus the water storage capacity of the soil, the later the translocated substances reach a specific depth. In the examples shown in Table 9.9, the transport time from the soil surface down to the measurement depth of 170 cm was less than one year in the Podzols, and in contrast, more than four years in the Luvisol. Therefore, in soils with higher field capacity, several maximums in the concentrations of readily soluble nutrients can be observed in the rooting zone, e.g. of NO_3–N (Fig. 9.9d), which can be attributed to the fertilization in different years and can still be significant for the plant nutrient supply.

For cationic elements, **Ca leaching** in soils of temperate humid climates is particularly high especially in soils containing $CaCO_3$ due to carbonate dissolution as well as in carbonate-free soils with high Ca saturation (up to 350 kg ha^{-1} a^{-1}), and in contrast, it is low in very strongly acidified forest soils (up to <15 kg ha^{-1}). With the addition of cations and anions through mineral fertilizer, e.g. with KCl fertilization, the sorption of K^+ ions mainly leads to desorption and leaching of Ca^{2+} ions together with Cl^- ions. In contrast, **Mg leaching** is generally much lower (up to 35 kg ha^{-1} a^{-1}) due to the lower Mg saturation in soils. It is low particularly in acidic sandy soils with low contents of Mg silicates (Table 9.9). In agricultural loess soils as well as in other clay-rich soils, **K leaching** is low due to their high K fixation capacity (especially in the subsoil) and is usually less than 5 kg K ha^{-1} a^{-1}. In clay-poor sandy soils and organic soils, in contrast, it can reach more than 50 kg K ha^{-1} a^{-1} with high K fertilization (Sect. 9.6.4). The leaching of **Al ions** only plays a significant role in strongly acidic soils (pH ≤4.5) and therefore especially in forest soils (Sect. 5.6.3).

For anions, field sites in temperate humid climate regions usually have the highest amounts of nitrate (Sect. 9.6.1) and chloride leaching. **Cl leaching** (<15–220 kg ha^{-1} a^{-1}) is essentially attributed to Cl input with K fertilization (Table 9.9, cf. fertilized arable land and unfertilized hay meadow). Until the end of the 1980s, **sulfate leaching** (Sect. 9.6.3) in field and forest soils of Central Europe was mainly attributed to high SO_2 emissions and the associated SO_4^{2-} deposition from the atmosphere (Table 9.9). Today, the input of S through the air and therefore also S leaching are strongly reduced. Thus, S leaching on central European arable land (20–80 kg ha^{-1} a^{-1}) mainly depends on the amount of S fertilization. Due to the strong sorption and fixation of phosphate in loamy and clayey

Table 9.10 Leaching of cationic micronutrient elements from arable land (unpublished results from Limburger Hof; Schimming 1991) and forest soils with beech and spruce stands of Central Europe (Mayer and Heinrichs 1980; Schimming 1991)

	Leaching (g ha^{-1} a^{-1})			
	pH	Mn	Cu	Zn
Arable soils	7–5	1–800	5–94	10–360
Forest soils	5–3	50–9300	2–110	140–2400

mineral soils, **P leaching** with seepage water is generally low (<1 kg P ha^{-1} a^{-1}). However, in sandy soils where the P binding capacity is exceeded due to long-term high inputs of mineral and organic fertilizers, and in soils with high preferential water flow, there can be significantly higher P leaching in dissolved and colloid form (up to >6.5 kg P ha^{-1} a^{-1}). There may also be stronger P leaching (5–15 kg P ha^{-1} a^{-1}) in peat soils, due to the low content of mineral sorbents.

The leaching of cationic **micronutrients** is low in alkaline to weakly acidic soil of temperate humid climate regions, because these pH values promote strong adsorption or fixation in the form of poorly soluble compounds. Leaching increases with decreasing pH, as can be seen in the comparison of field sites and more strongly acidic forest stands shown in Table 9.10. Soluble organic (complexing) ligands (Sect. 5.3.2) promote the mobilization of cationic micronutrient elements and increase their leaching, and anoxic conditions and reduction processes also promote the leaching of manganese and iron (Sect. 5.7.4).

9.5.2 Nutrient Availability and Nutrient Supply in Soils

Usually only a very small fraction of the total amount of nutrient elements contained in soils is present in the soil solution in a form that is directly plant-available. Significantly larger amounts are generally bound to soil solids in readily mobilized form (e.g. exchangeable K^+), moderately mobilized form (e.g. K^+ on the interlayer edges of illites), and poorly mobilized form (e.g. K^+ as lattice components of feldspars). The availability of a nutrient element therefore depends on the following factors (Fig. 9.6):

- The concentration or better the activity (=effective concentration) of the chemical forms (species; see Sect. 5.3.2) of a nutrient element in the soil solution, also called **intensity**. In addition, the relationships of the different nutrient and contaminant element species in the soil solution, as well as the formation of ion pairs, complexes and chelates are also significant.
- The total available quantity of a nutrient element or the amount in the solids of the rooted soil zone that can be mobilized (reserve) during a vegetation period, also called the **quantity**.
- The rate of replenishment from the available reserves of the solids into the solution phase or also vice versa, e.g. on the rate of fixation of dissolved fraction by the solids after the addition of soluble nutrients through fertilization. These transitions between solution and solid phases mainly involve adsorption (sorption), desorption and diffusion processes. In addition, the transport rate of nutrients to the plant root through mass flow with the soil solution and through diffusion in the soil solution is decisive.
- The mobilizing ability of the plants, which is determined by, among other things, the rooting density (cm of roots per cm^3 of soil), the type and quantity of mobilizing root exudates, and also by diverse microbial mobilization processes in the immediate surroundings of the root, the **rhizosphere**.

Among these influencing parameters, the **correlations** between the solution concentration (or activity) of a nutrient or also of a potentially toxic element (=intensity) and the total amount that can be mobilized (=quantity) are described using so-called **adsorption isotherms** (Sects. 5.5.6 and 9.6.4), which are therefore also called **quantity/intensity correlations** (Q/I correlations) (see curves in Fig. 5.13). The slope of

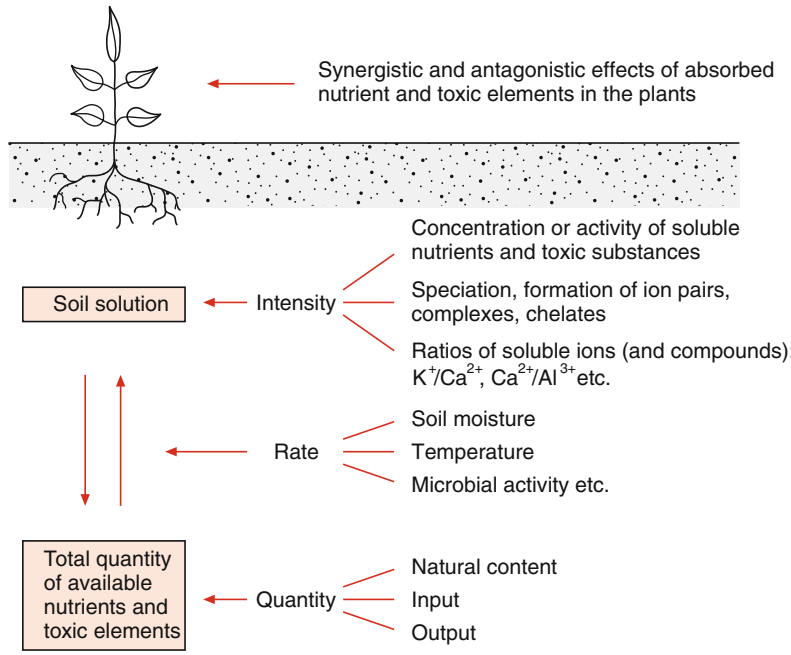

Fig. 9.6 Factors influencing nutrient and pollutant availability in soil (from Brümmer et al. 1986)

these curves in a defined range of the solution concentration ***c*** and of the available reserves of a nutrient ***q*** is also called the **buffer capacity *bc*** of a soil, because changes in the solution concentration (Δc) due to inputs or outputs can be partly compensated through changes in the available reserves (Δq): $\boldsymbol{bc = \Delta q/\Delta c}$. A steep curve characterizes a high buffer capacity (slight changes in the solution concentration), and a flat curve a low buffer capacity (large changes in concentration).

Plants roots are only capable of absorbing the nutrient element fractions that are present as ions in the soil solution, or in some cases as inorganic or low-molecular organic complexes. Therefore, the concentration or the activity and the respective chemical form (species) of the nutrient elements in the soil solution is decisive for uptake by plants (Fig. 9.6).

9.5.2.1 Nutrients in the Soil Solution

Table 5.2 shows the concentrations of nutrient and potentially harmful elements in the soil solution of central European arable and forest soils. Table 5.4 shows which species of nutrient and potentially toxic elements can be found in the soil solution. The concentration of dissolved nutrients is subject to great fluctuations during the year; in the soil solution of central European soils, it often lies between 0.1 and 0.8 g L^{-1} (or 2–15 mmol L^{-1}).

Furthermore, the relationship between the different nutrient and potentially toxic elements is also significant for nutrient uptake (Fig. 9.6). The uptake of ions from one nutrient element (e.g. Mg^{2+}) can be reduced by a surplus of other ions (e.g. Ca^{2+}, K^+) due to **ion competition**. In the same way, Al^{3+} ions reduce the uptake of K^+, Mg^{2+} and Ca^{2+} ions in strongly acidic soils. In polluted soils, arsenic competes with phosphate for uptake by plants, and potentially toxic heavy metals (Cd^{2+}, Pb^{2+}) with cationic micronutrient elements (Cu^{2+}, Zn^{2+}, Mn^{2+} u.a.). Therefore, a balanced composition of the soil solution is necessary for proper plant nutrition.

Altogether, the soil solution usually contains less than 2–20 % of the nutrients required by plants during the vegetation period. For this reason, the total reserves of available nutrients in the rooting zone (quantity, Fig. 9.6), the nutrient supply rate from the solids into the soil solution, and the transport rate to the plant roots are decisive for optimal plant growth.

9.5.2.2 Nutrient Supply and Transport

Nutrients removed from the soil solution by plants roots are rapidly replenished if the cations or anions are bound to the solids in an adsorbed form (desorption process). In contrast, the supply rate from poorly soluble compounds (e.g. carbonates, phosphates and oxides) is lower; it increases with decreasing grain size or increasing surface area of these compounds. The nutrients bound in organic matter (except for the exchangeable ions) are only plant-available after microbial decomposition. The replenishing rate is very low if the nutrient elements are only liberated from silicates through weathering processes. Especially in forestry or under long-term extensive cultivation, silicate weathering generally represents the only available source of nutrients. In Central Europe, at a soil pH ($CaCl_2$) of about 5, between <0.1 and 0.5 keq ha^{-1} K + Mg + Ca are liberated per year in a rooting zone of 10 dm, much less at higher pH values, and accordingly more at lower values. In contrast, a harvest of 8 t ha^{-1} of wheat with the corresponding quantity of straw requires ca. 5.7 keq ha^{-1} of available K + Mg + Ca in the rooting zone during the main growth period lasting only ca. 4 months. High agricultural yields therefore require adequate inputs of available nutrients through fertilization within a relatively short time.

After the nutrients have been liberated from the soil solids, they are transported to the plant roots through convection with the soil solution and through diffusion in the soil solution. **Mass flow** is a result of plant transpiration (Sects. 9.2.2 and 9.2.3). The water in the root zone is depleted in the process. This creates a gradient in the matric potential and thus a flow of the soil solution with the nutrients towards the plant roots. The transport rate of a nutrient by mass flow is determined by the concentration in the soil solution and the water flow rate. The latter depends on the transpiration rate of the plants and the water content of the soil, as well as the number, size and shape of the soil pores and thus also on the texture and soil structure.

Plant uptake of nutrients transported to the roots through mass flow leads to a reduction in the solution concentration, resulting in **diffusion** towards the roots. Transport of nutrients through diffusion can be approximately described by Fick's 1st Law for steady state flow in a liquid:

$$\frac{\partial Q}{\partial t} = -DA \cdot \frac{\partial c}{\partial x}$$

(Q = nutrient quantity that is transported in the time t through the cross-sectional area *A*, e.g. the root surface; D = diffusion coefficient, units are generally $cm^2\ s^{-1}$; c = concentration; x = transport path).

The diffusion rate is much lower in the soil solution than in free saline solutions. It decreases (a) with decreasing soil temperature as a result of reduced ion oscillation, (b) with increasing buffer capacity (*bc* see above) of the soil as a result of reduced solution concentration, and (c) especially with decreasing soil water content due to longer transport paths through thinner water films surrounding the soil particles and increasing electrostatic interactions between the ions in the solution and solid phases. While e.g. the diffusion coefficients of ions in free saline solution are around $10^{-5}\ cm^2\ s^{-1}$, for K^+, Mg^{2+} and Ca^{2+} in moist soils it is ca. $10^{-7}\ cm^2\ s^{-1}$, and for very strongly adsorbed ions, such as phosphate ions, is it ca. $10^{-9}\ cm^2\ s^{-1}$. In the interlayers of clay minerals or in micropores of iron oxides, where there are stronger electrostatic and steric interactions, the solid-state diffusion of K^+ or Mn^{2+}, Cu^{2+}, Zn^{2+} etc. have much lower values, reaching below $10^{-19}\ cm^2\ s^{-1}$.

The root surface towards which diffusion is moving (**diffusion sink**) provides an approximate measurement for the parameter A in the equation above. According to Fick's 1st Law, the transport rate of nutrients to the root ($\partial Q/\partial t$) increases with an increase in the root surface area (*A*) and an increase in the concentration gradient ($\partial c/\partial x$) due to a rise in the nutrient concentration (*c*), e.g. through fertilization, as well as a reduction of the transport path (*x*) through an increase in the soil water content.

Field experiments with various crops determined that the supply of nutrient elements to the plant roots mainly takes place through diffusion for NO_3–N (65–85 % of the total supply) as well

as for P (>95 %) and K (85–98 %). Mg and Cl are predominantly transported through mass flow, and for Ca, it is the rule. If the overall nutrient supply is lower than the absorption rate by the root, as may be the case e.g. with P and K, typical depletion zones of these nutrient elements develop immediately surrounding the roots, which usually comprise a few mm (Figs. 9.15 and 9.18). Nutrient availability is therefore also considerably affected by **root growth** and the **root surface** (especially root hairs and mycorrhiza). Plant roots grow towards the soil particles containing nutrients, a process also called **nutrient interception**. The higher the root density, the shorter the transport path for mass flow and diffusion. With a favorable soil structure, the root density, measured as root length in cm^{-3} of soil, can range from values of ca. 1 (legumes), 3–5 (cereals) up to 20 (grasses).

Furthermore, the replenishment of nutrients from the solids is directly affected by the **mobilizing ability** of the plant roots by means of **root excretions**, so-called **root exudates**. The active donation of protons causes the mobilization and absorption of cationic nutrients (e.g. of NH_4^+, K^+, Mn^{2+}, Zn^{2+} etc.); and can simultaneously lead to a liberation of Ca and P from Ca phosphates. The donation of OH^-, HCO_3^- and organic anions results in the absorption of anionic nutrients (e.g. NO_3^-, $H_2PO_4^-$, SO_4^{2-} etc.). Organic anions can also liberate sorbed phosphate, molybdate etc. from iron oxide surfaces through anion exchange. Precipitations of complexing and chelating organic acids (especially citric acid) as well as of non-proteinogenic amino acids, so-called siderophores (in grasses, including cereals) are also capable of mobilizing cationic trace elements. The excretion of reducing phenols can also lead to a mobilization of Mn^{2+}, Fe^{2+} and other trace elements through the reduction of Mn and Fe oxides. The precipitation of acidic phosphatase causes hydrolytic cleavage and thus a liberation of organically bound phosphate.

The plant roots also release other organic substances such as sugar and polysaccharides as well as dead cells, e.g. from root hairs and caps. All organic substances originating from the roots stimulate the activity of mycorrhiza fungi and microorganisms in the rhizosphere (Sect. 4.1.4). These also contribute to the mobilization of nutrient elements, especially of P, as well as to the N nutrition of plants through N_2 fixation.

9.5.2.3 Nutrient Uptake from the Subsoil

The subsoil also often has a great influence on the plant nutrient supply; the better and deeper it can be rooted, the greater the nutrient availability (Sect. 9.1). The fraction of nutrients absorbed from the **subsoil** is affected by various factors, such as the soil texture, nutrient content in the top- and subsoil, root development in the subsoil, plant growth, and the climate and weather conditions. It can also fluctuate considerably within the same soil from one year to the next, because root development in the subsoil can vary strongly, e.g. depending on the precipitation depth and distribution. In years with low amounts of precipitation, there is generally much stronger root development in the subsoil than in wet years. In field trials with cereals and sugar beet under central European conditions, the fractions of nutrient elements absorbed from the subsoil were found to be 15–50 % for NO_3–N, 20–40 % for P, 30–60 % for K, and 60 % on average for Ca.

The majority of nutrients absorbed from the subsoil was generally translocated into the subsoil through solution transport from the fertilized Ap horizon; furthermore, **soil fauna** activity (bioturbation) can also play a significant role here, as well as mixing through swelling and shrinking (peloturbation) in Vertisols (Sect. 8.4.2).

9.5.2.4 Measurement of the Nutrient Supply in Soils

The nutrient supply in soils can be determined by means of:

(a) **Field experiments**, where the quantity of the yields, the nutrient element contents of the crops, as well as the nutrient element removal with the harvested produce are measured under real site conditions and with natural soil layers. Long-term trials on

different soils and under various climate conditions provide information on the available nutrient reserves in the soil, and change in the yield levels as a result of changed nutrient reserves due to nutrient inputs (fertilization) or removal (plant extraction). Field experiments are also required to calibrate chemical soil test methods.

(b) **Pot experiments**, where all growth factors are kept constant and the effects of the investigated nutrients can be tested by specifically varying their contents. They are also used to test the quality of chemical extraction methods. However, the results from pot trials must always be compared to field trials, because the growth conditions in the (usually relatively small) test pots generally differ considerably from actual field conditions.

(c) Chemical **plant analyses**, where the nutrient element contents of the plants and their growth or yields provide information on the nutrient supply in the respective soils. For plant analyses, generally the entire shoot or specific plant parts (leaves, needles etc.) are sampled at the earliest possible well-defined growth stage. The analytical data can be interpreted using values from tables on the content ranges of the essential elements for an optimal supply of different plant species. However, plant analysis only delivers information on the nutrient requirements of a growing crop relatively late in the season, and is therefore mainly used for permanent crops such as fruit cultivation and forestry, and also as a method for verifying chemical soil testing procedures.

(d) Diagnosis of **deficiency symptoms** developing on aerial plant parts as a sign of insufficient supply of the plants with one or several nutrient elements. However, the symptoms are sometimes not so characteristic, so that it is not always possible to make clear and early diagnoses during the vegetation period.

(e) **Chemical soil testing procedures** that can be easily and quickly performed before the beginning of the vegetation period, and the test results can be used for timely fertilization. Chemical soil tests are classified into three sub-areas: representative sampling in the field, sample drying and preparation, chemical extraction and analysis of the nutrient elements.

For routine tests, soil samples are generally taken from the Ap horizon (0–30 or 40 cm depth), and in grassland, from a depth of up to 10 cm, because the main portion of the root mass (up to >90 %) and the available nutrients are found in these zones. For more precise tests, additional samples are taken from deeper horizons or from defined profile depths (0–30, 30–60, 60–90 cm). Representative conclusions are obtained by testing composite samples consisting of about 20 individual samples taken evenly distributed over the investigated area (usually no more than 1 ha). Today, on larger fields with heterogeneous subareas, e.g. in crest and depression zones, sometimes also site-specific, geo-referenced (GPS supported) sampling is performed that enable subsequent site-specific fertilization, e.g. within the scope of precision agriculture.

The composite samples are dried and prepared in the lab at 20–35 °C with subsequent sieving on a 2 mm mesh. The mass fraction >2 mm ∅ (=coarse soil consisting of gravels and stones), which does not contain any available nutrients, is measured, and the fraction <2 mm ∅ (=fine earth) is used for further testing.

For the **extraction** of plant-available nutrient elements, a defined soil quantity is then treated with a specific volume of extraction solution, and the filtered extract is then used for performing the **chemical analysis** for the respective nutrient elements. The following extraction agents are used for extracting the plant-available nutrient elements from the soil samples: water (for NO_3–N, P, B), saline solutions (for NO_3–N, NH_4–N; Ca, Mg, K, Na; mobile heavy metals), acids (for Cu and for poorly mobilizable fractions of other nutrient elements), and complexing/chelating solvents (e.g. NH_4F, DTPA and EDTA) for cationic micronutrient elements. Combinations of different solvents are also used, e.g. of a saline solution and a complexing ligand (e.g. a $CaCl_2$/DTPA mixed solution for the CAT method used

in Germany for Na, Mg, Mn, Cu, Zn, B) or of an acid, saline solution and a complexing ligand (e.g. for the Mehlich-3 method used in the USA for P and K).

The results obtained from the chemical analysis for the respective nutrient element is then given in mg per 100 g, mg kg^{-1} or g kg^{-1} of soil. In soils with higher organic matter contents and in horticultural substrates, the nutrient contents are given per unit of volume of soil (e.g. in mg per 100 cm^3 or mg dm^{-3}) after determining the volumetric mass. Using the soil volume as a basis generally improves the correlation between the soil analysis values and the nutrient supply of the plants, also because the plant roots always develop their roots in a specific soil volume.

To convert the available nutrient element contents in the Ap horizon (e.g. 65 mg kg^{-1} of plant-available P) into **nutrient element reserves** per ha, first the topsoil mass in kg ha^{-1} must be determined by multiplying the bulk density (e.g. 1.5 g cm^{-3}) with the topsoil depth (e.g. 30 cm) and surface area (1 ha in cm^2) (in this case 4.5×10^6 kg topsoil mass ha^{-1}), and this is then multiplied with the nutrient element content in mg kg^{-1} of soil, and is given as kg of nutrient element per ha (here 293 kg ha^{-1} of plant-available P). Mathematically, with an annual P removal of ca. 30 kg ha^{-1} through harvest products, the available P reserves would last for ca. 10 years without additional P fertilization. However, the time period is actually much longer, because there is also slow release from poorly available nutrient fractions.

9.5.2.5 Soil Test Categories for Nutrient Elements in Soils

Because the nutrient availability in the soil and uptake by plants are determined overall by diverse influences, the described simple extraction methods only indicate ranges for the nutrient supply of soils from "very low" to "very high". These ranges are generally divided into five categories for field and grassland soils (Table 9.11).

Nutrient element contents in the soil test categories A (very low) and B (low) provide an insufficient to suboptimal supply to the crops and thus generally result in yield losses; on the other hand, they are favorable especially for water protection. In soil test category C (optimum), an optimal supply to the crops and optimal yields can be expected. Fertilization should be dosed accordingly to achieve this range. Although soil test categories D (high) and E (very high) provide abundant nutrients to the crops, there is a risk of environmental pollution, especially water pollution. Fertilization should be reduced (D) or omitted (E).

For the evaluation of the trace nutrient element contents determined through soil chemical analysis (B, Mn, Cu, Zn), a three-stage classification of the soil test categories into A (very low and low content), C (desirable content) and E (high to very high content) have been found to be sufficient.

Table 9.11 Soil test categories for the contents of available nutrient elements (P, K, Mg) from arable and grassland soils (VDLUFA 1991–2004) and required fertilization measures

Soil test category	Required fertilization measures
A Very low content	Strongly increased fertilization
B Low content	Increased fertilization
C Optimum content	Maintenance fertilization
D High content	Reduced fertilization
E Very high content	No fertilization

9.5.3 Nutrient Fertilization

Determination of the fertilizer requirements of plants must take account of (a) their nutrient removal depending on the desired yields, as well as (b) the reserves in the soil of available nutrients in the rooting zone, and (c) the replenishment of nutrients through mineralization of soil inherent organic matter, harvest residues and organic fertilizers. Proper fertilization according to 'Good Agricultural Practices' aims to provide the crops with sufficient amounts of all required nutrients and to produce high-quality plant food and feed products, and at the same time, to avoid excessive fertilizer inputs and the associated soil,

water and air pollution (Sect. 9.5.1). Fertilization must therefore be adjusted to the crop and site requirements, and performed in an environmentally sound manner.

Table 9.12 gives the nutrient element contents of field crops at the time of harvest as mean values from a large data set from different central European production areas (micronutrient element contents in Table 9.16). The nutrient element contents in individual plants of a plant species sometimes fluctuate considerably around the given mean values (especially K in straw and silage maize) because of differences in the nutrient supply of the soils, fertilization, and weather conditions, particularly at harvest time (possible K losses through leaching). Nevertheless, the listed mean nutrient element contents represent mandatory values for nutrient element budgets in Germany (Sect. 9.5.1), in which the nutrient element extraction through removal of harvest products must be determined. They are also required to estimate the fertilizer requirements for the cultivated crops.

According to the nutrient element contents listed in Table 9.12, a wheat harvest of 8 t ha^{-1} of grain and 7.2 t ha^{-1} of straw extracts the following total quantities of nutrient elements from the soil (sum for grain and straw) in kg ha^{-1}: N 181 (145 + 36); P 37.5 (28 + 9.5); K 124 (40 + 84); Mg 18 (9.5 + 8.5); Ca 28.5 (5.5 + 23). If the straw remains on the field, the removal is reduced and as a result, also the fertilization for subsequent crop. Similarly, the removal can also be calculated as a basis for the fertilization of other crops.

The listed nutrient element removals show that the plant-available nutrient fractions in soils without inputs from mineral and organic sources are depleted by the removal of harvest products. In soils with an optimal nutrient supply (soil test category C), this is generally the case with nitrogen within 2 years, with potassium within 3–10 years, and with phosphorus within decades. This results in decreasing yields. In contrast, if there is a considerable shortage of the nutrient elements P and K in the soil, an increase in the available P and K values by respectively 10 mg kg^{-1} (based on CAL methods), depending on the soil properties, requires 80–250 kg P ha^{-1} or 50–400 kg K ha^{-1} (Sects. 9.6.2 and 9.6.4).

In soils with a good nutrient supply, fertilization with the different nutrient elements can be performed based on the expected extraction by the subsequent crop, taking account of any other inputs or outputs (Sect. 9.5.1) (nutrient **removal fertilization**). If soil analysis results are available, the fertilization for the respective existing soil test category can be optimized. For soil test

Table 9.12 Mean contents of nutrient elements of field crops in different production areas of Central Europe at the time of harvest in the fresh mass (FM) (in kg (100 kg)$^{-1}$ FM; %-fraction of the dry mass (DM) in the fresh mass)

Plant		Nutrient element content in kg (100 kg)$^{-1}$ FM					
		DM (%)	N	P	K	Mg	Ca
Wheat	Grain	86	1.81	0.35	0.50	0.12	0.07
	Straw	86	0.50	0.13	1.16	0.12	0.32
Maize	Grain	86	1.51	0.35	0.42	0.12	0.18
	Straw	86	0.90	0.09	1.66	0.15	0.43
Rape	Grain	91	3.35	0.78	0.83	0.30	0.45
	Straw	86	0.70	0.17	2.08	0.09	1.32
Field bean	Bean	86	4.10	0.52	1.16	0.12	0.11
	Straw	86	1.50	0.13	2.16	0.24	0.76
Sugar beet	Beet	23	0.18	0.04	0.21	0.05	0.05
	Leaves	18	0.40	0.05	0.50	0.06	0.17
Potato	Tuber	22	0.35	0.06	0.50	0.02	0.02
Silage maize	(whole plant)	32	0.43	0.08	0.42	0.08	0.12

category C (optimal), only **maintenance fertilization** is recommended (Table 9.11). In doing so, the expected nutrient extraction by the subsequent crop is compensated by suitable fertilization after subtracting any other inputs, so that category C is maintained on the long term. For soil test categories A (very low) and B (low), it is recommended to supplement the maintenance fertilization, e.g. by 66 % or 33 %, and in contrast, reductions are recommended for D (high), e.g. by 50 %, and no fertilization for E (very high).

Element- and method-specific range values have been defined to delimit these five soil test categories (Sects. 9.6 and 9.7). They vary in the different countries of Central Europe as well as worldwide, because the soils, site factors and cultivation methods also differ.

9.6 Essential Nutrient Elements

Macronutrient elements for plants are, in order of decreasing contents in the plant material, the elements N, K, Ca, Mg, P and S. Si and Na are also essential elements for several plant species, for example, Si for rice and the horsetail family, Na for C_4 plants (e.g. maize, millet), Crassulaceae etc. They also represent beneficial elements for the growth of many other plants (Sect. 9.8).

9.6.1 Nitrogen

Nitrogen (N) belongs to the macronutrient elements for plants and microorganisms, and is transferred to animals and humans when they eat plants. With its different oxidation levels from -3 to +5, nitrogen forms a great number of compounds. In terms of quantity, it is generally the predominant primary nutrient in plant material and is a component of many organic N compounds such as amino acids, proteins, vitamins and chlorophyll. However, nitrogen is only present in very small amounts in the parent rock for soil formation and in the mineral soil material, and must therefore be regularly supplemented with organic and/or mineral fertilizers under agricultural use. The N supply to the crops can often be a yield-limiting factor. A significant part of the high yield increases in past decades in Central Europe can be attributed to optimized N fertilization. However, regular fertilization with high and excessive N inputs also leads to nitrate leaching out of the soil and sometimes also to strong nitrate pollution in groundwater and surface waters, as well as increased liberation of the greenhouse gas N_2O, but also of NH_3 from the soil into the atmosphere. In undisturbed native ecosystems, elevated NH_4^+ (and NO_3^-) depositions from the atmosphere are known to be a cause for eutrophication, soil and acidification as well as decreasing biodiversity. For this reason, many countries have issued legal ordinances to minimize environmental pollution by agricultural land use, in Europe e.g. the EU Nitrates Directive (1991), EU Water Framework Directive (2000), EU Groundwater Directive (2006), and EU Directive on National Emission Ceilings (2001). Overall, agricultural and horticultural land use requires precisely monitored nitrogen management because of ecological responsibility and economic reasons, but also because of legal constraints.

9.6.1.1 Biological N_2 Fixation and Nitrogen Cycle

With its high N_2 content, the atmosphere represents the largest N reservoir (Sect. 9.3.1). As gaseous N_2, however, nitrogen is not available to plants, it must first be brought into the soil through biological N_2 fixation. Commercial N fertilizers are also produced from atmospheric N_2 (Haber-Bosch method). Biological N_2 fixation introduces atmospheric nitrogen into the soil, where it is transformed into organic and inorganic compounds through different processes, and finally transferred back into the atmosphere in the form of various gases such as N_2, N_2O, NO and NH_3. These phase transitions are called the nitrogen cycle (Fig. 9.7).

Biological N_2 fixation is performed by different bacterial species (Sects. 4.1.4 and 4.3.1).

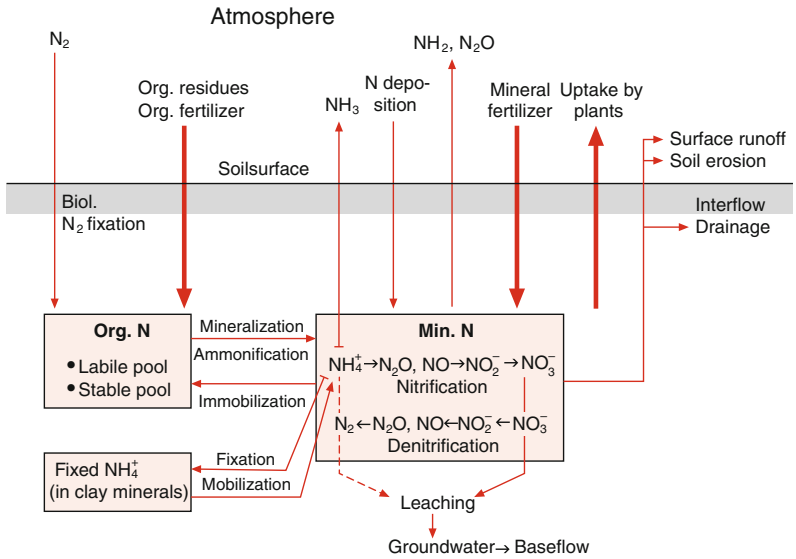

Fig. 9.7 The nitrogen cycle in soil agroecosystems

Under central European conditions, N_2 fixation by autonomous, heterotrophic bacteria amounts to 1–30 kg N ha^{-1} a^{-1}. It is partly limited by the supply of readily decomposable soil organic matter. N fertilization also reduces N_2 fixation. Overall, the quantities of N fixed by autonomous bacteria are not sufficient to cover the N requirements of high-yield crops (for wheat ca. 190 kg N ha^{-1}).

Particularly in tropical regions, several autonomous bacteria can also be observed in association with the roots of higher plants, using their assimilates as an energy source. This enables higher N_2 fixation ranging from 20–100 kg ha^{-1} a^{-1}.

C-autotrophic cyanobacteria assimilate N_2 utilizing the energy of light. They are of considerable significance in paddy soils, and in association with higher plants, e.g. *Anabaena* with *Azolla* (water fern), they can supply more than 100 kg N ha^{-1} a^{-1} for the cultivation of rice.

Symbiotic N_2 fixation is mainly observed in Rhizobia living symbiotically with legumes. Rhizobia require well-drained soils, weakly acidic to weakly alkaline pH values, and a good Fe, Mo and Co supply. The amount of N fixed by legumes is 20–140 kg ha^{-1} for peas, 60–170 kg ha^{-1} for field beans, 80–270 kg ha^{-1} for clover species, and 150–350 kg ha^{-1} for alfalfa. A portion of this fixed nitrogen is left behind in the soil for the subsequent crop, e.g. 20–40 kg N ha^{-1} with field beans and up to ca. 100 kg N ha^{-1} with clover as a catch crop.

Actinomycetes are also observed in symbiosis with a series of woody plants, e.g. in alders and in sea buckthorn, and particularly in the oleaster family in the tropics and subtropics. These symbioses with woody plants can lead to N additions to the soil of more than 100 kg N ha^{-1} a^{-1}.

Altogether, the quantities of N fixed by microbial activity vary strongly depending on climatic influences such as solar radiation, temperature and precipitation, as well as fertilization and N conversion in the soil. The quantities of N bound in the microbial biomass always represent a considerable N pool (80–300 kg ha^{-1} a^{-1}) in the Ap horizons of arable soils in temperate humid regions.

9.6.1.2 N Compounds and N Contents

In humic topsoils, more than 90 % of the nitrogen transferred from the atmosphere into the soil is fixed in an organic form. In fertilized loamy to clayey topsoils, however, inorganic nitrogen can rise to more than 20 % as a result of NH_4^+ fixation by clay minerals (Fig. 9.7). Some soils in

hot deserts (e.g. Central Sahara, highlands of Chile) and cold deserts (continental Antarctica) are also rich in mineral nitrogen compounds and contain $NaNO_3$ and $Ca(NO_3)_2$ added through precipitation or bird droppings (Sect. 7.2.4.5).

The **organically bound nitrogen** comes from vegetation and soil organism residues as well as their metabolic products, and is also bound in humic substances. The greatest portion is found in amide and peptide structures, and also in proteins, amino acids and amino sugars. The latter are characteristic for microbial residues. Humic substances also contain large fractions of amide nitrogen and heterocyclically bound nitrogen. Amides and peptides are sometimes found in binding forms where they are largely protected from microbial decomposition, and thus represent a very **stable N pool** (Fig. 9.7) that can last for millennia. This pool also includes heterocyclic N fractions that are bound in humic substances. In addition, there is an **unstable N pool** with readily degradable organic N compounds, generally consisting of plant amino acids and proteins. The fractions of the various organic N compounds vary considerably among different soils as well as depending on the land use and climate conditions.

The total **N content (N_t)** in Ap horizons of mineral soils in temperate humid climates generally ranges from 0.7–2 g kg^{-1} of soil. This means that there can be N_t reserves in Ap horizons of 3–9 t ha^{-1}, and in deep Chernozems (Ap + Ah), even more than 14 t ha^{-1}. Although the Ah horizons of grasslands (usually 2–6 g N_t kg^{-1}) as well as Ah, AhE (usually 2–5 g N_t kg^{-1}) and O horizons (usually 10–20 g N_t kg^{-1}) of forest soils have higher N_t contents, the quantity of nitrogen is generally lower than in arable soils because the horizons are usually thinner. Fen soils (Limnic Histosols)have the highest N_t contents (H horizons 10–25 g N_t kg^{-1}), and when they are drained and cultivated, decomposition processes are intensified and the liberated CO_2 can significantly contribute to environmental pollution.

The N_t content of soils is closely related to their SOC content. In sandy soils of temperate humid regions, changes in land use such as the ploughing up of grassland and subsequent arable land use can lead to a reduction in the N_t and SOC content by more than 50 % within a few years; in silty-loamy soils, it takes more than 50 years until a new equilibrium is established. With an opposite change in land use, it would take 150 years or more to achieve a doubling of the N_t content. Regular spreading of solid manure or compost also leads to long-term accumulation of N_t and SOC in arable soils (by up to 25 %).

The SOC/N_t or C/N ratio in Ap and Ah horizons of high-yielding arable and grassland soils in temperate humid regions is usually <10–15. In contrast, strongly acidified forest soils with high contents of poorly decomposed litter (O horizons) have very wide C/N ratios (25–38); this is particularly true also for peat bog soils (Fibric Histosols) (40–60). However, the high atmospheric N input under central European conditions today (Fig. 9.7) has led to significant N fixation in the organic matter on these nature-oriented sites, and to a narrowing of the natural C/N ratio. For example, test results for forest soils with hornbeam litter show that the N_t content in the litter increased considerably during a summer half year, while the C/N ratio became more narrow (Table 9.13). This can be attributed to the incorporation of airborne NH_4^+ and NO_3^- in organic matter mainly through microbial processes, but apparently sometimes also through abiotic processes (e.g. with the participation of MnO_2).

Because all microbially regulated processes of the N cycle (Fig. 9.7) as well as the type of predominant vegetation depend on the respective

Table 9.13 Contents of organic carbon (SOC) and total nitrogen (N_t) and the C/N ratio of hornbeam litter after 0, 3, 7, 15 and 25 weeks at the surface of a Stagnosol developed from loess over Rhine Main Terrace (Central Europe, Bonn) (after Geissen and Brümmer 1999)

Trial duration (weeks)	SOC	N_t	C/N
	g kg^{-1}		
0	433	9.9	43.7
3	416	9.5	43.7
7	438	11.5	38.2
15	406	11.5	35.4
25	438	15.1	28.9

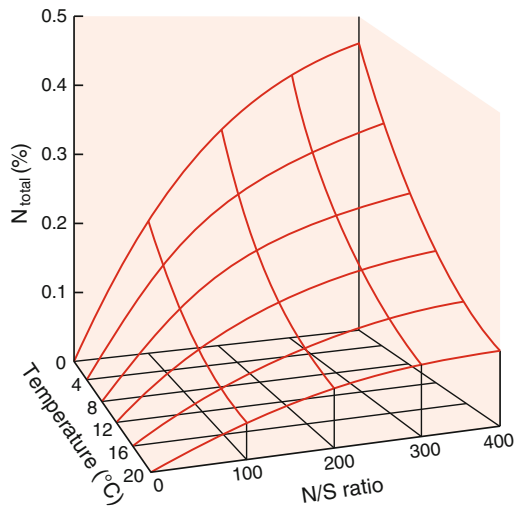

Fig. 9.8 Nitrogen contents as predicted from mean annual temperature and the ratio of precipitation/saturation deficit (from Jenny 1980)

climate, the N_t (and SOC) contents of soils are also affected by the climate. The influence of **temperature** and **P/S quotient** (precipitation/saturation deficit) on the N_t content is demonstrated using the example of arable soils (A_p horizons) from comparable parent sediments preceded by steppe vegetation in the USA (Fig. 9.8). With the same temperature, the N_t content increases with increasing P/S quotients, represented by the curves from the left to the right. The rise in N_t (and SOC) is most pronounced at low temperatures (border to Canada) and is lowest at higher temperatures (Texas). With the same P/S quotients, the N_t content decreases with increasing temperature as a result of increased mineralization, represented by the curves from the back (Canada) towards the front (near Mexico). Loamy soils in Central USA therefore contain much less SON and SOC than comparable soils along the northern border. The composition of the organic N compounds in soils is also affected by the climate. In a similar climate sequence under natural grassland (Ah horizons), for example, the amino sugar contents reach a maximum at mean annual temperatures of 12–15 °C, and decrease significantly with higher and with lower mean annual temperatures. In contrast, the amino acid contents reach a minimum in this temperature range.

The principal **plant-available nitrogen compounds** are nitrate (NO_3^-) and ammonium (NH_4^+), the former being readily soluble and thus also readily leached, and the latter being mainly bound in an adsorbed form and therefore largely protected from leaching. In aerated soils of temperate humid climates, however, the NH_4^+ fraction of N_t is usually less than 1 %, and only exhibits higher fractions after NH_4^+ fertilization or spreading of liquid manure. Organic N compounds with relatively small molecular sizes, such as amino acids, are also plant-available, but are generally utilized by competing rhizosphere bacteria. For this reason, the **mineral N forms** (**N_{min}**), NO_3^- and NH_4^+ are most significant for plant nutrition.

9.6.1.3 Ammonification and NH_4^+ Fixation, Nitrification and Denitrification

N mineralization or **ammonification** (Fig. 9.7) is defined as the microbial transformation of organic N compounds, mainly amino(–NH_2) groups, into NH_4^+ ions. In doing so, first the macromolecules (e.g. proteins) are broken down by enzymes (hydrolases) from numerous heterotrophic microorganisms into smaller constituents (e.g. amino acids), from which NH_4^+ ions are then released through deamination. Microorganisms require decomposable organic matter as an energy source for these processes, and use the liberated nitrogen, carbon and other nutrient elements to build their body substance, which is characterized by a very narrow C/N ratio, especially in bacteria.

If more nitrogen is liberated than required by the microorganisms, the liberated NH_4^+ ions from the soil solution change into the adsorbed form or are subject to nitrification. If, in contrast, the N content of the decomposed substances is too low, mineral nitrogen is absorbed by the microorganisms from the soil reserves and is therefore temporarily fixed in their biomass. This process is called **N immobilization** (Fig. 9.7). Such immobilization mainly takes place when organic matter

with a wide C/N ratio, e.g. cereal straw (C/N 50–100), is plowed into the soil. In this way, excess mineral nitrogen (N_{min}) can be fixed in the soil and largely protected from leaching during the winter half year. However, in the case of insufficient N reserves, the microbial decomposition of straw may require additional fertilization with up to 1 kg N per 100 kg of straw. These additions of N must then be considered in the next vegetation period. At a C/N ratio of ca. 25, there is neither liberation of nitrogen from the organic matter nor microbial fixation of N_{min}. In contrast, nitrogen is liberated from organic parent materials with a narrow C/N ratio, e.g. dead soil bacteria (C/N 5–8), legume roots (C/N ca. 10) or grass and legume cuttings (C/N 10–20).

N mineralization or ammonification is strongly affected by the soil temperature, alternating soil moisture and the pH value. It is low at 0 °C and increases up to ca. 50 °C. For example, a humid hot climate causes high N mineralization and therefore rapid losses of organic matter in the soil. However, it is relatively independent of the soil moisture, but rises considerably when wet phases follow dry phases. The optimal pH-range is between 5 and 8. At lower and higher pH values, the ammonification rate decreases.

NH_4^+ ions formed by ammonification or added through atmospheric inputs and fertilization can also be fixed by clay minerals in silicate-rich soils (Fig. 9.7). Especially highly charged 2:1 layer silicates such as illite, vermiculite and smectite can fix NH_4^+ ions in their interlayers instead of K^+ ions due to their similar ionic radius. In silt-rich central European soils, **NH_4^+ fixation** can reach 0.1–0.33 g N kg^{-1} of soil or 0.5–1.0 g N kg^{-1} of clay. In soils developed from loess and other unconsolidated sediments, sometimes NH_4^+ was already fixed by expanded clay minerals at the beginning of soil development in the Holocene (=native NH_4^+). Freshly spread NH_4^+, e.g. from liquid manure, is also fixed. Pot trials with different soils demonstrated that in topsoils, 7–100 % of the NH_4^+ ions added with liquid manure are fixed by clay minerals after incorporation in the soil, and 49–100 % in subsoils. The majority of this NH_4^+ fraction was then mobilized again during the course of about two years, and absorbed by the cultivated plants. In contrast, the native NH_4^+ that was already fixed inside the interlayers is very immobile and hardly plant-available, while the recently fixed NH_4^+ at the edges of the interlayers is slowly released into the soil solution again through diffusion processes and thus becomes available. NH_4^+ liberation takes place when the NH_4^+ concentration in the soil solution is strongly lowered due to plant uptake or nitrification. The amount of K^+ fertilization and thus the K^+ saturation and fixation affect the NH_4^+ fixation by clay minerals. It decreases with increasing dominance of competing K^+ ions in the soil. Especially in the topsoil, the portion of the fixed NH_4^+ fraction is subject to considerable fluctuations.

Nitrification is defined as the oxidation of ammonium (NH_4^+) to nitrate (NO_3^-) by microorganisms. It takes place in two stages,

$$NH_4^+ + 3/2O_2 \rightarrow NO_2^- + H_2O + 2H^+ \Delta G_r^0 = -195.5\,\text{kJ mol}^{-1} \tag{9.1}$$

$$NO_2^- + 1/2O_2 \rightarrow NO_3^- \Delta G_r^0 = -73.7\,\text{kJ mol}^{-1} \tag{9.2}$$

whereby the first reaction can take place in several partial steps, with the formation of **NO** and **N_2O**, among others. Both reactions are exergonic, require oxygen and deliver the energy to the microorganisms involved. They are therefore mainly triggered by aerobic chemoautotrophic bacteria from *Nitrosomonas* (reaction 9.1) and *Nitrobacter* (reaction 9.1) genera, which are generally associated with each other. Reaction (9.1) shows how the formation of nitrite (NO_2^-) results in the liberation of protons, leading to an increase in soil acidity. Optimal conditions for the complete transformation of NH_4^+ to NO_3^- are found under aerobic conditions with C/N ratios in the topsoil <25, temperatures of 25–35 °C, and pH values of ca. 5.5–8. With decreasing temperature, nitrate formation is delayed (reaction 9.2), and at temperatures of 0–2 °C, it is only detectable to a limited extent. Also at pH <5.5, there is still oxidation of NH_4^+ to NO_3^-, whereby

mainly fungi are involved with increasing acidity, especially in very strongly acidic forest soils. Overall, reaction (9.1) depends less on the temperature and pH than reaction (9.2).

Because of the dominating nitrification processes in aerated soils of temperate humid climate regions, the NH_4^+ formed by ammonification is very rapidly transformed into NO_3^-, so that the NH_4^+ fraction in these soils is generally very low. At low temperatures (<6 °C) or with poor aeration, in contrast, ammonification takes place faster than nitrification. Soils of the tundra as well as Stagnosols and Gleysols therefore contain relatively high amounts of ammonium. Ammonification also takes place faster than nitrification in tropical soils at temperatures >30 °C.

In the reaction chain of nitrification, the oxidation of NH_4^+ to NO_2^- (reaction 9.1) can be delayed by using **nitrification inhibitors**, through which especially NH_4^+ fixed in adsorbed form remains stable for a longer period of time. They are used in agriculture to reduce N losses through N_2O volatilization and NO_3^- leaching.

Denitrification is defined as the reduction of nitrate (NO_3^-) through nitrite (NO_2^-) to form gaseous nitrogen oxides (NO, N_2O) and molecular nitrogen (N_2), whereby the oxidation level of the nitrogen is lowered from +5 to 0:

$$N^{(+5)}O_3^- \rightarrow N^{(+3)}O_2^- \rightarrow N^{(+2)}O \rightarrow N_2^{(+1)}O \rightarrow N_2{}^0 \tag{9.3}$$

Denitrification mainly takes place at high levels of water saturation in the soil (above 70–80 % of the total pore volume) and therefore with limited aeration. With decreasing O_2 contents in the soil air, soil microorganisms from the *Pseudomonas, Alcaligenes* etc. genera are capable of using N compounds containing oxygen instead of molecular oxygen as an electron acceptor. Furthermore, they require readily decomposable organic carbon as an energy source (electron donor) and for the synthesis of their body substance. This carbon comes from the soil organic matter and especially from dead plant material, harvest residues and organic fertilizers. For this reason, in mineral soils, denitrification mainly takes place in the topsoil and is very low in subsoils with low SOC contents. It can reach particularly high values in N-rich fen soils, (Limnic Histosols) and with suitable thickness, it can still also be active up to depths of more than 10 dm.

In some soils with high contents of readily available carbon in narrow pores, denitrification can also take place at water contents below 60–70 % of the total pore volume. The microbial activity in these pores is then increased to such an extent that the oxygen requirements of the microorganisms exceed the oxygen supply through diffusion, and therefore O_2-poor or -free microspaces are formed where denitrification takes place. Denitrification is therefore also affected by several soil physical parameters, which determine the rate of gas exchange between the soil and atmosphere.

Among the gaseous products NO, N_2O and N_2, usually only small amounts of NO and, depending on the conditions, various amounts of N_2O and N_2 are transferred from the soil to the atmosphere (Sect. 9.6.1.5). Because different microorganisms are involved in the overall reaction chain from NO_3^- to N_2, there are also different requirements for the reaction conditions for the individual partial reactions. For the entire reaction chain up to N_2, the formation of N_2 begins at ca. 5 °C and rises to a maximum at >50 °C. Many years of high N fertilization and the addition of readily decomposable organic matter (e.g. spreading of liquid manure, green manure etc.), which lead to elevated microbial activity and a high N mineralization potential in the soil, can cause increased denitrification. The optimal pH here lies between pH 6 and 8. Complete **denitrification up to N_2** is significantly reduced with decreasing pH. In contrast, incomplete **denitrification up to N_2O** still takes place at lower pH values and also at lower temperatures, e.g. in the winter months, so that a considerable increase in the N_2O fraction in the sum of the formed N_2 and N_2O is also observed in strongly acidic forest soils and in arable soils during the winter months.

Overall, in mineral soils used for agriculture in Central Europe, N losses through denitrification range from 3 to >30 kg N ha^{-1} a^{-1} or 1 to >16 % (on average 7 %) of the applied quantity

of N fertilizer. Denitrification is particularly high in clay-rich soils with dense packing and in poorly drained soils, especially also after intense precipitation alternating with dry phases. Particularly high denitrification losses (up to 200 kg N ha^{-1} a^{-1}) can also occur in N-rich fen soils (Limnic Histosols) after they have been drained, because the organic matter starts to decompose. Due to the heterogeneity of soils and various cultivation methods, denitrification losses are also subject to considerable spatial and temporal fluctuations even within the same field.

In contrast to soils used for agriculture, denitrification losses in strongly acidic forest soils are generally low (0.1–1 kg N ha^{-1} a^{-1}) and mainly consist of N_2O emissions . Higher N losses (up to 7 kg N ha^{-1} a^{-1}, of which 4.9 kg N_2O–N ha^{-1} a^{-1}) were measured under alder populations with symbiotic N accumulation in the soil.

Denitrification processes can also take place in groundwater-affected Gr horizons of Gleysols and marsh soils with reduced sulfur compounds (sulfides), whereby the nitrates leached out of the topsoil are reduced by chemo-autotrophic bacteria (*Thiobacillus denitrificans*), and sulfides are simultaneously oxidized. Under strongly reducing conditions, e.g. in bog and subhydric soils, nitrates can even be transformed into ammonium. This process is then called **nitrate ammonification**.

Sewage purification in sewage treatment plants also involves the transformation of nitrates into gaseous N_2 through denitrification to remove them from the wastewater.

9.6.1.4 N Budget, N Fertilization and Crop Yields

The annual consumption of mineral N fertilizers in intensive agriculture is very high. For example, in 1988 in West Germany, it averaged 132 kg N ha^{-1} on agricultural fields, and then decreased to 93 kg N ha^{-1} in 2009/10. Until the end of the 1990s, there was also an average of ca. 100 kg N ha^{-1} a^{-1} of nitrogen added through manuring. Only a portion of the nitrogen added to the soil can be used by plants; the remainder leads to water pollution when it is leached (as NO_3^-), and/or conversion to gases (N_2, N_2O, NO, NH_3) leads to atmospheric pollution. To reduce such environmental impacts, many countries issued Fertilizer Ordinances prescribing how N fertilization is to be performed. In Germany, every farm is required by law to establish nutrient budgets, particularly for N and P (farmgate nutrient balance; Sect. 9.5.1). Since 2011, the N budget may only have a surplus of 60 kg N ha^{-1} a^{-1}. This excess is tolerated because on some agricultural soils, there is a deficit of 40–80 kg N ha^{-1} a^{-1} in the budget that cannot be attributed to any measurable or calculable outputs. They are probably caused by gaseous N losses through denitrification and nitrification (Sect. 9.6.1.3), especially in soils with high groundwater levels and strong influence of stagnant water, as well a by NH_3 losses when spraying liquid manure (Sect. 9.6.1.5) or by N accumulation in the soil's organic N pool (Fig. 9.7).

The **N requirements** of the cultivated field crops, as a basis for **N fertilization** under central European conditions, can be calculated for the respective yield expectations (for wheat e.g. 8 t grain ha^{-1}) using the average N contents given in Table 9.12 (for wheat e.g. 190 kg N ha^{-1} a^{-1} for grain and straw). However, before spreading significant quantities of N, the Fertilizer Ordinance prescribes that the N quantities still available in the soil (usually up to a depth of 9 dm) be determined for every field or every cultivation unit at the relevant times (e.g. in the spring). This can be performed through soil analysis or using guideline values (published by the Chambers of Agriculture). Soil analysis determines the soluble and exchangeable **mineral N compounds** (**NO_3^- plus NH_4^+**), which are called **N_{min}** (see below). Under temperate humid climate conditions, depending on the management, weather conditions and soil conditions, the N_{min} contents can range between 10 and 200 kg N ha^{-1}. They depend on, among other things, the fertilization level and the type of previous crop, and e.g. in silty-loamy soils after cereals, it can average ca. 60 kg, after sugar beet ca. 80 kg, after legumes as a catch crop ca. 100 kg, and after strongly fertilized vegetables ca. 160 kg N ha^{-1}. On sandy soils with low clay contents, the N reserves after high-precipitation winters are very low and can be

neglected in the N fertilization. However, after low-precipitation winters, quantities similar to silty-loamy soils are found. The N_{min} contents usually increase with increasing water storage capacity of the soil as a result of decreasing NO_3^- leaching losses.

N depositions from the air, especially with high inputs, must still be considered in the planned N fertilization. The average N inputs in Central Europe are of 28 kg ha^{-1} a^{-1} (on average ca. 50 % NO_3^-–N and NH_4^+–N) with a variation range of 5–132 kg ha^{-1} a^{-1} (Table 9.8). In several regions of Central Europe, airborne N fractions of 50–60 kg N ha^{-1} a^{-1} were measured in the harvest mass on silty-loamy soils. Inputs of more than 100 kg N ha^{-1} a^{-1} are observed in Central Europe mainly in areas with industrial livestock farming and associated high NH_4^+ deposition. In Central USA, in contrast, the N deposition is only ca. 5 kg ha^{-1} a^{-1}; in the humid tropics it can rise to >20 kg N ha^{-1} a^{-1} as a result of NO_3^- formation and inputs through frequent thunderstorms.

Another source of N to be considered is the **N replenishment** from unstable N soil reserves through mineralization during the vegetation period. The annual **N mineralization rate** is usually 0.2–2 % of the total organic bound nitrogen in soils. Higher rates are generally the exception. Mineralized quantities <10–220 kg N ha^{-1} a^{-1} were measured with large annual fluctuations, even on the same sites, depending on the soil moisture and temperature. For this reason, prediction of the N supply is still associated with considerable uncertainty. Quantities between 20 and 80 kg N ha^{-1} a^{-1} are often replenished, especially in the period between May and August. An indication of the supplied quantities of N can be obtained from the nutritional state of the plants on small control plots with low N starter additions, and this can be considered for the further N inputs.

The N quantities still necessary to cover the plants' N requirements can be spread as mineral and/or organic N fertilizer. To achieve optimal yields in winter wheat (8 t grain plus straw), for example, N reserves of ca. 120 kg ha^{-1} are required (N reserves plus starter addition) at the beginning of vegetation in the spring, which are then usually supplemented by two further N additions (shoot and late additions) up to ca. 200 kg N ha^{-1}.

The most commonly used fast-acting mineral N fertilizer with readily soluble N salts in Central Europe are mainly calcium ammonium nitrate (NH_4NO_3 plus $CaCO_3$) and also urea ($CO(NH_2)_2$), ammonium nitrate urea solution as well as several other fertilizers, enabling precise and timely requirement-adapted fertilization.

The Fertilizer Ordinance prescribes that the N_t content (as well as the P_t content) be determined for all **organic fertilizer**s, such as farmyard fertilizers, and also the NH_4^+ content (through chemical analysis or using average values) for liquid fertilizers (liquid manure, slurry, sewage sludge), to enable calculation of the N quantities to be spread. The N_t content of e.g. slurry is 1.7–2.8 kg m^{-3}, of liquid manure 3.2–6.6 kg m^{-3}, of biocomposts 4.9 kg t^{-1}, and for solid manure 5.5–7.0 kg t^{-1}, with an NH_4^+-N fraction in slurry of ca. 90 %, in cattle and swine liquid manure of ca. 50–70 %, and in biocomposts and solid manure of ca. 10 %. The NH_4^+ fractions are directly plant-available. Other N fractions are liberated through mineralization during the course of the vegetation period. This process generally takes place in two phases, with a high mineralization rate in the first 2–8 weeks that then goes down to a lower rate. In the year of application, usually 10–40 % of the N_t content in green manures is available to the plants, and usually 20–25 % in solid manure, where there also is further replenishment in the second year (ca. 5 %) and sometimes even in the third year. Organic vegetable production generally uses horn meal with a short-term effect of 50–75 % of the N_t content, Ricinus meal (60–70 % short-term effect), legume meal (35–45 % short-term effect), and a series of industrial processed organic fertilizers (50–70 % short-term effect).

Various simulation models have been developed to collect data on the N dynamics in soil-plant systems, such as DAISY, EXPERT-N, HERMES and NLEAP, which estimate the N removal by the plants, NO_3-leaching during the winter half year and the N_{min} reserves still existing in the soil in the spring, and thus enable

fertilization recommendations for the new vegetation period. However, they require the input of a huge amount of weather, soil and cultivation data. Coupling such models with global navigation satellite systems and geographic information systems enables site-specific fertilization recommendations for "precision agriculture". The models INCA and SWAT-N were developed to simulate the behavior of nitrogen in entire catchment areas.

In Germany, analytical determination of the existing mineral nitrogen (N_{min}) reserves in the soil is performed using field-fresh samples that are cooled during transport to the laboratory, usually from depths of 0–30, 30–60 and 60–90 cm, immediately after the samples have been collected and prepared (or after storage at 4 °C for a maximum of maximal 8 days, otherwise they must be frozen at −25 °C), in order to avoid microbial changes of the N_{min} content. NO_3^- and NH_4^+ are extracted from the field-fresh soil sample (150 g) using a 0.0125 molar $CaCl_2$ solution (600 ml). Based on the determined N_{min} values and other additional information, fertilization consulting systems were developed that have proven their worth in practice. In the USA, N_{min} is determined using the presidedress soil nitrate test (PSNT) on soil samples that were dried immediately after sampling. With this method, 5 g of dry soil are extracted with 50 ml of a 0.01 M $CaSO_4$ or 0.01 M $CaCl_2$ solution (agitated for 15 min). According to this test method, >25 mg NO_3–N kg^{-1} are considered to be sufficient at the beginning of the vegetation period. Precision agriculture makes use of N sensors during the application of N fertilizer, which measure the intensity of the chlorophyll coloration using reflectometry, and then calculate the N requirements of winter cereals, enabling site-specific N fertilization. This method is increasingly used in practice today.

9.6.1.5 Environmental Pollution Through Nitrogen Leaching

N losses out of soils mainly take place in **gaseous** or **dissolved forms**. The gases released from the soil into the atmosphere include molecular nitrogen (N_2), nitrous oxide (laughing gas, N_2O), nitrogen monoxide (NO) and ammonia (NH_3); among these, N_2O is a particularly significant climate-relevant trace gas, while NH_3 as atmospheric NH_3-/NH_4^+ deposition mainly causes damage in natural and nature-oriented ecosystems through eutrophication and through acidification after nitrification. Losses in dissolved form mainly involve nitrate (NO_3^-), which can contaminate groundwater and surface waters and cause eutrophication, and therefore is particularly problematic for the drinking water supply (EU drinking water threshold values for NO_3^-: 50 mg L^{-1}; USA: 10 mg N L^{-1}, this corresponds to 44.3 mg NO_3 L^{-1}). NH_4^+ leaching can also occasionally be significant only on sandy and permeable soils.

N_2O (laughing gas) is a trace gas that is relevant for the greenhouse effect, and also contributes to the destruction of the protective ozone layer in the troposphere. Here, soils are considered to be the main source (ca. 70 %) of atmospheric N_2O. It is produced as an intermediate product both with microbial denitrification and with microbial nitrification (Sect. 9.6.1.3), and is transferred from the soil into the atmosphere through gas exchange. N_2O formation and emission is mainly observed under unsaturated conditions (60–70 % water saturation), but with strongly reduced O_2 contents in the soil. Under these conditions, microbial denitrification only partly progresses from NO_3^- to N_2, and also microbial nitrification only partly from NH_4^+ to NO_3^-, so that larger quantities of N_2O can develop as an intermediate product of both reactions. The conditions of formation are intermittently reached in soils, e.g. also with an alternation of wet and dry phases, and then lead to phases of elevated N_2O emissions. With high water saturation, the absence of oxygen and thus completely anoxic conditions, complete denitrification from NO_3^- to N_2 dominates, while in well-drained soils, complete nitrification from NH_4^+ to NO_3^- dominates.

N_2O emission also increases with the level of N fertilization. The annually emitted fraction of N_2O-N of the applied N in Central Europe has a median value of 1.8 %, with a variation range of 0.2–15.5 %. Apparently, there were no

significant differences between field and grassland sites. A high content of readily decomposable organic matter in the soil, which leads to elevated microbial activity after abundant precipitation and thus relatively fast depletion of O_2 in the soil air, can also result in increased N_2O emissions. For example, the spreading of liquid manure by injection in the soil can also lead to a short-term 2–3-fold increase in the N_2O emission. In contrast, soil incorporation reduces NH_3 losses, which, in turn, are considerably higher with surface spreading (see below). Under temperate humid conditions, N_2O formation and emission is optimal at pH 5.5–6.5. It is also less temperature-dependent than other microbial processes in the soil (Sect. 9.6.1.3). Accordingly, considerable amounts of N_2O are emitted also in the winter months with an alternation of freezing and thawing. In regions with corresponding characteristic climate conditions, such as in parts of Southern Germany and neighboring countries, the N_2O emission during the winter half year is about 50 % of the altogether generally relatively high total emissions. In comparison, N_2O emission is low in arid regions of Eastern Germany and neighboring east European countries with mostly well-drained soils. Altogether, the annual emission rate from agricultural soils in Central Europe is 0.04–17.1 kg N_2O–N ha^{-1}, and is considerably lower under forest use with 0.02–0.14 kg N_2O–N ha^{-1} a^{-1}. Under largely natural conditions in west African soils under savanna vegetation, ca. 0.6 kg N_2O–N ha^{-1} a^{-1} were emitted, and in unfertilized agricultural soils of the same region, ca. 0.2 kg N_2O–N ha^{-1} a^{-1}.

Ammonia (NH_3) emissions are mainly observed after spreading liquid manure, slurry and other farmyard organic fertilizers, as well as ammonia, ammonium salt or urea ($CO(NH_2)_2$) on neutral to alkaline soils. The effect of pH on NH_3 emissions is described by the following two equations:

$$\begin{aligned} &NH_4{}^+ + OH^- \leftrightarrow NH_3 + H_2O\ (3); \\ &NH_3 + H^+ \leftrightarrow NH_4{}^+. \end{aligned} \tag{9.4}$$

With increasing OH^- concentration, the equilibrium is shifted towards the formation of NH_3 (9.3). The higher the pH, the greater the potential for NH_3 losses. Therefore, this mainly affects calcareous, biologically active soils. In acidic soils, in contrast, NH_3 is converted to more stable $NH_4{}^+$, so that NH_3 losses are considerably reduced. However, with the spreading of urea [$CO(NH_2)_2$], which is converted in the soil by the enzyme urease to form NH_3 or NH_4OH and CO_2, acidic soils can also exhibit short-term and localized alkaline reactions and associated NH_3 losses.

NH_3 emissions also increase for chemical reasons with increasing temperature and $NH_4{}^+$ concentration in the soil solution, as well as with decreasing NH_3 or $NH_4{}^+$ adsorption capacity of the soil. It is also affected by soil physical and meteorological influencing parameters, such as the NH_3 transport rate through the soil pores and NH_3 removal at the soil surface depending on the wind speed, air temperature and humidity. When spreading liquid manure with 50–70 % of the N_t as NH_3/NH_4–N, or slurry with ca. 90 % of the N_t as NH_3/NH_4–N, desiccation of the soil surface also increases the NH_3 emissions, just as with surface application of liquid manure and slurry on wet soil with a low infiltration rate. Under unfavorable conditions, up to 90 % of the NH_3–N applied with liquid manure/slurry can be lost; commonly observed losses are of ca. 25 %. Injection in the soil can reduce NH_3 losses to 5–10 %. Significant NH_3 emissions are also observed in high-intensity pasture management, reaching 14 kg NH_3–N per livestock unit in 180 days of grazing under temperate humid climate conditions.

A portion of the NH_3 released from the soil can be absorbed by a plant cover. The fractions reaching the atmosphere are deposited in other soils or waters. In regions with intensive animal husbandry like in the Netherlands and in northwestern Germany, it can reach more than 100 kg N ha^{-1} a^{-1} (Sect. 9.6.1.4), which leads to corresponding damage in nature-oriented ecosystems. Altogether, agriculture is estimated to account for up to 90 % of the anthropogenic NH_3 emissions in Central Europe.

N leaching out of the rooting zone into the groundwater mainly occurs as nitrate, and in some readily permeable sandy soils also as

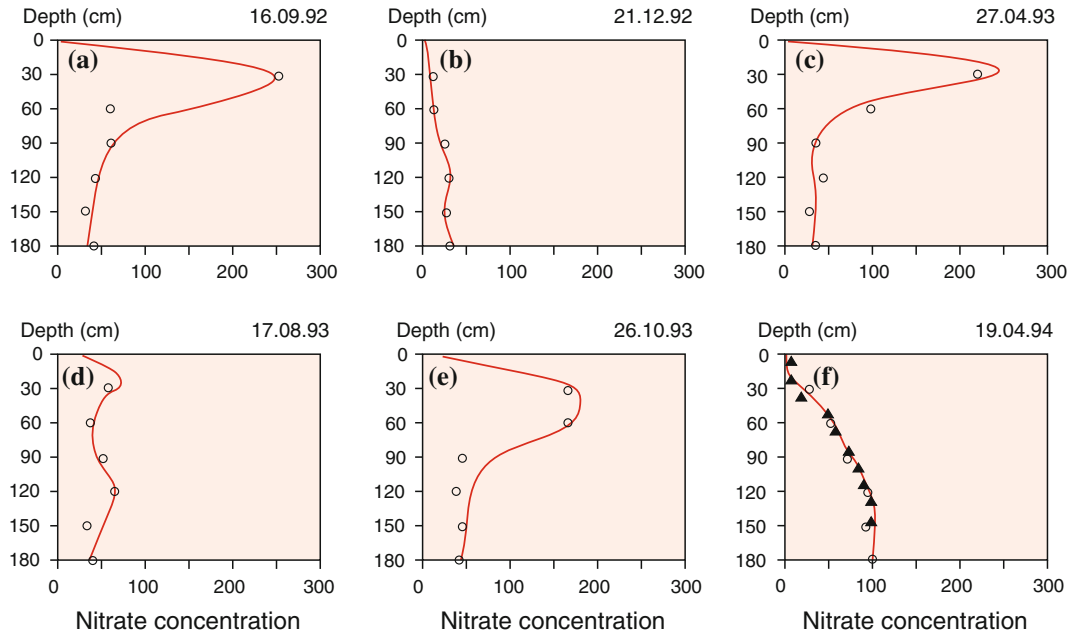

Fig. 9.9 The NO_3 concentration in seepage water

ammonium and in soluble organic compounds ($SON_{\cdot}$), such as e.g. after the spreading of liquid manure. The amount of leaching depends on the seepage water volume and on the NO_3^- concentration in the seepage water. The volume of **seepage water** that leaves the rooting zone is mainly determined by the precipitation depth and intensity, the soil water storage capacity and the plants' water consumption. Therefore, in regions with relatively low precipitation, e.g. in arid regions of Eastern Germany, Eastern Europe and several mid-western and western states of the USA with <500–600 mm of annual precipitation, as well as in landscapes with deep silty-loamy soils with high field capacities (Sect. 9.2.1), such as loess and calcareous glacial till regions of several European countries and the USA, and with management methods with virtually year-round greening, there is no formation of seepage water or only comparatively low quantities of seepage water. In such areas, N surpluses can still be stored in the soil for several years and can be used by subsequent crops. In contrast, in regions with higher precipitation and sandy soils, e.g. in the northwest European lowland plains (750–850 mm a^{-1}), there is always considerable seepage water formation and therefore also always NO_3^- leaching. Under central European conditions, seepage water is mainly formed in the winter months. Because of the higher **groundwater recharge** rates observed in Northwest European landscapes with predominantly sandy soils and high permeability, but low buffering and transforming capacities, these regions are often also defined as groundwater protection areas with special constraints for their management.

The **NO_3 concentration** in seepage water is subject to strong fluctuations during the course of the year (Fig. 9.9). It is determined by the long-term N fertilization level as well as the time, distribution and dosage of the applied N fertilizer and the N uptake by the plants. N leaching can only be minimized through targeted N fertilization that is **adapted to the crop requirements**, and simultaneously considering the N_{min} reserves in the entire rooting zone and the N supply through mineralization. Furthermore, inherent soil processes such as N mineralization, microbial N fixation and denitrification also affect the NO_3^- concentration in the seepage water. For this reason, there is often significant N mineralization from harvest residues in the fall, which,

particularly with legumes as a previous crop, can lead to high NO_3^- contents in the topsoil, and especially on sandy soils under central European conditions, to strong NO_3^- leaching during the winter. The spreading of barn manure or liquid manure in the fall can also have this effect. However, the cultivation of catch crops, winter cereals or rape can considerably reduce NO_3^- leaching during the winter.

For example, on an organically managed field after field beans, strong NO_3^- accumulation was measured at a depth of 30 cm late in the summer (Fig. 9.9a). Still, the cultivation of a catch crop with adequate N uptake (Fig. 9.9b) was able to strongly reduce N leaching. The N reserves stored in the organic material of the catch crop were then mineralized again the following spring and during the subsequent vegetation period (Fig. 9.9c), and were absorbed by the cultivated plants (in this case spring wheat) (Fig. 9.9d). After harvesting in the fall, N mineralization once again took place. Without the cultivation of a catch crop during the winter, the high NO_3^- contents in the topsoil (Fig. 9.9e) were then translocated to a depth or more than 120 cm (Fig. 9.9f), and were therefore no longer available to the plants in the new vegetation period.

Under temperate humid climate conditions and comparable soil conditions, N leaching is generally higher in conventional agriculture than in organic farming. For example, with long-term conventional and organic farming on two comparable riparian floodplain soils of the River Rhine, the two-year average was of 99 and 26 kg N ha^{-1} a^{-1}. With a high proportion of legumes in the crop rotation or high inputs of N fertilizers, N leaching on organic farms can also be much higher. Altogether, N leaching is generally highest with intensive vegetable cultivation and decreases in the sequence conventional agriculture, intensive pasture management, extensive pasture/grassland management, forestry. For this reason, particularly in sandy catchment basins, a reduction in the NO_3^- input into the groundwater requires a sufficient proportional area of grassland and forest to avoid exceeding the drinking water threshold values in the entire catchment basin.

Spatially inclusive and comprehensive **measurement of N leaching** is very expensive and laborious. For this reason, the use of models such as **HERMES, INCA** or **SWAT-N** is increasing in popularity.

Representative investigations by order of the European Environment Agency (EEA) on **NO_3^- contamination** of the **groundwater** in Central Europe demonstrate that 14 % of the EEA measuring points have NO_3^- contents of >50 mg L^{-1} in the topmost aquifers, and can therefore no longer be used for drinking water without prior treatment. 24 % of the measuring points comprising mainly arable land in their catchment area have values exceeding the thresholds (of which ca. 8 % with >90 mg L^{-1}); and with predominantly grassland and forest, it is only ca. 7 or 4 %. However, nitrate degradation by microbial denitrification to form gaseous N_2 in the groundwater can also lead to a reduction of the NO_3^- contents. However, this requires reducing conditions as well as sufficient reserves of electron donors, such as microbially available organic carbon or sulfides, and also sufficient turnover times in the groundwater. Although these requirements may be fulfilled in some catchment basins, the associated denitrification always results in a consumption of the mostly non-regenerable reserves of electron donors.

NO_3^- inputs into surface waters and the resulting eutrophication processes take place through lateral flow of groundwater, through drainage systems as well as through surface runoff and soil erosion. In Central Europe, these NO_3^- inputs originating from diffuse sources represent ca. 65 % (Rhine, Elbe) to 86 % (Danube) of the total N-inputs in flowing waters, which in turn pollute the oceans. Therefore, ca. 73 and 76 % of the inputs in German parts of the North Sea and Baltic Sea come from the rivers.

9.6.2 Phosphorus

Phosphorus is an indispensable primary nutrient for all life forms, which is transferred in the food chain from soils and plants to animals and human beings, and is stored e.g. in their bones and teeth

as apatite. It is absorbed by plant roots as $H_2PO_4^-$ and HPO_4^{2-} ions. In the plant material, phosphorus is bound as phosphate ester in phospholipids, nucleic acids and phytin, and is significant for energy transfer (see ATP, ADP), for the synthesis of organic substances, and as a cellular component. P deficiency symptoms in plants include growth inhibitions in the shoots, leaves (small, narrow leaves, leaf roll) and roots, often also reddish discoloration on older leaves (anthocyan formation) and sometimes also chlorosis and necrosis. The removal of harvest products from agricultural fields as well as of wood from forests depletes the P in soils, so that P fertilization is required to maintain soil fertility. However, strong P over-fertilization of soils under humid conditions is associated with elevated P losses. It may result in proportional inputs into the groundwater and surface waters and represent a significant cause for water eutrophication

9.6.2.1 P Contents of Rocks and Soils

The Earth's crust contains on average ca. 0.1 % P. Rocks are the biggest global **P reservoir** (ca. 10^{13} Tg P), followed by soils and oceans (ca. 2 and 1 × 10^5 Tg) and the terrestrial biomass (3 × 10^3 Tg). The phosphorus in rocks (native P) consists of phosphates, which are mainly found in the form of apatites (see below) and represent both the parent mineral for soil phosphates and the parent material (apatite mineral deposits) for phosphate fertilizers. The P contents in unfertilized soils are mainly determined by the P content of the parent rocks. Contents <100 mg P kg^{-1} are found in sandy soils, e.g. Podzols in temperate humid regions, but also in strongly weathered, kaolinite- and oxide-rich Ferralsols, Plinthisols and Acrisols, as well as in smectite-rich, clayey Vertisols in the tropics and subtropics. In many silty, loamy and clayey soils of temperate climates, the P contents vary between 200 and 800 mg kg^{-1}. P contents of more than 1000 mg kg^{-1} are observed in young soils developed from P-rich basalts and basaltic ashes.

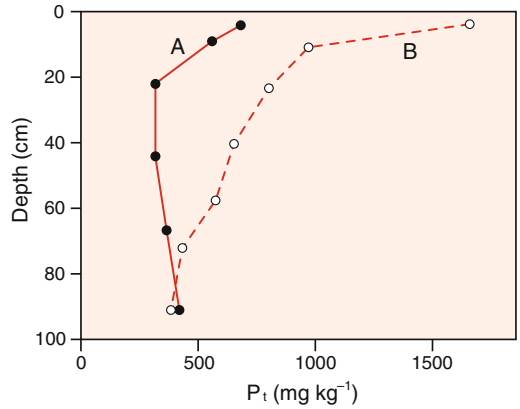

Fig. 9.10 Vegetation residues also lead to an accumulation of P in unfertilized topsoils

The highest P contents, with more than 10 % P, are found in Ornithic Cryosols (permafrost soils in Antarctica developed from penguin droppings) (Sect. 8.4.9).

With decades of high P inputs through mineral and organic fertilizers, agricultural soils can also exhibit significantly higher P contents (up to more than 2000 mg kg^{-1}) (Fig. 9.10). The fertilized phosphate initially accumulates in the topsoil, but under humid conditions, it is always also translocated in small amounts with seepage water into the subsoil. As shown in the example in Fig. 9.10, compared to an unfertilized pasture on comparable soils, intensively managed permanent pasture after ca. 50 years of high P fertilization exhibits P accumulation up to a depth of about 70 cm with respect to the original P contents. Vegetation residues also lead to an accumulation of P in unfertilized topsoils (Fig. 9.10). P is then found as a component of humic substances, among others. In hilly landscapes, the soils on slopes can be depleted of P through erosion, while soils in depressions mainly accumulate P in their colluvial soil horizons. Such P redistributions can provide an indication of the extent of soil erosion in the different landscapes since the beginning of fertilization. Anthropogenic influences on the P contents of soils are also observed on old settlement sites due to elevated P contents in the form of apatites (remains of animal bones).

9.6.2.2 P Forms and P Minerals in Soils

Phosphorus is typically found in soils as orthophosphate, and as such, the vast majority is in a bound form. The P fraction in the soil solution usually comprises less than 0.1 % of the total P (P_t). In soils, the P_t content generally increases from the sand to the clay fraction and with the humus content. The P liberated from apatite in the parent rock during pedogenesis is either bound by constituents of the clay fraction (Fe and Al oxides, clay minerals), precipitated as newly formed (secondary) minerals, or incorporated into humic substances. Altogether, phosphate is found in the following forms in soils: (a) in dissolved form, (b) sorbed on the surface of Fe and Al oxides and clay minerals, and occluded in Fe and Al oxides, (c) in the form of defined phosphate minerals, and (d) in organic substances and soil organisms.

(a) **P in the soil solution**

The predominant inorganic P species found in the soil solution are $H_2PO_4^-$ and HPO_4^{2-} ions. $H_2PO_4^-$ ions dominate in the pH range from 2.1 to 7.2, and HPO_4^{2-} ions at pH 7.2–12.0. PO_4^{3-} ions only represent the dominant P species in aqueous solutions at pH >12, and are therefore only significant in saline soils containing Na_2CO_3, such as Solonchaks. In addition to the free anions, soluble Ca phosphate complexes such as $CaH_2PO_4^+$ and $CaHPO_4^o$ can also be found in the soil solution. Another portion of the dissolved phosphate can be bound in organic form (DOP) and can represent 20–70 % of the total dissolved P in humic topsoils.

In unfertilized soils, the phosphate concentration in the soil solution varies between 0.001 and 0.1 mg P L^{-1}, and in fertilized A horizons, depending on the level of fertilization, usually between 0.1 and 5 mg P L^{-1}. The P concentration is significantly lower in subsoils (usually <0.1 mg P L^{-1}), depending on their P_t contents (Fig. 9.10). However, also elevated P concentrations can be observed in subsoils due to preferential flow or bioturbation. With comparable contents of sorbed P, soils with high P sorption capacity have lower P solution concentrations than soils with low sorption capacity (Fig. 9.11). For optimum plant yields, a P solution concentration of 0.3–0.8 mg P L^{-1} is regarded as being necessary.

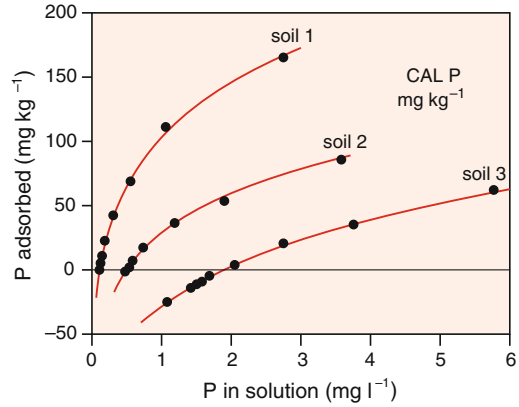

Fig. 9.11 Soils with high P sorption capacity have lower P solution concentrations than soils with low sorption capacity

(b) **Sorbed and occluded phosphate**

The phosphate concentration in the soil solution is at equilibrium with the **sorbed phosphates** on the surfaces of Fe and Al oxides and clay minerals. As an oxyanion, phosphate forms stable inner-sphere surface complexes with the functional groups of these soil minerals (Fig. 5.9). This type of bonding is also called **specific sorption**. In doing so, phosphate is mainly bound through exchange against OH^- ions from the sorbent. P sorption therefore strongly depends on the pH. With a reduction in the phosphate concentration in the soil solution, sorbed phosphates are released into the solution phase; with an increase in the solution concentration, the sorbed phosphate fraction increases. The **sorption capacity of soils** for phosphate is determined using **sorption curves**. To do so, soil samples are equilibrated with solutions of increasing P concentration, and then the fixed (+ΔP) or liberated (−ΔP) quantity of P resulting from the reduction or increase in P concentration in the equilibrium solution is determined (Fig. 9.11). In this way, quantity-intensity (Q/I) relationships are obtained

(Sect. 9.5.2; Fig. 9.6), which can be used to derive parameters such as the **P buffering** (slope of the curves) and the content of sorbed (unstable) P at a specific P solution concentration, as well as the P concentration in the soil equilibrium solution (intersection with the X axis at Y = 0) for different soils. As shown in Fig. 9.11, the steepness of the curves decreases with increasing P contents in the soil (CAL P) (decreasing P buffering) and the **P equilibrium concentration** increases (up to 2 mg L^{-1}). This leads to an increase in P availability. P removal causes corresponding opposite changes.

The most important P sorbents in soils are amorphous Al oxides, allophanes, ferrihydrites, goethites and other Fe oxides, as well as Fe and Al fixed in humic substances. In central European soils, mainly Fe oxides such as ferrihydrite and goethite, as well as Fe and Al organic compounds are decisive for P sorption. The sorption capacity of different soils for phosphate can therefore be estimated using the contents of these sorbents. In doing so, phosphates that are already sorbed must be considered as part of the total P sorption capacity. Therefore, with increasing P fertilization levels, the remaining P sorption capacity also decreases (Fig. 9.11) and the availability of fertilized phosphates increases. In soils developed from volcanic deposits such as Andosols, a high content of allophanes leads to a very high P sorption capacity and P fixation; high Fe and Al oxide contents in strongly weathered Ferralsols and Plinthisols of the tropics have the same effect. In the latter, P from the apatite in the parent rock was completely transformed into Al and Fe oxide-bound P. P accumulations are also usually observed in Fe oxide-rich Bg horizons of central European Gleysols and in Bs horizons of Podzols.

Especially porous P sorbents such as amorphous Al oxides, ferrihydrite and goethite contain micropores leading inside the oxide particles, resulting in sorption sites on internal surfaces in addition to those on outer surfaces. Because of this, the selected reaction time for

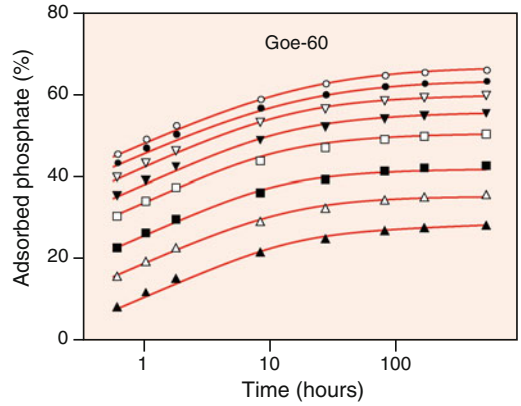

Fig. 9.12 Analytical results on P sorption by goethite as the most important Fe oxide in central European soils besides ferrihydrite

P sorption represents a critical parameter for laboratory tests for determining P sorption curves (see above). With a reaction time of a few hours, initially only a '"quick" P sorption on the outer surfaces of the sorbents can take place, while the diffusion-regulated "slow" P sorption on inner surfaces requires reaction times of several weeks to months; only then is equilibrium fully established between:

P solution concentration ↔ P sorption on outer surfaces ↔ P sorption on inner surfaces.

This is also demonstrated by analytical results on P sorption by goethite as the most important Fe oxide in central European soils besides ferrihydrite (Fig. 9.12). For this reason, the P sorption of soil samples is up to 2–3 times higher after reaction times of several weeks than after a few hours. Under field conditions, the establishment of P sorption equilibriums after P fertilization of the soil requires much more time.

Figure 9.13 shows how the total sorbed P fractions are distributed on external and internal surfaces depending on the reaction time for three goethites with different specific surface areas. After the addition of P, the goethite with the largest specific surface area and a high micropore fraction (Goe-132) initially fixed the highest P fractions on outer surfaces after a short reaction time. With increasing reaction time, there is P diffusion

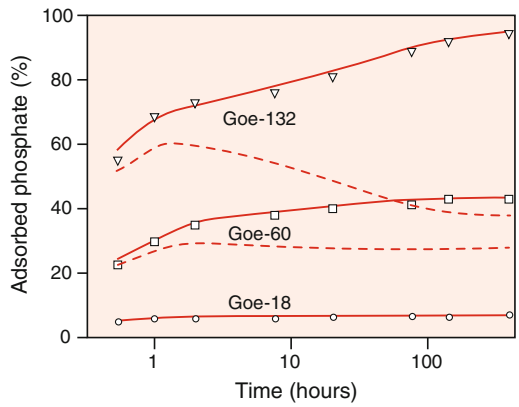

Fig. 9.13 Total sorbed P fractions are distributed on external and internal surfaces depending on the reaction time for three goethites with different specific surface areas

towards inner surfaces and a reduction of the P fractions on outer surfaces, until equilibrium conditions are reached. These processes lead to a reduction in the P availability. The goethite with the smallest specific surface area and low micropore fractions (Goe-18) has the lowest overall P sorption, and the P fixation on inner surfaces is negligible. The P sorption behavior of ferrihydrite is approximately comparable to that of fine crystallized goethite (Goe-132).

There is similar P diffusion in the pores of Fe concretions and mottles. For this reason, investigations using electron microprobe analysis (EMA) also always demonstrate uniform P distribution in porous oxide accumulations. These diffusion processes can lead to the formation of **phosphates occluded** in oxides, and in addition, through the growth of Fe concretions and P occlusion. Especially in Ferralsols and Plinthisols of the tropics, phosphates are often fixed in occluded form, resulting in widespread P deficiency in these soils.

Furthermore, P sorption by goethite as well as by other Fe and Al oxides and by clay minerals is strongly pH dependent (Fig. 9.12). It increases considerably with decreasing pH from 9 to 2. But also in the alkaline pH range, there is still considerable P sorption by Fe oxides. This was also confirmed for calcareous soils by EMA investigations. Furthermore, Ca^{2+} ions can enable phosphate sorption on iron oxides via bond formation in exchange against H^+ ions from OH groups, e.g. as

$$= Fe-O-Ca-OPO(OH)_2.$$

The results from chemical tests also demonstrate that at weakly acidic to neutral soil pH, e.g. in A horizons of loess soils, 50–70 % of the P is fixed on Fe and Al oxides. With decreasing pH, this fraction continues to increase.

Therefore, the formation of sorbed and occluded P in soils depending on the pH can be mainly explained through the sorption properties of Fe and Al oxides. The P availability of fertilized soluble phosphates (e.g. superphosphate) is significantly reduced by P sorption on inner oxide surfaces. In accordance with the laws of diffusion, P supply through back-diffusion represents a much slower process than the diffusion into the oxides. This back and forth diffusion can be impeded by blockage of the micropore openings, e.g. due to deposited organic substances. Competition with other anions for sorption sites, e.g. with organic anions (fulvate, citrate u. a.), can also reduce P sorption and thus increase the P availability. In the same way, the chelation of Fe and Al by organic substances and the dissolution of oxide surfaces can cause P mobilization. For example, the spreading of liquid manure, in addition to the associated addition of P, can also lead to an improvement of the P availability in soils. Organic complexing ligands excreted by plant roots or formed by microorganisms, such as citrate, can have similar effects.

(c) **Phosphate minerals**

The anions of phosphoric acid (H_3PO_4) have a high affinity to Ca^{2+}, Al^{3+}, Fe^{3+} and Fe^{2+} ions, with which they can form poorly soluble phosphates in the soil. For this reason, these cations are also used in sewage treatment for P precipitation. **Ca phosphates** are divided into mono-, di- and tri-Ca phosphates according to the number of protons of the phosphoric acid that were replaced by Ca.

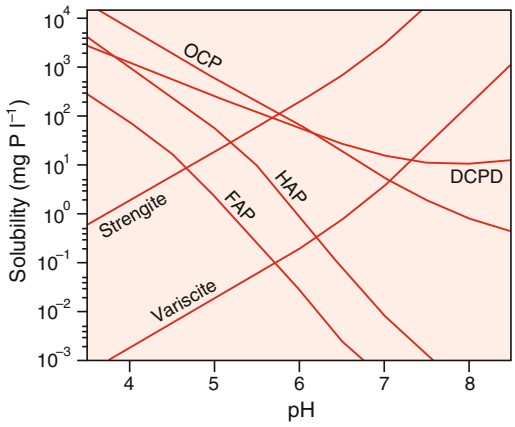

Fig. 9.14 Solubility diagram for different P species as a function of pH (FAP = fluorapatite, HAP p = hydroxyapatite, OCP = octacalcium phosphate, DCDP = dicalcium phosphate)

The most important tricalcium phosphate is **apatite**, representing the primary source of P for soils through rock weathering, and for production of P fertilizers through the mining of natural mineral deposits. Apatite is found as **hydroxyapatite** ($Ca_5(PO_4)_3OH$), **fluorapatite** ($Ca_5(PO_4)_3F$) and **carbonate apatite** $Ca_{10}(PO_4)_5(CO_3)(OH,F)_3$) in rocks, natural mineral deposits and soils. F^- and OH^- ions have a similar ionic radius and can substitute each other through anion exchange. With carbonate apatite, CO_3^{2-} is incorporated into the lattice at equivalent fractions of the PO_4^{3-} ions or also OH^- or F^- ions. Fluorapatite has the lowest solubility, and carbonate apatite has the highest (Fig. 9.14). For this reason, the latter is sometimes also directly used as a P fertilizer on acidic soils in the form of finely ground raw phosphate, just like hydroxyapatite. In both soils and rocks, apatites are generally found in the form of silt-sized crystals.

Readily soluble monocalcium phosphate, $Ca(H_2PO_4)_2$, is commonly used as a fertilizer (superphosphate, triplephosphate). Transformation products of $Ca(H_2PO_4)_2$ found in soils include **dicalcium phosphate**, $CaHPO_4 \cdot 2H_2O$ (brushite) at acidic to alkaline pH, and **octacalcium phosphate** (OCP), $Ca_4H(PO_4)_3 \cdot 3H_2O$, at alkaline pH values. OCP is also called defect apatite, in which substitution of Ca^{2+} by H^+ ions took place. Transformation into secondary apatite is also considered probable in low-humus alkaline soils. Formation of **taranakite**, $(K, NH_4)_3Al_5H_6(PO_4)_8 \cdot 18H_2O$, was also observed on fertilized, acidic sandy soils. Furthermore, a formation of **variscite**, $AlPO_4 \cdot 2H_2O$, is probable in strongly acidic soils with dissolved and sorbed Al^{3+} (Fig. 9.14). However, the development of **strengite**, $FePO_4 \cdot 2H_2O$ (Fig. 9.14), could not be observed in strongly acidic soils until now. In contrast, it is certain that increasing P sorption by Fe (Al) oxides due to increasing substitution of $OH^- \leftrightarrow H_2PO_4^-$ takes place with decreasing pH values. Fe(II) phosphate, **vivianite** ($Fe_3(PO_4)_2 \cdot 8H_2O$), which is white in a pure state, was detected in soils and sediments. It can be formed particularly in Gleysols and fen soils under reducing conditions in the presence of Fe^{2+} in sites with decomposing P-rich biomass, and was also detected in fluvial sediments with strong P contamination. With an influx of O_2, vivianite is colored bright blue due to the partial oxidation of Fe(II).

The **solubility of Ca phosphates** is described by their solubility products. The solubility product K_{sp} quantifies the activities of the dissolved ionic constituents of a compound at equilibrium with its solid phase. For the dissolving reaction of hydroxylapatite by protons in the soil solution

$$Ca_5(PO_4)_3OH + 7H^+ \Leftrightarrow 5Ca^{2+} + 3H_2PO_4^- + H_2O \tag{9.5}$$

the following solubility product (K_{sp}) can be formulated (a = activity, Sect. 5.3.1):

$$K_{sp} = \frac{a^5 Ca^{2+} \cdot a^3{}_{H_2PO_4^-}}{a^7{}_{H^+}} \tag{9.6}$$

After taking the logarithm and inserting the pH for –log (a_{H+}), this results in:

$$\log K_{sp} = 5 \log a_{Ca^{2+}} + 3 \log a_{H_2PO_4^-} + 7\,pH \quad (9.7)$$

$$\log a_{H_2PO_4^-} = 1/3\,(14.46 - 7\,pH - 5 \log a_{Ca^{+2}}) \quad (9.8)$$

After converting Eq. (9.7) and inserting the value of log K_{sp} (=14.46) for hydroxylapatite, Eq. (9.8) can be used to calculate the activity and concentration (Sect. 5.3.1) and thus the solubility of $H_2PO_4^-$, expressed as log mol L^{-1} for any required pH and any Ca activity (log $a_{Ca^{2+}}$). For a soil with pH 6 and a Ca activity of 0.0025 mol L^{-1} (100 mg L^{-1}), for example, the calculated P concentration of the soil solution at equilibrium with hydroxylapatite is ca. 0.4 mg L^{-1}, and at pH 5 under otherwise unchanging conditions, ca. 95 mg L^{-1}. The equilibrium activity of $H_2PO_4^-$ as a function of the pH and Ca activity of the soil can be described for other Ca phosphate minerals in a similar way (Fig. 9.14). At pH 6, it is much lower (ca. 0.6 μg P L^{-1}) for fluorapatite than for hydroxylapatite, and much higher (ca. 53–74 mg P L^{-1}) for brushite and octacalcium phosphate (Fig. 9.14). As a general rule, increasing soil acidification leads to an increase in the P solubility of Ca phosphates, while liming leads to a decrease, because both the pH and Ca activity increase through liming.

The opposite is true for the **solubility of Al and Fe(III) phosphates** (variscite, strengite), which increases with increasing pH, because the rising OH^- concentration leads to increasing transformation of Al and Fe(III) phosphates into Al and Fe(III) oxides and hydroxides, thereby releasing more $H_2PO_4^-$ into the soil solution (Fig. 9.14):

$$AlPO_4 \cdot 2H_2O + OH^- \Leftrightarrow Al(OH)_3 + H_2PO_4^- \quad (9.9)$$

In the same way, increasing pH values lead to increased liberation of sorbed phosphate from Fe (Al) oxides (Sect. 9.6.2.2b). Therefore, it can be generally said that all phosphates bound to **Fe(III) and Al**, are grouped in a broad sense as "**Fe, Al phosphates**", and exhibit increasing solubility **with a rise in** pH. The commonly determined optimum P availability in soils with a pH-range around 6.0–6.5 can also be explained by the rising solubility isotherms of Fe(III) and Al phosphates with increasing pH, as well as rising solubility isotherms of Ca phosphates with decreasing pH, which deliver the optimal P solubility at their intersection at pH 6.0–6.5.

(d) **P in organic matter and microorganisms**

The fraction of soil **organic P** in the total P usually varies between 5 and 35 % in fertilized A horizons of mineral soils, and decreases in the soil profile from top to bottom according to the humus content. Higher fractions are found in unfertilized topsoils, and particularly in organic humus layers and in peat soils. Phytates, i.e. the salts of phytic acid, represent the most important form of organic phosphorus (>50 %). In addition, phospholipids and nucleotide phosphates are also found. All of these compounds are of biogenic origin and contain P as phosphate ester with the functional group ≡C–OPO$(OH)_2$. Like with phosphoric acid, the protons of this group can dissociate and be replaced by Ca, Fe and Al ions, which then form poorly soluble organic P compounds. Furthermore, at weakly acidic to alkaline soil pH, there is probably also phosphate fixation via Ca^{2+} bonds onto humic substances according to ≡C–O–Ca–OPO$(OH)_2$, and in the acidic range, phosphate fixation onto organically bound Al and Fe. The enzyme phytase, produced by bacteria and fungi, can progressively cleave the phosphate ester group of organic substances, and make it partly available to plants.

In related soils, the quantity of organic P generally increases with the SOC. In different humus forms, the C/P ratio of the organic matter varies between 100 and 1000 and is therefore much higher than the C/N ratio, but increases in the same way from mull humus

over moder to mor humus. The quantity of P contained in the microorganisms of Ap horizons is ca. 60–120 kg P ha^{-1}; because of its rapid conversion, it is a relatively mobile and therefore plant-available fraction.

9.6.2.3 P Mobilization Under Reducing Conditions

Under hydromorphic conditions, P solubility and availability is strongly influenced by redox processes. After saturation of the soil and the development of reducing conditions, Fe oxides are reductively dissolved by facultative and obligate anaerobic microorganisms, and the sorbed phosphates are liberated into the soil solution, e.g. according to the following reaction:

$$4\left(=\mathrm{Fe-OPO(OH)_2}\right)^{2+} + \mathrm{CH_2O} + \mathrm{H_2O} \Leftrightarrow 4\mathrm{Fe}^{2+} + 4\mathrm{H_2PO_4^-} + \mathrm{CO_2} + 4\mathrm{H}^+ \quad (9.10)$$

Equation (9.10) shows the liberation of phosphate fixed to Fe(III) with the simultaneous formation of Fe^{2+}. The CH_2O symbolically represents microbially decomposable organic matter. In a similar way, sorbed P is liberated through the reduction of Fe(III) oxides with =Fe–O–Ca–OPO $(OH)_2$ groups. Hydrogen sulfide (H_2S) formed under reducing conditions can also reduce Fe oxides in Bgr horizons of sulfur-rich soils (e.g. marsh soils) and especially in subhydric soils and limnic sediments, and transform them completely into Fe sulfides, whereby the sorbed and occluded phosphates are then fully liberated:

$$2\left(=\mathrm{Fe-OPO(OH)_2}\right)^{2+} + \mathrm{H_2S} \Leftrightarrow 2\mathrm{Fe}^{2+} + 2\mathrm{H_2PO_4^-} + \mathrm{S}^0 + 2\mathrm{H}^+ \quad (9.11)$$

$$\mathrm{Fe}^{2+} + \mathrm{H_2S} \Leftrightarrow \mathrm{FeS} + 2\mathrm{H}^+ \quad (9.12)$$

Reductive P mobilization takes place e.g. in paddy soils after flooding and significantly improves the P supply to the rice plants. In mudflat soils and other subhydric soils, the liberation of P depending on the transformation of Fe oxides into Fe sulfides (Eqs. 9.11 and 9.12) is particularly significant (Table 9.14). Such liberation of P is also observed in anoxic sediments of eutrophied waters, which contain topsoil material rich in P due to the discharge of sewage or erosion from fertilized arable lands in their catchment basin. Here, reductive P mobilization is a significant cause for the occurring eutrophication processes.

Table 9.14 Redox potential (Eh), ratio of iron from iron sulfides (Fe_{FeS}) to dithionite extractable iron (Fe_d) and P concentration in the soil solution in a marine tidal mudflat profile at pH 7.2–7.6 (North Sea coast) (Brümmer and Schroeder unpublished)

Depth (cm)	Eh (mV)	$\frac{Fe_{FeS}}{Fe_d}$	P in solution (mg P L^{-1})
0–1	+50 to –50	0.02	0.5
1–5	–100	0.41	0.5
5–20	–120	0.49	7.4
20–35	–170	0.71	14.6
35–50	–190	0.87	16.4

9.6.2.4 P Supply to Plants, P Fertilization and P Budget

Because plant roots only absorb dissolved phosphate and its concentration in the soil solution is very low, the dissolved P quantity of several 100 g ha^{-1} is far from being sufficient to ensure the P supply of the plants. A good wheat harvest requires altogether about 100 times the amount of dissolved P. As shown in Fig. 9.15, a maize root can lower the P concentration of the soil solution in its rhizosphere from 0.8 to 0.03 mg P L^{-1} within three days. For this reason, P must constantly be replenished from the solid material into the P-depleted soil solution in the rhizosphere. This mainly takes place through the desorption of sorbed P, but also through dissolution of Ca phosphates and through mineralization of organic P. The liberated P then diffuses in the soil solution towards the rhizosphere. The driving force of diffusion is the concentration gradient towards the depleted rhizosphere. The processes and influencing parameters for the diffusion of nutrients are described in detail in Sect. 9.5.2.2. The depletion zone of the rhizosphere is approximately as wide as the zone of the root hairs, e.g. ca. 0.7 mm for maize and 1.3 mm for rape. Root hairs are therefore significantly involved in P uptake and P utilization.

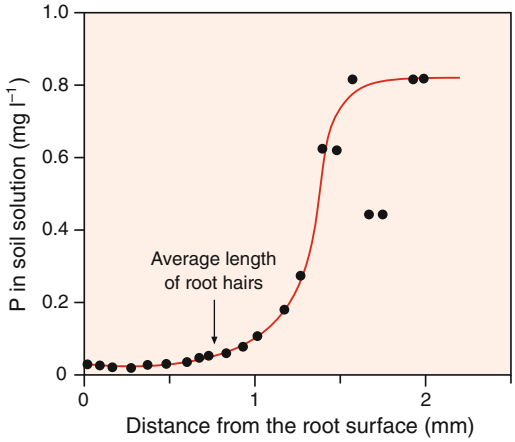

Fig. 9.15 P uptake from the rhizosphere of maize after three days in sandy soil (from Jungk and Claassen 1997)

Altogether, P diffusion represents the rate-determining step of P uptake, indicated by the P depletion of the rhizosphere (Fig. 9.15). The P supply to the plants is therefore better the higher the P concentration in the soil solution, i.e. the more saturated the P sorbents and the faster the phosphate is desorbed, or the more soluble the phosphates in the solid material. These processes are accelerated by the excretion of organic anions (e.g. citrate) and protons from roots and microorganisms. The secreted protons increase the solubility of Ca phosphates (Eq. 9.5), while organic anions desorb sorbed phosphates, or mobilize them through Fe and Al complex formation or chelation, and thus increase the P availability. For this reason, the **P fertilizer requirements** to raise the P concentration of the soil solution to optimal concentrations of 0.3–0.8 mg P L^{-1} decrease significantly when the arable soil has a good humus supply. The spreading of liquid manure and compost or the incorporation of crop residues (e.g. straw) has a similar effect. Mineral anions such as silicate compete with phosphate for bonding sites. For this reason, the addition of soluble silicate increases P mobility in strongly desilificized soils of the humid tropics. Furthermore, with the help of mycorrhiza, plants can mobilize phosphorus from poorly available chemical forms. However, this is only significant in soils with poor P supply.

In practice, the quantities of P required during a vegetation period, e.g. a total of ca. 40 kg P ha^{-1} (ca. 30 kg for the grain, ca. 10 kg for the straw; Table 9.12) for a wheat harvest of 8 t ha^{-1}, are mainly applied as readily soluble monocalcium phosphate ($Ca(H_2PO_4)_2$) in the form of superphosphate or triple phosphate (constituent of compound fertilizers). On acidic soils with pH ($CaCl_2$) <5.5, finely ground raw phosphates are also suitable (Sect. 9.6.2.2c). The majority of phosphate species formed in the soil solution depending on the pH, such as $H_2PO_4^-$, HPO_4^{2-} and $CaH_2PO_4^+$ (Sect. 9.6.2.2a), are then sorbed in the soil (Sect. 9.6.2.2b). Repeated extractions with water can liberate a considerable portion of the fertilized phosphates, whereby the decreasing P liberation with each extraction follows the course of a desorption curve.

At high $Ca(H_2PO_4)_2$ concentrations, e.g. around fertilizer grains, **metastable phosphate minerals** such as dicalcium phosphates (e.g. brushite; Sect. 9.6.2.2c) can be formed. At acidic pH values, this is possible through disproportionation:

$$Ca(H_2PO_4)_2 + 2H_2O \Leftrightarrow CaHPO_4{\cdot}2H_2O + H_2PO_4^- + H^+ \quad (9.13)$$

Furthermore, with simultaneous application of soluble phosphates and ammonium (e.g. as ammon phosphate), acidic soils also exhibit formation of metastable taranakite (Sect. 9.6.2.2c). In neutral to weakly alkaline soils, the transformation of $Ca(H_2PO_4)_2$ to brushite can take place as follows:

$$Ca(H_2PO_4)_2 + Ca^{2+} + 2OH^- \Leftrightarrow 2CaHPO_4{\cdot}2H_2O \quad (9.14)$$

In Ca-rich soils with alkaline pH, formation of octacalcium phosphate (Sect. 9.6.2.2c) from $Ca(H_2PO_4)_2$ as well as from $CaHPO_4{\cdot}2H_2O$ is possible:

$$2Ca(H_2PO_4)_2 + 2Ca^{2+} + 6OH^- \Leftrightarrow Ca_4H(PO_4)_3{\cdot}3H_2O + HPO_4^{2-} + 3H_2O \quad (9.15)$$

It is sometimes presumed that there is further transformation to hydroxylapatite, however, it could not yet be detected in humic topsoils. Apparently, the kinetics of this process, which is also inhibited by the presence of organic matter, are also very slow. For low-humus subsoils containing carbonates, in contrast, EMA investigations have demonstrated that hydroxylapatite forms in iron concretions with phosphate and Ca accumulations. This suggests that initially a sorption of P and Ca takes place in the iron concretions, until the concentration of both elements is so high that efflorescence of hydroxylapatite can occur.

Prediction of the **P fertilizer requirements** necessitates soil analyses before the beginning of the vegetation period to determine the contents of available phosphates (Sect. 9.5.2.4). The extraction solution generally used for this purpose in Germany and Austria is a **Ca-acetate-lactate** solution buffered at pH 4.1 (**P CAL**). Extraction with **pure water** is used in several European and other countries to determine the available P contents (**P_{water}**). In Anglo-Saxon regions, in contrast, extraction is performed according to the Olsen method with 0.5 M **$NaHCO_3$** at pH 8.5 or according to Mehlich-3 with a solvent mixture consisting of CH_3COOH, NH_4NO_3, NH_4F, HNO_3 and EDTA. The CAL method mainly detects phosphates that are sorbed via Ca bonds, readily soluble Ca phosphate minerals, and partially sorbed phosphates, while $NaHCO_3$ mainly extracts phosphates that are sorbed on Fe–Al oxides and organically bound. Mehlich-3 also mainly records sorbed phosphates and readily soluble Ca phosphates. All of the above-mentioned methods mainly extract the total amount (quantity) of the potentially available phosphates, while decisive influencing parameters for P uptake such as intensity, rate and buffering of the phosphates are not taken into account (Sect. 9.5.2; Fig. 9.11). For this reason, the extracted contents of available phosphates generally correlate poorly with the plant yields. However, the relationships improve with decreasing P-supply in the soil. Therefore, on arable land, P fertilization is recommended only in soil test categories A (very low) and B (low; Table 9.11), where there is a clear P fertilization effect. For soil test category C, which has an optimum P supply, **maintenance fertilization** with P is recommended at a rate approximately corresponding to the quantity removed by the harvest products. The quantities of P, as well as K and Mg remaining on the field with the harvest residues (e.g. straw) are completely plant-available on the medium term, and must therefore be considered accordingly in the fertilizer requirement prediction. Soils in soil test categories D and E require considerably reduced P fertilization or none at all. Data on the P contents for soil test categories A–E varies considerably among different countries; they vary depending on the soil properties, site conditions and cultivation systems. The general principle of nutrient fertilization according to the soil test categories has proven to be viable. The CAL and Mehlich-3 methods are suitable for the simultaneous determination of the potassium and magnesium supply of the soil.

For ecological and economic reasons, phosphorus counts among the nutrient elements like nitrogen for which annual **nutrient budgets** must be established based on the total P inputs and outputs during a farming year (Sect. 9.5.1). On a 6-year average, P surpluses up to just under 9 kg P ha^{-1} a^{-1} is authorized in Central Europe. Under certain conditions, this limit does not apply to undersupplied soils in soil test categories A and B.

In the past, more P was added to soils of Central Europe than was removed. The statistical mean mineral fertilization rate reached its peak value in Germany from 1970 to 1980 with ca. 30 kg P ha^{-1} a^{-1}. In addition, ca. 20 kg P ha^{-1} a^{-1} were added through nutrient imports from livestock feeds acquired from outside the farm. For this reason, especially farms with high stocking densities often have P inputs that greatly exceed the P outputs. Today, ca. 21 % of the arable land in Germany falls in the soil test categories A and B (grassland ca. 31 %), 38 % (35 %) in soil test category C, and 41 % (34 %) in soil test categories D and E. Since 1980, the annual **P budget** surpluses have been reduced by almost 80 %, mainly because of

decreasing mineral fertilization. In the farming year 2009/10, the average mineral P fertilization was only 6.0 kg P ha^{-1} of agricultural land, and the organic P fertilization dropped to ca. 8 kg ha^{-1}. Today, the legally prescribed controlled application of farmyard fertilizers enables savings in the use of mineral fertilizer P and also preserves the already limited existing P natural mineral deposits. Depending on the future worldwide consumption of mineral P fertilizers, it is estimated that the still available P reserves will last for a minimum of 60 years and a maximum of 130 years. The P supply of soils and plants is therefore also called the bottleneck for global food security.

9.6.2.5 Water Pollution by P Losses

The P over-fertilization taking place over decades in Central Europe, especially on farms with high stocking densities, has already led to P accumulation down in deeper subsoil horizons, particularly in sandy soils with low P sorption capacity (Sect. 9.6.2) (cf. Fig. 9.10). Also in clay-rich drained soils, which swell and shrink depending on the soil moisture, there is strong discharge/losses of phosphates through drainage pipes with preferential flow. Especially with low depths to the water table, e.g. in lowland plains, flood plains, and flat coastal regions, this leads to elevated P inputs into the groundwater, which can be both in dissolved and colloid form. In Central Europe, depending on the soil and the applied test methods, the colloid-bound P losses with seepage and drainage water can account for 1–37 % or even up to 80 % of the total applied P quantities. P (and N) inputs into surface waters take place with lateral flowing groundwater. Other diffuse sources for P pollution of surface waters include drainage water discharge and surface runoff, as well as inputs through erosion material from fertilized fields. To limit the P pollution of lakes and flowing waters, orientation values are suggested for seepage water entering groundwater and drainage water of 0.20 mg L^{-1} total P or 0.15 mg L^{-1} orthophosphate P for discharge into the groundwater, and 0.12 mg L^{-1} total P or 0.08 mg L^{-1} orthophosphate P for drainage water. For flowing waters, the concentrations required for mesotrophic conditions of <0.10 mg L^{-1} total P or <0.04 mg L^{-1} orthophosphate P are aimed for on the long term.

Calculations using models for the P losses from entire catchment basins delivered outputs of >2 kg P ha^{-1} a^{-1} with maximum values of 6.5–13 kg ha^{-1} a^{-1} for sensitive central European soils. Losses of 5–15 kg P ha^{-1} a^{-1} were measured in moors with low mineral contents and therefore low P sorption capacity. In contrast, in deep mineral soils with medium to high P sorption capacity, the P outputs are of only a few 100 g ha^{-1} a^{-1}. Inputs of <0.5 kg P ha^{-1} a^{-1} are considered to be tolerable for lakes in Central Europe. In the period from 1998 to 2000, 60–80 % of the total P inputs from the Elbe, Weser, Rhine and Danube originated from groundwater and drainage water, <1–4 % from surface runoff, and 2–3 % from soil erosion. 73–77 % of the P inputs in the German regions of the North Sea and Baltic Sea came from the mentioned diffuse sources of agricultural land use.

9.6.3 Sulfur

Sulfur is an indispensable nutrient element for plants, animals and human beings. It is a component of many plant constituents as well as sulfuric acid esters ($R–O–SO_3H$), essential amino acids (cysteine, cystine and methionine), and thus also of proteins, enzymes, and vitamins, as well as a series of secondary metabolites such as leek oils and the anti-carcinogenic sulforaphane contained in broccoli. Plants mainly absorb sulfur from the soil as sulfate (SO_4^{2-}). S deficiency causes disruptions in protein and chlorophyll synthesis by plants. Deficiency symptoms are pale green to yellow discoloration on the youngest leaves, later chlorosis in the entire foliage (similar to N deficiency, Sect. 9.6.1), in rape there are spoon-shaped malformations of the leaves and white coloration of the flowers, and in cereals a rigid appearance of the plants. S deficiency leads to yield losses; in rape, strong S deficiency can result in almost total yield losses.

9.6.3.1 S Contents of Rocks and Soils

The S content of igneous rocks is 0.2 × 3 g kg^{-1}. It is higher in basic rocks than in acidic rocks, and is mainly found in the form of sulfides of Fe, Zn, Pb, Cu, Hg, Ni, Ag, etc. During the course of weathering, sulfides are oxidized to sulfates, so that mineral-bound sulfur in soils and sediments under aerobic conditions is almost only found in the form of gypsum ($CaSO_4 \cdot 2H_2O$). Gypsum rocks can contain up to 15 % SO_4 sulfur. Under strongly **anoxic conditions,** in contrast, sulfur in semiterrestrial and subhydric soils and sediments is mainly found as **iron sulfide** (mackinawite: FeS; pyrite: FeS_2), but can also accumulate as elemental sulfur.

In terrestrial soils of humid climate regions, the S content is usually 0.1–0.5 g kg^{-1}, in bog soils, in contrast, it can reach up to 10 g kg^{-1}, and in acid sulfate soils up to 35 g kg^{-1}. Gypsiric Leptosols can even consist predominantly of gypsum. Other than these exceptions, there is no significant accumulation of SO_4 in soils of humid climate regions, because sulfates are relatively readily soluble (ca. 2 g L^{-1}) and are translocated or leached into the subsoil.

In arid soils, however, sulfates can accumulate through input with precipitation, rising of groundwater containing SO_4, or as a result of channel and sprinkler irrigation. Under these conditions, there can be a precipitation of gypsum. Gypsisols, as typical soils of many deserts, have high sulfate contents (Sect. 8.4.4), just like some soils in dry steppes and in semi-deserts such as Kastanozems. Calcisols and Durisols, which may also exhibit sulfate-rich horizons.

9.6.3.2 S Forms and Minerals in Soils

Depending on the redox conditions, sulfur is found at different oxidation levels, from −2 (e.g. sulfides), ±0 (elemental sulfur), +2 (thiosulfates), +4 (sulfites) up to +6 (sulfates). There is a corresponding high number of mineral and organic compounds and binding forms. Under oxidizing conditions, mainly oxidation level +6 is found, and under strongly reducing conditions, oxidation levels –2 (S^{2-}) or ±0 (S^0) dominate.

In soils of humid climate regions, 80–98 % of sulfur under **oxidizing conditions** is found in organic compounds of H, O, and A horizons. In subsoils, the mineral binding forms dominate. On the one hand, **organically bound S fractions** include sulfur that is directly bound to C (C-S fixation) like in amino acids and proteins containing S (cysteine, methionine) as well as sulfonates. On the other hand, sulfates may bind to C via O-bonds, like organic sulfate esters (–C–O–SO_3H). This fraction probably also includes sulfur from organic Al-SO_4 complexes, which can represent higher fractions in strongly acidic soils, e.g. in Bs horizons of Podzols. Particularly the organic sulfate esters represent a readily mineralizable SO_4 fraction for soil microbes. The C/S ratio in the organic matter is usually 60–200, and also up to >400 on sites with S deficiency.

In the soil mineral fraction, beside the formation of free sulfate salts, sulfur can also be occluded as sulfate in carbonates. Adsorbed sulfate is found in acidic soils, and its quantity increases with rising pH and reaches maximum contents at pH values around 4. In this pH range, after reacting with hydroxy-Al-polymers, sulfate can be fixed as jurbanite ($AlOHSO_4 \cdot 5H_2O$) and alunite ($KAl_3(OH)_6(SO_4)_2$). Especially in acidic forest soils, **jurbanite** is apparently of special significance for S dynamics. At pH <4, mainly SO_4 adsorption and occlusion by Fe oxides takes place. At pH 3–4, hydroxy-Fe-sulfates such as **schwertmannite** ($Fe_8O_8(OH)_6SO_4$) are also formed, and **jarosite** [$KFe_3(OH)_6(SO_4)_2$] at pH <3 (Sect. 7.2.5). These compounds are of special significance for extremely acidified sulfur-rich soils in marine coastal and delta regions, e.g. in several marsh soils of the North Sea coast, as well as worldwide in Thionic Tidal Fluvisols. Altogether, these so-called alkaline Al and Fe sulfates account for a significant portion of the base-neutralizing capacity of strongly acidified soils.

The **SO_4 concentration** of the **soil solution** in terrestrial soils of Central Europe is 5–350, and often 10–150 mg L^{-1}. In semi-terrestrial soils, higher concentrations are generally measured. In addition to soluble inorganic sulfate, soluble organic S compounds formed with the spreading of road salt, such as sulfate ester, amino acids,

and fulvic acids containing S can be present in the soil solution, and also escape out of the soil as gases. Under humid climate conditions, subsoils often exhibit higher contents of soluble sulfates than topsoils.

Under **reducing conditions**, S accumulation in the form of iron sulfides can occur if sulfates are added to the soils or sediments with the groundwater or flood water. Microbial reduction of Fe(III) oxides to Fe^{2+} ions and the formation of hydrogen sulfide through microbial reduction of sulfates (desulfurication) or through the decomposition of S-rich organic matter leads to a precipitation of FeS (amorphous or mackinawite) and polysulfides such as Fe_3S_4 (greigite):

$$Fe^{2+} + H_2S \Leftrightarrow FeS + 2\,H^+ \qquad (9.16)$$

With time, these iron sulfides can be transformed into the very stable disulfides (FeS_2) pyrite and marcasite. In addition to H_2S, mercaptanes (e.g. CH_3SH) are also formed through microbial activity under strongly reducing conditions. Incomplete oxidation of H_2S and FeS can also lead to the production of elemental sulfur as a metastable intermediate product. At the transition to aerobic soil conditions, H_2SO_4 is formed through the oxidation of sulfides, which can cause a strong drop in pH in the soil with high initial sulfide contents and the absence of $CaCO_3$—in extreme cases, down to pH 2, e.g. in acid sulfate soils. Under these conditions, alkaline Fe and Al sulfates are then formed, e.g. jarosite:

$$3Fe(OH)_3 + K^+ + 3H^+ + 2SO_4^{2-} \Leftrightarrow KFe_3(OH)_6(SO_4)_2 + 3H_2O \qquad (9.17)$$

9.6.3.3 S Supply to Plants, S Leaching and S Fertilization

The S content of plants is usually 1–10 g kg^{-1} DM, and for rape up to 15 g kg^{-1}. Cruciferous plants generally have a particularly high S requirement. Yield losses are observed in rape if the S content of the leaves is <4 g kg^{-1} DM, and for cereals, below 2–3 g kg^{-1}.

Plants cover their **S** demands from the SO_4 reserves in soils, from atmospheric inputs (especially in Ferralsols, Plinthisols and Acrisols), as well as sometimes from the groundwater or floodwater. Cereal plants absorb a significant portion of their sulfur from the subsoil (ca. 45 %). The **S extraction** by the plants is 30 kg S ha^{-1} for cereals (grain yield), sugar beet including the leaves, and for the growth of pasture, and in contrast, rape (grain yield) can reach up to 45 kg ha^{-1}. Potato and maize as well as forest trees have lower S requirements (ca. 2 kg S ha^{-1}).

S leaching mainly involves mobile, plant-available sulfates, a large portion of which are leached out of arable soils with pH values >5.5 and therefore very low SO_4 sorption during the winter half year. Depending on the SO_4 reserves and the volume of seepage water, S leaching in Central Europe ranges from 20 to 120, on average 50–60 kg S ha^{-1} a^{-1}. The S losses are not compensated by the S inputs from the atmosphere. Due to the success of air pollution reduction measures in the last decades, the wet and dry S deposition in Central Europe has dropped to 2–50, on average 11 kg ha^{-1} a^{-1} (Table 9.8). Especially near the coasts, the precipitation has a relatively high sulfur content (up to ~25 kg S ha^{-1} a^{-1}), which mainly consists of sprayed seawater salts. In remote regions far away from industrial, urban and coastal areas, the annual sulfur input through precipitation is much lower. In New Zealand, for example, it is only 1 kg S ha^{-1} a^{-1}, so that S deficiency on cultivated soils is common there, as well as in different states of the USA and in other countries. Altogether, many regions of North and Central Europe also sometimes have significant S shortages in crops during the vegetation period, so that **SO_4 fertilization** of 15–40 kg S ha^{-1}, depending on the plant requirements, is needed.

SO_4^{2-} can only act as a harmful substance if it is present as readily soluble magnesium sulfate at high concentrations, like in some saline soils. In contrast, high gypsum contents are not toxic because of their low solubility, as can been seen on the example of Gypsiric Leptosols. If the sulfur is present in sulfide form, elevated concentrations of hydrogen sulfide (strong phytotoxin) can more or less completely inhibit plant growth. High SO_2 or SO_3 concentration in the air

can also have harmful effects, clearly demonstrated in former times by the yellowing of the leaves and needles of trees growing near industrial plants (waste gas damage).

The methods used for testing the S supply of soils are associated with considerable uncertainty, because it is difficult to predict how much sulfur will be liberated during each vegetation period through mineralization from the organic matter. Furthermore, the S stock in the deeper layers of the rooting zone is also relevant for the S supply to plants. The best results are obtained by analyzing the content of readily soluble **mineral sulfate-sulfur (S_{min})** simultaneously with the N_{min} analysis (method Sect. 9.6.1.4). Extractions with different saline solutions, e.g. with 0.01 M $Ca(H_2PO_4)_2$ or with 1 M NH_4NO_3 solution, deliver similar results. For an adequate supply to the crops, at least 10 mg S_{min} kg^{-1} of soil in the entire rooting zone is considered to be adequate for plant nutrition.

9.6.4 Potassium

Potassium is an essential element for all life forms. Plants absorb potassium as a cation (K^+) from the soil solution. In plants, it is responsible for the adjustment of the osmotic pressure and the regulation of the water balance, for example. It also activates various enzymes. A good K^+ supply to the plants increases their drought and frost resistance. K deficiency leads to an increased tendency to exhibit wilting symptoms; chlorosis develops from the edges of older leaves, and later necrosis.

9.6.4.1 K Contents of Rocks and Soils

The **rocks** in the Earth's crust contain on average 1.9 % K, which is mainly fixed in feldspars and micas. During weathering and pedogenesis, this native potassium is progressively liberated, leached and transported to the oceans. There, over the course of longer periods of time, K is incorporated into clay minerals again through sediment diagenesis, which are then transformed back into mica or illite. Particularly during the Upper Permian (Zechstein or Lopingian), large salt accumulations formed in shallow coastal basins in arid climates, where evaporation leads to the precipitation of sea salt and the formation of natural mineral deposits of K and other salts. Today, these are mined and applied to the soil again as K fertilizer. The largest reserves of potassium are found in rocks (ca. 5×10^{17} t), followed by soils and the oceans.

In young illitic-smectitic soils with Holocene soil development, the total potassium content usually ranges from 0.2 to 3.3 % K, and 2–4 % K in the clay fraction. The K content is therefore very low in clay-poor sandy soils, and increases with the clay content. Much lower values of 0.1–0.8 % K are found in old, deeply weathered tropical soils like Ferralsols, where the majority of feldspars, micas and clay minerals containing K have been transformed into K-free kaolinite and Fe and Al oxides.

9.6.4.2 K Minerals and Forms in Soils

In mineral soils, the majority of the potassium is bound as lattice components in silicates, especially in alkali feldspars, micas and illites. The K fraction in **organic compounds** is very low. Humic substances contain practically no potassium. However, the microbial biomass contains about 25–50 kg K ha^{-1}. Another portion of the potassium is bound/fixed in the plant biomass. For example, this fraction accounts for 50–60 kg ha^{-1} a^{-1} in a beech forest. Other K forms include the K fixed in the interlayers of 2:1 layer silicates, as well as **exchangeable K** and **dissolved K**. Depending on the mineral composition of the soil and the amount of K fertilization, exchangeable K in the Ap horizon can range from 100 to 1000 kg K ha^{-1}. The K concentration in the soil solution usually lies between 2 and 20 mg L^{-1}. The difference between the total K and exchangeable K is conventionally called non-exchangeable K, which essentially consists of the K incorporated in the crystal lattice of silicates and fixed in the interlayers of layered silicates.

Through the soil solution, the different forms of potassium are at equilibrium with each other.

However, the transitions between them take place at different rates. **Exchangeable K** moves into the soil solution very rapidly. The establishment of equilibrium is much slower for K that is specifically fixed in the interlayers of illites and micas. This K is liberated through very slow diffusion processes (D_{eff}: ca.10^{-20} cm^2 s^{-1}) only after the interlayers have swelled. The inverse process involves the diffusion of dissolved K or exchangeable K into the interlayers of expanded/swollen 2:1 clay minerals. This causes the silicate layers to contract to 1 nm layer distance and a transformation of swollen/expanded clay minerals into illite. This is called **K fixation**, and the K bound in this specific way is called fixed K.

Fixed interlayer potassium is progressively liberated when the K concentration drops in the soil solution, e.g. when plants extract K from the soil. In contrast, the fixed K increases with rising K concentration, e.g. through K fertilization, until the fixing capacity of the inner surfaces has been largely saturated. Only then can the reserve of exchangeable K build up on the outer surfaces. In addition to the K supply, the extent and intensity of K fixation mainly depend on the presence of 2:1 layer silicates, and therefore usually increase in central European soils with the clay content. In the silt and coarse clay fraction, K is mainly fixed by vermiculite with a layer charge >0.6 charges per unit/elementary cell, and in the fine clay fraction, mainly by illites that are expanded at the edges and by smectites with a charge of >0.4 charges per unit/elementary cell. Soils with a strong K-fixing capacity are found in river floodplains in temperate humid regions, where fine clay was deposited by the low transport force of water. These soils are capable of fixing the native and fertilized K so strongly that the plants can develop K deficiency. The **K fixing capacity** of soils is determined by adding a specific quantity of dissolved K to a soil sample, and then, with or without interim desiccation, measuring the remaining exchangeable K. The difference between the added and the remaining extractable K delivers the so-called wet or dry K fixing capacity of the soil.

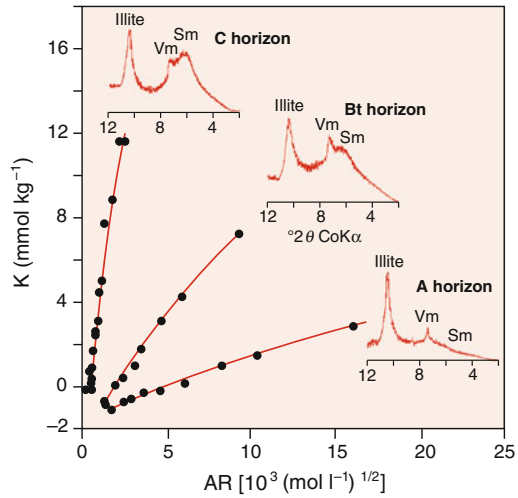

Fig. 9.16 K-Ca exchange diagrams of the A, Bt, and C horizons in a Luvisol derived from loess. The X-ray diffractograms are shown at the top of each curve. AR is the activity ratio. Figure drawn after Niederbudde (1975)

The K fixing capacity changes during pedogenesis. The K fixing capacity increases when micas lose their interlayer K through weathering and transformation into vermiculites. In Luvisols developed from loess, for example, the K liberated from biotites in the B horizon is fixed by highly charged smectites already present in the loess, which then are transformed into illites again. Through mineral K fertilization, such **illitization** processes also take place in A horizons, when they contain vermiculites, highly charged smectites, and illites that are expanded at the edges. This is concluded from X-ray diffractograms (Fig. 9.16): The smectite content increases from the A to the C horizon, and in contrast, the illite content along with the K content in the clay fraction <0.2 μm decreases.

A pedogenic process in strongly acidic soils that decreases the K fixing capacity is the embedding of Al hydroxypolymers in expanded interlayers of 2:1 layer silicates. This makes the interlayer space inaccessible for K ions. Liming and an increase in pH can partly reverse these processes through $Al(OH)_3$ precipitation, and can therefore increase the K fixing capacity.

9.6.4.3 Correlations Between Exchangeable and Dissolved K

The quantity of exchangeable K increases with the K concentration in the soil solution. This correlation can be represented by adsorption isotherms, e.g. by Langmuir and Freundlich (=quantity/intensity (*Q*/*I*) correlations; see Sects. 5.5.6.1 and 9.5.2). At a given K concentration in the soil solution (K intensity), however, the quantity of sorbed K (K quantity) also depends on the type and concentration of competing cations and on the type and quantity of the sorbents (clay minerals). In the absence of Al ions, the exchange behavior of K^+ is mainly determined by Ca^{2+} (and Mg^{2+}) ions, so that their concentration in the soil solution must also be considered to understand the K^+ sorption.

So-called **K/Ca exchange curves** are used to characterize the K-Ca exchange, where the amount of sorbed K is considered as the quantity and the K and Ca concentration in the soil solution as the intensity. The curves are obtained by equilibrating soil samples with solutions containing K^+ and Ca^{2+}, which, like many soil solutions from weakly acidic soils, have ca. 0.05 molar of Ca^{2+} and 0–10^{-3} molar of K^+. Through sorption or desorption of K, the soil changes the K content in the solution, and the sorbed (+ΔK) or desorbed (–ΔK) K quantity is plotted against the **K/Ca activity ratio** ($AR = a_K/a_{Ca}^{1/2}$) of the soil solution. Here, the exponent ½ of a_{Ca} corresponds to the bivalency of Ca^{2+} (see Sect. 5.5.6.2).

The intersection of such *Q*/*I* curves with the abscissa is called AR_0, because here K is neither sorbed nor desorbed (ΔK = 0) (Figs. 9.16 and 9.17). AR_0 corresponds approximately to the *AR* in the soil. The K quantity that is desorbed into the K-free Ca solution (lowest point on the Q/I curve, Fig. 9.17) is called **unstable K**; it is correlated with the exchangeable K. The slope of the Q/I curves (ΔK/Δ*AR*) characterizes the soils' **K buffer capacity** (*KBC*). It indicates the extent to which a soil can counteract changes in *AR* through the exchange of K^+ by Ca^{2+} and vice versa. As shown in Figs. 9.16 and 9.17, the *KBC* decreases with increasing *AR*, because the soils are gradually saturated with K and can therefore absorb less and less additional K.

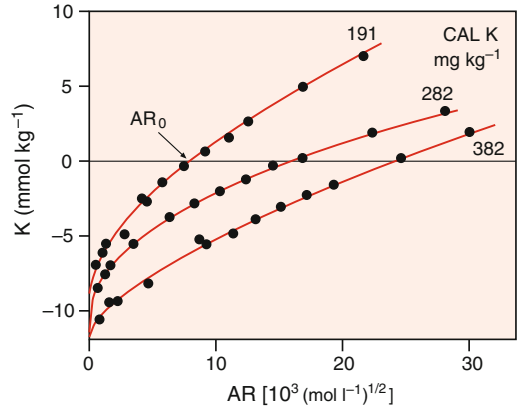

Fig. 9.17 K-Ca exchange rates in soils with different supply of available K (AR = activity ratio)

The changes in ΔK as a function of K/Ca-*AR* shown in Fig. 9.16 demonstrate the effect of clay mineral constituents and K fertilization on the K availability in soils. In the C horizon of Luvisols, high vermiculite and smectite contents cause a much lower AR_0 value and therefore less K^+ in the soil solution than in the Bt and Ah horizon. At the same time, the K buffer capacity (*KBC*) (=slope of the *Q*/*I* curve) and thus the K sorption and fixation in the C horizon is at its highest. In contrast, because of K fertilization and the associated illitization, AR_0 is highest in the Ah horizon and the *KBC* is lowest, therefore providing the best K supply to the plants. Similarly, Fig. 9.17 shows that AR_0 increases with increasing contents of available K (CAL K), while *KBC* decreases. In contrast, low-clay soils as well as clay-rich kaolinitic soils also exhibit a low KBC at low K concentrations or low K/Ca *AR*, and therefore have a low K supply potential from the unstable K. However, even with a low K concentration, soils with illitic-smectitic clay mineral constituents are usually still capable of supplying considerable amounts of K from the non-exchangeable K reserves (see below).

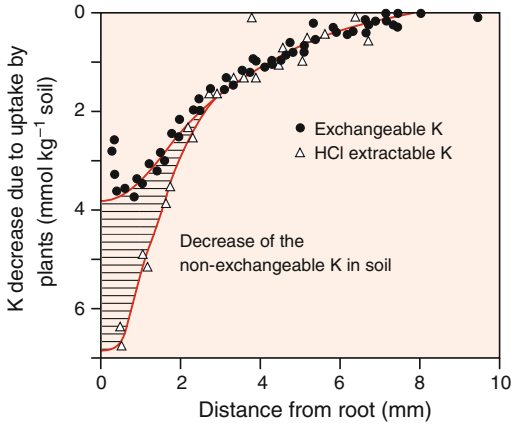

Fig. 9.18 Depletion profiles of exchangeable and non-exchangeable K in the rape rhizosphere (after Seggewiss and Jungk 1988)

9.6.4.4 K Supply to Plants, K Fertilization and K Leaching

The K contents in the soil solution that are directly available to plants on fertilized arable land range between ca. 5 and 15 kg ha^{-1}. However, a wheat harvest of 8 t ha^{-1} requires ca. 125 kg K ha^{-1} (40 kg for the grain, 85 kg for the straw; see Table 9.12). Therefore, large quantities of fixed K must be replenished through diffusion from the solids into the soil solution during the vegetation period. K uptake by plant roots can reduce the K concentration in the soil solution down to ca. 0.1 mg L^{-1}, and therefore create a concentration gradient for the flow of K out of the pool of K sorbed on outer and inner surfaces of clay minerals into the soil solution. The K from feldspars hardly plays a role for the K supply of agricultural crops because of the relatively high pH in fertilized soils and the resulting slow weathering, as opposed to the K supply of tree populations on strongly acidified forest soils.

Figure 9.18 shows the K depletion in the rhizosphere of rape roots: within seven days, the roots caused a significant reduction not only in the exchangeable K, but also in the non-exchangeable (extractable with hot HCl) K. Non-exchangeable K is mainly liberated with high rooting intensities and thus short diffusion paths, but also through a rising concentration of competing Ca^{2+} ions. For this reason, the K/Ca *AR* is also used for the determination of K *Q/I* curves. The increasing liberation of K with decreasing K concentration is presumably also the reason why in illitic-smectitic soils, the so-called **plant-available K** (CAL K) hardly drops below ca. 50 mg kg^{-1} of soil.

The **K supply in soils**, just like the P supply, is determined **in Germany and Austria** using the K quantities extractable with Ca-acetate-lactate (pH 4.1) (CAL K). In Anglo-Saxon regions, the Mehlich-3 method is often used (Sect. 9.6.2.4). Extraction with 1 M NH_4 acetate is also a well-tried method. All methods mainly determine the soluble and exchangeable K. Similar to P, the available K only correlates with crop yields in cases of soils with poor K supply (soil test categories A and B; see Sect. 9.5.2.5). Above about 100 mg available K kg^{-1} of soil, K fertilization does not achieve higher yields of agricultural crops on most central European soils. Apparently, the K supply from K pool of the 2:1 layer silicates is then sufficient for optimal yields. Furthermore, the plant roots also absorb K from the subsoil (10–60 % of the K uptake), especially if the K supply in the topsoil is low. For this reason, in soils in the optimal K soil test category C, which, like with the other soil test categories, is subdivided according to soil texture or CEC because of the great significance of the clay content and the cation exchange capacity (CEC), **K fertilization** can be calculated according to the K removal from the field with the harvest products.

The consumption of mineral K fertilizer in Western Europe until 1980 was ca. 80 kg K ha^{-1} a^{-1}, and dropped until 2009/10 to an average of ca. 18 kg ha^{-1}. For the period between 1950 and 1988, mainly the fields on farms with high stocking densities and high liquid manure additions have large K budget surpluses. Here, **K leaching** in soils with more than 10 % clay (predominantly as 2:1 layer silicates) is negligible, however, with high K fertilization rates and seepage water quantities of more than 200 mm per year, it can rise up to 20–50 kg K ha^{-1} a^{-1} on sandy soils (see Table 9.9).

9.6.5 Calcium

Calcium is an essential element for plants, animals and human beings, entering the food chain through transfer from the soil. Plants absorb calcium as Ca^{2+} ions from the soil solution. It is a component of important compounds in plants, e.g. of phytin, pectin and Ca phosphate. Ca deficiency generally rarely occurs in crops.

9.6.5.1 Ca Contents, Minerals and Forms in Soils

The **Ca content of soils** generally lies between 0.1 and 1.2 % Ca, in soils containing carbonate and gypsum and in saline soils often considerably higher, and usually much lower in soils consisting of quartz-rich sands as well as in extremely acidified forests. **Minerals** from the silicate group that contain Ca in soils are mainly plagioclases, pyroxenes, amphiboles and epidotes, and Ca is also found in the form of carbonates such as calcite ($CaCO_3$) and dolomite [$CaMg(CO_3)_2$] as well as gypsum ($CaSO_4 \cdot 2H_2O$). Because these minerals are readily weatherable, Ca is liberated with the onset of acidification and is then bound by the exchange media in the soil. Therefore, a significant portion of the total Ca is always present in an **exchangeable form**. In soils of temperate humid climate regions with pH > 6, the Ca fraction in the exchangeable cations is usually above 80 %, however, in extremely acidified forest soils it is sometimes only <1–5 %.

In soils of Central Europe containing $CaCO_3$, the carbonate content generally originates from the parent rocks, and in agricultural soils sometimes also from fertilization. The solubility of $CaCO_3$ strongly depends on the CO_2 partial pressure (see Fig. 5.17) and is based on the formation of soluble calcium hydrogen carbonate [$Ca(HCO_3)_2$]. Calcium sulfate (gypsum) also sometimes enters the soil through fertilization, e.g. with superphosphate (gypsum content about 50 %). There can also be secondary formation from sulfates in readily soluble mineral fertilizers, like K_2SO_4, $(NH_4)_2SO_4$ and $MgSO_4$, due to reaction with adsorbed Ca, but it is not stable in soils of humid regions because of its high solubility (2.6 g L^{-1} at 20 °C).

The **Ca content of the soil solution** in carbonate-free arable soils usually lies between 40 and 160 mg L^{-1}. However, they can be much higher in soils containing $CaCO_3$ and $CaSO_4$, and much lower in acidified soils. In extremely acidified forest soils, Ca solution concentrations of <0.1–5 mg L^{-1} can be observed. The most important Ca species in the soil solution are Ca^{2+}, organic Ca complexes and sometimes $CaSO_4^0$, as well as $CaHCO_3^+$ and others in soils containing $CaCO_3$.

9.6.5.2 Ca Supply to Plants, Ca Fertilization and Ca Leaching

The Ca contents of different plants and plant parts usually range from 0.5 to 50 g kg^{-1} dry matter (DM). Crops with Ca contents <5–10 g kg^{-1} DM in the green plant parts exhibit **Ca deficiency**. In one year old spruce needles, the boundary for Ca deficiency is <2–2.5 g kg^{-1} DM.

Ca deficiency is rare in arable soils of Central Europe, because the Ca content of the soil solution is generally above the required concentration of 20 mg Ca L^{-1}. The content of exchangeable Ca (Ca_{exch}) that is extractable from the soil using 1 M NH_4 acetate (Sect. 9.6.4.3) or Mehlich-3 solution (Sect. 9.6.2.4) gives an indication of the Ca supply to the plants. In cereals, latent Ca deficiency occurs at $Ca_{exch.}$ contents <200 mg kg^{-1}. Ca is sometimes significant in fruit cultivation (bitter pit in apple) and also in vegetable cultivation (blossom end rot in tomato, blackheart in celery and cauliflower).

Especially on very strongly to extremely acidified forest stands, Ca deficiency is observed at concentrations <0.1–5 mg Ca L^{-1} in the soil solution. On these sites, there are often also high Al and sometimes Mn concentrations in the soil solution, which, with simultaneous very low Ca (and Mg) concentrations, can lead to root damage and other nutritional disruptions in forest trees, as well as to the soil flora and fauna due to antagonistic effects with ion absorption. Most forest trees exhibit strong root damage at pH values <4.0 and Ca/Al molar ratios in the soil solution of <0.2 to <0.1. In spruce seedlings, a molar ratio between the sums of the exchangeable base cations Ca, Mg and K and the exchangeable Al

leads to considerable root damage at ratios of basic cations to Al <1.0. Ca deficiency is also widespread in oxide-rich tropical soils with variable charge and acidic soil pH (e.g. Ferralsols).

The harvesting of crops usually removes 5.5 (only cereal grains) or 28.5 (cereal grains plus straw) to 150 kg Ca ha^{-1} a^{-1} from the soil (see Table 9.12). Under temperate humid climate conditions, there are generally also annual leaching losses of 30–350 kg Ca ha^{-1} a^{-1}. In contrast, Ca inputs with precipitation only amount to 2–20 Ca ha^{-1} a^{-1}, on average 6 kg. Therefore, Ca losses must be compensated on agricultural soils through regular **liming** (Sect. 5.6.5). If clay-rich soils are frequently fertilized with Ca despite sufficient Ca concentration in the soil solution, this is usually done in order to improve soil structure. On forested soils in Central Europe, so-called **compensative liming** with 3 t of finely ground dolomite per ha is performed to compensate for acid inputs and to improve the Ca (and Mg) supply of the forest trees.

9.6.6 Magnesium

Magnesium is an essential macronutrient element for all life forms, absorbed by plants as Mg^{2+} ions out of the soil solution and passed on to the higher members of the food chain. A sufficient supply of Mg for human beings and animals is therefore associated with sufficient Mg supply in the soil and for plants. Magnesium is a component of important plant constituents (chlorophyll, phytin etc.), activates many enzymes, and influences the swelling state of cells, among other things. Mg deficiency leads to chlorosis between the leaf veins on older leaves. In conifers, the tips of older needles become orange-yellow in color.

9.6.6.1 Mg Contents, Minerals and Forms in Soils

In temperate humid climate regions, the Mg contents in soils with low salt and carbonate contents usually lie between 0.5 and 5 g kg^{-1}. The main portion is found in **silicates**, especially in amphiboles, pyroxenes, olivines, biotites, and some clay minerals like chlorites and vermiculites. For this reason, quartz-rich sandy soils generally have low Mg contents, and silicate-rich clayey soils have higher contents. In soils with pH ($CaCl_2$) > 6.5, magnesium is also found in **carbonates** such as dolomite [$CaMg(CO_3)_2$], magnesite ($MgCO_3$), and 1–3 % in calcite ($CaCO_3$), and in saline soils of arid and semiarid regions, also as readily soluble **Mg salts** (e.g. $MgSO_4$, $MgCl_2$).

Part of the Mg liberated by weathering is bound by the exchange media as **exchangeable Mg^{2+}**. In soils of temperate humid climate regions, this fraction increases with increasing clay and silt contents and also usually with increasing profile depth. Very low Mg contents are observed in podzolized sandy soils, very strongly acidified forest soils, and some tropical soils (e.g. Ferralsols, Acrisols), where Mg deficiency can also occur. The fraction of exchangeable magnesium in the total exchangeable cations (**Mg saturation**) in agricultural soils of Central Europe generally lies between 5 and 25 %. Fractions of about 15 % are optimal for the plant supply. In clay-rich coastal Fluvisols and Vertisols, as well as in soils formed from Mg-rich igneous rocks (e.g. basalts, peridotites) and dolomites as well as in some saline and alkali soils, the Mg saturation can be considerably higher, and especially in subsoils, it can sometimes even exceed the Ca saturation. In contrast, the Mg saturation only reaches values <0.01–1 % in very strongly acidified forest soils. At Mg/Al ratios <0.07 at the exchange complex, the Mg supply of spruce is considered to be critical.

The **Mg concentration in the soil solution** is mainly determined by the Mg saturation. It fluctuates in soils of temperate humid climate regions across a broad range from <0.1 to 60 mg L^{-1}. While it often lies between 5 and 25 mg L^{-1} in arable soils, it drops down to <0.1–10 mg L^{-1} in extremely to very strongly acidified forest soils. The Mg species found in the solution phase are mainly Mg^{2+} ions and smaller fractions of organic Mg complexes, and sometimes $MgSO_4^0$ and other species.

9.6.6.2 Mg Supply to Plants, Mg Fertilization and Mg Leaching

The Mg contents of plants in the green plant parts generally lie between 1 and 10 g kg^{-1} DM. Mg deficiency is observed at Mg contents <2 g kg^{-1} DM in the vegetative parts of agricultural crops, and in forest trees (spruce) below 0.6–0.8 g kg^{-1} DM in the youngest needle generation. In grassland, the Mg content of the biomass should be at least 2.0 g kg^{-1} with regard to animal health (prevention of grass tetany in cattle). Human nutrition also sometimes shows signs (e.g. cramps in the calf muscles) of suboptimal to low Mg supply.

The Mg concentration in the soil solution and the content of exchangeable Mg in the soil are most significant for the Mg supply to plants. In silty, loamy and clayey soils under agricultural use, a high content of exchangeable Mg in the subsoil also significantly contributes to the Mg supply. On fertilized soils, Mg uptake by plants from the soil solution can be strongly reduced by high NH_4^+, K^+ and Ca^{2+} concentrations due to ion competition, so that only suboptimal Mg supply to the plants or even Mg deficiency can be the result. In strongly acidified soils, e.g. in many forest soils, very low Mg concentrations in the soil solution (up to <0.1 mg L^{-1}) can lead to strong ion competition by H^+ and Al^{3+} as well as Mn^{2+}, which can lead to Mg deficiency in forest ecosystems.

In trials with nutrient solutions, strongly reduced Mg contents in the fine roots of forest trees and considerable root damage were observed at Mg/Al molar ratios of 0.025. However, Mg deficiency can probably already be expected at Mg/Al <0.2 in forest trees. In addition to the soluble and exchangeable Mg, non-exchangeable Mg from octahedral sheets of trioctahedral micas and clay minerals or from the interlayers of clay minerals can also be made plant-available in strongly acidified soils. In very strongly acidic soils, liming with dolomite has a particularly positive effect on Mg uptake by plants, because the rise in pH reduces ion competition by H^+, Al^{3+} and sometimes also Mn^{2+} ions, and also increases the Mg content in the soil solution and on the exchange media.

Determination of the **Mg supply in soils** is based on the measurement of the dissolved and exchangeable Mg^{2+}. This is usually achieved by extraction with 1 M NH_4 acetate (Sect. 9.6.4.3) or with Mehlich-3 solution (Sect. 9.6.2.4). In Germany, extraction with a 0.0125 M $CaCl_2$ solution according to the method by Schachtschabel is most commonly used. The CAT method is also used to determine the Mg as well as Na, Cu, Mn, Zn and B supply in soils. (extraction solution: 0.01 M $CaCl_2$ and 0.002 M DTPA).

Extensive field experiments have demonstrated that Mg deficiency symptoms in young potato and oat plants on Pleistocene sandy soils almost only occur at contents <50 mg $Mg(CaCl_2)$ per kg, especially at comparatively high K contents and thus a wide K/Mg ratio in the soil. Higher yields through Mg fertilization were often achieved on sandy soils at $Mg(CaCl_2)$ contents in the Ap horizon of less than 20–30 mg kg^{-1}. On clay-rich soils with $Mg(CaCl_2)$ contents <50 mg kg^{-1}, in contrast, higher yields were seldom achieved with Mg fertilization, even with high contents of exchangeable potassium in the Ap horizon. The optimal soil test category C desired for arable land is 30–40 mg Mg per kg of soil in sandy soils, 40–60 for loamy sands to loams, 60–90 for clayey loams to clays, and 80–120 for all grassland soils .

The **Mg removal** with wheat yields of 8 t ha^{-1} is of ca. 19 kg Mg ha^{-1} (grain ca. 10, straw ca. 9 kg ha^{-1}), and for fodder beet up to ca. 50 kg Mg ha^{-1} a^{-1} (beets ca. 27, leaves ca. 23 kg, see Table 9.12). With an optimal Mg supply in the soil (category C), **Mg maintenance fertilization** is recommended, which consists of the Mg removal by the harvested field crops plus the Mg leaching depending on the precipitation depth and the soil texture. **Mg leaching** generally increases with the Mg supply from sandy to clayey soils, and often lies between 6 and 22 kg ha^{-1} a^{-1} under temperate humid conditions. In Central Europe, **Mg inputs** with open field precipitation lie between 0.5 and 8, on average 1 kg ha^{-1} a^{-1}. Inputs can reach 8 kg ha^{-1} a^{-1} only in coastal regions. Mg addition with precipitation is therefore of only low significance for the Mg balance in soils of areas far away from the coast. Mg maintenance fertilization for soil

test category C, depending on the cultivated field crops and soil texture, often requires 20–70 kg Mg ha^{-1} a^{-1}, for grassland up to 40 kg Mg ha^{-1} a^{-1}.

Mg fertilization can be performed in different ways. Dolomite ($CaMg(CO_3)_2$) works particularly well on very strongly acidified forest soils. In addition to the rise in pH, the often poor Mg (and Ca) supply in forest soils is considerably improved by so-called compensative liming with 3 t ha^{-1} of finely ground dolomite.

9.6.7 Sodium

Sodium is essential for animals and human beings, as well as for most C_4 plants (e.g. millet) and for halophytes; however, this has not been proven beyond a doubt for C_3 plants. For the latter, it is sometimes a "beneficial" element, because it promotes growth in several plant species, e.g. in sugar beet. In terms of the quantity required by most C_4 plants, Na may be assigned to the trace elements (see Table 9.7). However, in other plants it is utilized in similar amounts as potassium. It is capable of adopting some of the general ion functions of potassium and is significant particularly in the regulation of the water balance of plants. Pronounced Na deficiency in plants has not been observed.

The average Na content in the Earth's crust is 21 g kg^{-1}. Sodium is mainly found in alkali feldspars (ca. 8 %), plagioclases (ca. 3–6 %), and in muscovites (ca. 3–4 %). The total **Na contents** of central European soils lie between 1 and 10 g kg^{-1}. The highest contents are usually found in the silt fraction, where Na is mainly bound on feldspars.

According to the Na contents of plants, a distinction is made between **natrophilic** (e.g. sugar beet, spinach, celery) with 10–35 g Na kg^{-1} DM and **natrophobic** plants (e.g. wheat, maize, potato) with 0.1–1.5 g Na kg^{-1} DM. Because of the significance of sodium for animal nutrition, a Na content of 2.0 g kg^{-1} DM is considered to be necessary for pasture grasses; however, this content is often not reached.

The Na^+ concentration in the soil solution and the content of exchangeable Na^+ in the soil are most significant for Na uptake by plants. In temperate humid climate regions, the Na concentration in the soil solution in A horizons of arable and forest soils generally lies between 1 and 20 mg Na L^{-1}. At high K^+ contents in the soil solution, the Na uptake by plants is reduced due to preferential K uptake. The Na saturation in central European soils, with the exception of several coastal Fluvisols, generally lies below 3 %. Stronger Na accumulation does not take place even with higher Na additions, because sodium is only very weakly bound and is therefore easily leached out. Soils in arid and semiarid regions (Solonchaks, Solonetzes), in contrast, exhibit higher contents of dissolved and exchangeable Na and sometimes also Na salts (mostly NaCl), especially also under the influence of artificial irrigation. In these cases, the Na concentration of the soil solution can rise up to 100–200 mg Na L^{-1} and then impede the growth of most plants (see Sect. 10.2.5).

Na removal, e.g. by sugar beet (incl. leaves), can reach ca. 70 kg ha^{-1}. **Na input through wet and dry deposition** in Central Europe generally lies between 1 and 17, on average 4 kg Na ha^{-1} a^{-1}; however, it can be much higher in coastal regions (up to ca. 30 kg ha^{-1} a^{-1}). **Na fertilization** mainly takes place with the spreading of potassium salts and farmyard fertilizers (e.g. cattle liquid manure). The Na supply in soils can be determined with 1 M NH_4 acetate, with a Mehlich-3 solution or with the CAT method (see Sect. 9.6.6.2). According to the CAT method, arable and grassland soils should have contents of 16–30 or 40–69 mg Na per kg^{-1} of soil (soil test category C).

9.7 Micronutrient Elements

Plants only require trace quantities of the elements Cl, Fe, Mn, B, Zn, Cu, Ni and Mo (in the sequence of their contents in plant material); they are therefore called **micronutrient elements**. In the sequence of the periodical system, Mn, Fe, Cu, Zn and Ni occur as cations, and B, Mo and Cl as anions. Nickel is required in such small quantities that no deficiencies are observed under field conditions. Table 9.15 provides an overview

Table 9.15 Mean removal of micronutrient elements by wheat and sugar beet in Germany (calculated according to the DLG feed value tables)

Plant	Wheat		Sugar beet	
	Grain	Straw	Beet	Leaves
Yield (t ha^{-1})	8	7.2	65	39.4
Element	Removal (g ha^{-1})			
Mn	240	410	990	1130
Fe	310	1870	3500	1615
Cu	48	50	83	73
Zn	450	250	585	455
Mo	2.2	1.2	1.8	2.9
Co	0.6	0.4	1.4	2.4

of the mean extraction of micronutrient elements by wheat and sugar beet with high yields.

9.7.1 Manganese

Manganese is an essential element for all life forms. For example, growth and fertility disorders in cattle can sometimes be attributed to Mn deficiency. Plants absorb Mn mainly as Mn^{2+} ions from the soil solution. It activates enzymes for photosynthesis as well as for the synthesis of chlorophyll and protein. Mn deficiency is often observed as interveinal chlorosis of young leaves, and stronger deficiency as brownish-black necrotic specks (e.g. "grey specks" in oats), resulting in lower yields.

9.7.1.1 Mn Contents, Minerals and Forms in Soils

The mean Mn content in the continental crust is 800 mg kg^{-1}, and in various rocks 50–1600 mg kg^{-1}. The Mn contents of **soils** generally range between 40 and 1000 mg kg^{-1} (Table 9.16). Soil horizons with pedogenic Mn accumulation, however, can contain >3000 mg kg^{-1}, and quartz-rich sands less than 20 mg kg^{-1}. Mn in soils is mostly fixed in Mn oxides (Sect. 2.2.6.5) as well as in silicates and carbonates (as $MnCO_3$). Mn oxides can also be associated with Fe oxides. Furthermore, Mn is found in organic complexes and in exchangeable and dissolved form as Mn^{2+} in the soil. In pedogenic Mn oxides, it is found in changing proportions in 2- and 4-valent form, and more rarely in the unstable 3-valent form. Heavy metals such as Co, Ni, Zn, Cd and Pb often accumulate in Mn oxides. During the course of soil development, manganese is more strongly translocated and leached out than iron. Particularly acidic soils, such as Podzols and Stagnosols, can be strongly depleted in Mn.

Under aerobic conditions, the Mn content of the **soil solution** of arable soils (Ap horizons) in temperate humid regions varies between 0.001 and 3 mg L^{-1}, and in acidic forest soils, 0.02–30 mg L^{-1}. Here, dissolved Mn is found in the form of ions and organic complexes. In neutral and alkaline soils, mainly soluble organic Mn complexes determine the solubility of Mn, which can account for more than 90 % of the dissolved Mn. In acidic soils, the soil solution mostly contains free Mn^{2+} ions, which are at equilibrium with the sorbed Mn^{2+}. In addition, Mn^{2+} is mostly liberated from Mn oxides, which, in addition to organic Mn complexes, represent the most important Mn reserves for plant nutrition. They are at equilibrium with the Mn^{2+} ions in the soil solution, depending on the **pH** and **Eh**, e.g.:

$$MnO_2 + 4H^+ + 2e^- \Leftrightarrow Mn^{2+} + 2H_2O \quad (9.18)$$

If the H^+ concentration increases, the equilibrium is shifted to the right, and more Mn^{2+} is formed. Theoretically, a decrease of one pH unit can lead to an increase of up to 100-fold in the Mn^{2+} concentration in the solution, and therefore simultaneously cause a corresponding increase in the sorbed Mn^{2+}. Figure 9.19 shows the relationship between Mn^{2+} and the **pH** in central European sandy soils; the fraction of exchangeable Mn^{2+} in the **active manganese** (=sum of the exchangeable Mn and Mn from finely distributed, readily reduced Mn oxides) increases with decreasing soil pH. According to Eq. (9.18), the Mn^{2+} concentration in the soil solution is higher the more electrons are available for

Table 9.16 Average geogenic base levels (mg kg^{-1}) of some micronutrient elements and potentially toxic trace elements in rocks and background contents of soils (A horizons) developed from various parent rocks in Central Europe (data from different authors was compiled; () = individual values)

	Mn	Cu	Zn	B	Mo	Co	V	Cr	Ni	As	Cd	Sn	Sb	Hg	Tl	Pb
Continental crust	800	35	70	10	1.5	18	109	88	45	3.5	0.1	2.5	0.3	0.02	0.5	15
Ultrabasic rocks	1600	10	50	2	0.3	150	40	1600	2000	1	0.05	0.5	0.1	0.02	0.06	1
Basalt/gabbro	1400	90	100	5	1	50	200	170	130	1.5	0.15	1.5	1	0.02	0.08	4
Mica schist, phyllite	700	25	80	50	(1.5)	13	100	75	25	4.3	0.15	5	(0.5)	0.02	0.65	20
Granite	325	15	50	15	1.8	4	30	12	7	1.5	0.09	3	0.2	0.03	1.1	30
Claystones	850	45	95	100	1.3	20	130	90	70	10	0.3	10	2	0.45	0.7	22
Sandstone	50	5	15	35	0.2	0.3	20	35	2	1	0.05	0.5	0.05	0.03	0.8	7
Limestone	700	4	25	20	0.4	2	20	11	15	2.5	0.16	0.5	0.2	0.03	0.05	5
Loess	500	13	45	(60)	1.2	8	45	35	20	7	0.3	4.5	0.5	0.05	0.1	25
Glacial till, loam	500	11	40	(50)	1	6	40	30	18	5	0.3	4.5	0.5	0.04	0.03	20
Soils developed from:																
Sand	80	3	15	(12)	(0.4)	2	10	5	6	2	0.2	0.5	0.2	0.03	0.02	10
Glacial till	500	11	50	(45)	(1)	5	40	25	12	6	0.3	4.5	0.5	0.08	0.04	25
Loess	500	15	55	(55)	(1.5)	5	40	30	20	7	0.3	4.5	0.5	0.08	0.1	35
Basalt	1000	45	135			(60)	(200)	(180)	150	3	0.3	(1)	0.4	0.06		42
Common range in soils	40–1000	2–40	10–80	5–80	0.2–5	1–40	8–60	5–100	3–50	1–20	0.1–0.6	0.3–10	0.1–3	0.02–0.2	0.02–0.4	2–80

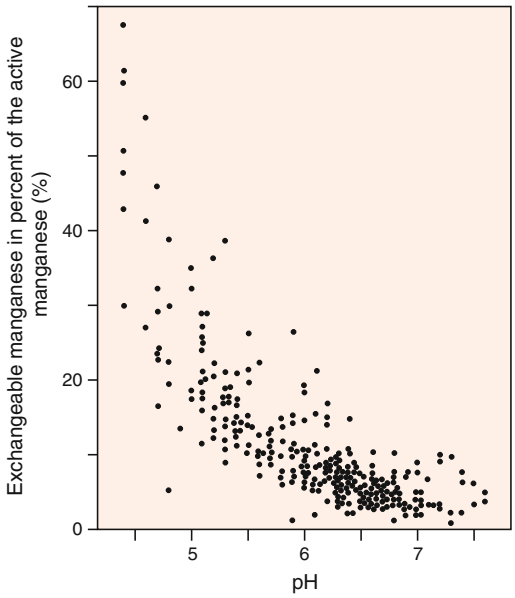

Fig. 9.19 Proportions of exchangeable Mn as a function of soil pH in sandy soil (after Schachtschabel 1957)

reduction processes and therefore the lower the **redox potential** (Eh) (Sect. 5.7). Under reducing conditions, Mn(III, IV) oxides are reduced to Mn^{2+} by the activity of anaerobic bacteria. Up to more than 100 mg Mn^{2+} L^{-1} were measured in the soil solution under strongly reducing conditions. When the soil dries out again, the formed Mn^{2+} is oxidized back to Mn(III, IV) oxides, often by Mn oxidizing bacteria.

9.7.1.2 Mn Supply to Plants, Mn Extraction and Leaching, Mn Fertilization

The concentration of plant-available Mn^{2+} in the soil solution depends to a great extent on the soil pH, on the redox conditions, and on the reserves of active Mn in the soil. When the Mn^{2+} concentrations are too low, plants can sometimes initiate mobilization of Mn^{2+} through the excretion of root exudates (e.g. maleic acid). With rising pH and therefore decreasing proportions of dissolved and exchangeable Mn^{2+} (Fig. 9.19), Mn uptake by plants decreases. For this reason, weakly acidic to alkaline soils can exhibit Mn deficiency, especially at low contents of **active manganese** (see above). For example, Mn deficiency symptoms (gray speck) has often been observed in young oat plants on many sandy soils of Central Europe with pH >5.7 in conjunction with a low content of plant-available active manganese. The same is true for other crops. In contrast to active Mn, the total content of Mn oxides together with the pH is not a good measurement for Mn availability, because Mn oxides in many soils like Podzols, Gleysols or Stagnosols sometimes occur in the form of poorly available concretions and as occlusions of Fe oxides.

The dependence of the Mn availability on the redox conditions is clearly demonstrated by the fact that Mn deficiency symptoms sometimes developing in dry periods during the early growth stages (see above) usually disappear again when the rains return, because higher **soil moisture** leads to a reduction of Mn oxides to Mn^{2+} ions. For this reason, Mn deficiency symptoms are generally not observed in wet springs.

In temperate humid climate regions, **Mn deficiency** is observed particularly on Mn-poor sandy soils and drained fens at pH($CaCl_2$) ≥ 6, as well as on calcareous soils (pH > 7). In contrast, Mn deficiency is rarely observed on carbonate-free silty, loamy and clayey soils with high contents of active manganese, and usually only on dry sites. In arid climates, Mn deficiency is widespread on soils containing carbonates. Peas, oats, beets and potatoes react particularly sensitively to Mn deficiency. Mn deficiency symptoms develop in many crops at Mn contents less than 15–20 mg kg^{-1} in the dry matter (DM). Latent Mn deficiency without visible symptoms can also occur at higher Mn contents in the plant. For cattle fodder, an Mn content of ca. 50 mg kg^{-1} DM is considered to be sufficient. Contents of 40–150 mg Mn kg^{-1} DM represent an optimum supply to the plants.

Toxic effect for plants may occur in strongly acidic, clay-rich soils (pH[$CaCl_2$] < 5) at high Mn^{2+} concentrations in the soil solution, especially with poor drainage or intermittent flooding. This is reflected by high Mn contents in the plants. Mn contents >1000 mg kg^{-1} in the DM of crops generally characterize **Mn toxicity** and associated yield losses. On very strongly acidified central European forest soils developed on

loess, more than 5000 mg Mn kg^{-1} DM of spruce needles were measured. However, spruce is very resistant to Mn toxicity. In contrast, Mn contents of 150–200 mg kg^{-1} of DM in barley plants already lead to yield losses, whereas in cotton, this only happens at contents of 2000–5000 mg kg^{-1} DM. On very strongly acidic soils, Mn toxicity is often associated with Al toxicity and a deficiency of various nutrient elements (Mg, Ca, K etc.). Mn toxicity can be remediated by liming the soil and raising the pH (see Fig. 9.19).

Under central European conditions, the removal of Mn by crops generally represents 240 (wheat grain) to 2120 (sugar beet with leaves) g ha^{-1} a^{-1} (Table 9.16). **Mn leaching** with seepage water on arable land ranges between 1 and 800 g ha^{-1} a^{-1}. However, inputs with mineral and organic fertilizers (usually ca. 10 kg ha^{-1} a^{-1}) result in a positive balance. In acidic forest soils, in contrast, the balance is usually clearly negative, with Mn leaching reaching up to 9000 g ha^{-1} a^{-1}.

Remediation of **Mn deficiency** is possible through foliar fertilization with $MnSO_4$ or Mn chelates. When adding Mn to the soil, high inputs of 100–400 kg ha^{-1} of manganese sulfate are required for a reliable and lasting remediation of the deficiency. In $CaCO_3$-free soils, another measure used to eliminate Mn deficiency is a decrease in pH through fertilization with physiologically acidic fertilizers.

In Anglo-Saxonian countries, extractions with buffered 0.005 M DTPA (pH 7.3 or 7.6) or with 0.05 M EDTA (pH 7.0) are commonly used soil analyses to determine the Mn supply in soils. With these methods, the data on the contents for an optimal Mn supply in soils fluctuate depending on the soil properties, site conditions and cultivation methods. In Germany, the SCHACHTSCHABEL method is used to determine the **active manganese**, among others. Here, Na sulfite (pH 8.0) is added as a reducing agent to the solution for extracting the soluble and exchangeable Mn^{2+} (0.5 M $MgSO_4$), which then also extracts the finely distributed, instable Mn oxides after reduction to Mn^{2+} ions. According to this method, the range of optimal supply (cf Sect. 9.5.2.5) for sandy soils with pH($CaCl_2$) >5.8 lies between 10 and 20 mg Mn kg^{-1}. Recently, the available Mn, as well as Cu, Zn and B, are also determined using the CAT method (see Sect. 9.6.6.2). This method measures the exchangeable and organically fixed Mn, as well as parts of the finely distributed oxidic Mn. According to this method under central European climatic conditions, the Mn contents for the desired soil test category C in field and grassland soils, depending on the pH ($CaCl_2$), are 5–15 (at pH <5.5), 20–40 (at pH 5.6–6.0), and 40–60 mg kg^{-1} (at pH >6.5). In the case of an optimal Mn supply, maintenance fertilization with 2 kg Mn ha^{-1} a^{-1} is recommended.

9.7.2 Iron

Iron is an indispensable element for plants, animals and human beings, which is only required in trace amounts by all life forms. In plants, it is a component of chlorophyll and proteins, and activates different enzymes for photosynthesis and metabolic activities. Plants cover their Fe requirements mainly from organic Fe(II) and Fe (III) complexes that are present in the soil solution. In the process, Fe(III) is reduced to Fe^{2+} on the root surface and then absorbed. Grasses can also absorb dissolved organic Fe(III) complexes. Because Fe is required for the formation of chlorophyll, among other things, young leaves with Fe deficiency are colored yellow to white, whereby the leaf veins initially stay green.

After aluminum, iron is the most common metal in the continental crust with average contents of 4.2 %. The mean Fe contents of **rocks** is highest in basalt-gabbro rocks (8.6 %) and claystones (4.8 %), and lowest in sandstones (0.9 %) and fluvic sands (0.2 %). The total Fe contents in **soils** often vary between 0.2 and 5 % and therefore in the same range as rocks. Iron accumulates in the form of oxides in some soil horizons (e.g. Bs of Podzols, Bo of Gleysols), in mottles and Fe concretions of redoximorphic soils, as well as in Plinthosols. The Fe content in concretions and in Bo horizons containing bog iron ore and in laterite crusts (petroplinthite layers) can reach more than 40 %.

Under **aerobic** conditions in soils, iron is mainly found in the form of **Fe(III) oxides** (Sect. 2.2.6.3) and in silicate compounds, and sometimes in organo-mineral compounds. Among the oxides, well-crystallized goethite and hematite represent exceptionally stable compounds, where under oxidizing conditions, the iron is present in a form that is hardly available to plants. Fe is mainly replenished from poorly crystallized, oxalate-extractable ferrihydrite and from organo-mineral compounds. Because of the low solubility of all Fe(III) oxides, the Fe concentration in the **soil solution** under oxidizing conditions is very low (usually <0.02–0.3 mg L^{-1}). Only at pH($CaCl_2$) values <3.0, as they are found in forest soils and acid sulfate soils, the contents of dissolved and exchangeable Fe^{3+} increase due to the onset of ferrihydrite dissolution. At pH values >3.5, the soil solution contains almost only soluble organic Fe complexes. The high Fe concentrations in seepage water, groundwater and fluvial water (0.1–10 mg L^{-1}) sometimes observed under aerobic conditions are attributed to the presence of organic Fe complexes and finely dispersed Fe oxide colloids. Under **anoxic** conditions, however, after reduction of Fe(III) oxides to Fe^{2+} ions, there may be high Fe^{2+} concentrations in the soil solution and in the groundwater (up to >1000 mg L^{-1}, see Sect. 5.7.4).

Under **aerobic** conditions, the **Fe availability** in soils is mainly determined by interactions between poorly crystallized Fe(III) oxides and soluble organic complexing ligands, which form soluble Fe(II, III) complexes. The mobilization of iron and of other nutrients and potentially harmful elements associated with rhizosphere effects is caused by complexing ligands that are produced by microbial activity or liberated during the decomposition of organic matter, by root exudates from plants, and by soluble fulvic and humic acids.

In temperate humid climate regions, the Fe contents of green plant parts generally range between 30 and 500 mg kg^{-1} DM. There may be Fe **deficiency** at Fe contents in the shoot <50–80 mg kg^{-1}. This is seldom observed on central European soils; however, it is relatively widespread around the world in soils containing $CaCO_3$, despite generally high Fe oxide contents. Furthermore, it can occur when the soil is limed to pH >7 (lime-induced chlorosis) and is particularly common in fruit trees. However, the total Fe contents in the deficient plants often do not differ much from those of plants without symptoms. In this case, a considerable portion of the iron in deficient plants is in a physiologically ineffective form. In calcareous soils, especially in wet phases, an important cause for this is the high HCO_3^- concentration in the soil solution (together with high Ca, Mg and P concentrations), which cause Fe immobilization in the plant through various physiological effects. Fe deficiency can also occur in soils of subtropical and tropical-arid regions containing only well-crystallized oxides such as goethite and hematite, which hardly replenish any Fe. Fe deficiency was also sometimes also observed on acidic, Fe-poor high moor soils and peat substrates in horticulture. Fe deficiency can be remediated by applying Fe chelates as a foliar fertilizer or by adding them to the soil or peat. Green manure can also lead to Fe mobilization in the soil due to increased formation of organic ligands, as well as the application of acidifying fertilizers.

Due to the complex causes for the appearance of Fe deficiency in plants, the determination of Fe availability through soil tests involves problems and provides only very uncertain conclusions. However, a visual diagnosis of Fe deficiency symptoms is possible at an early stage. On the other hand, high heavy metal contents in soils can also cause toxicity symptoms resembling Fe deficiency symptoms. In this case, an elevated uptake of heavy metals can be the cause for reduced Fe uptake. **Fe toxicity** can be triggered by high Fe^{2+} concentrations in the soil solution under **anoxic** conditions, e.g. in paddy soils. High Fe^{2+} uptake by rice plants mainly takes place when there is a simultaneous deficiency of macronutrients; it leads to the formation of reddish-brown spots (bronzing) on the leaves.

9.7.3 Copper

Copper is an essential element for the nutrition of all life forms, and it is transferred from the soil through plants to animals and human beings. Plants absorb copper from the soil solution as Cu^{2+} ions, probably also in the form of low-molecular organic complexes and sometimes from inorganic complexes. It is a component in various enzymes and is therefore involved in photosynthesis and the synthesis of chlorophyll and proteins, among others. Cu deficiency symptoms include chlorosis and pale yellow and white colored leaves, curled and withered leaf tips (whip tailing), and yield losses. Cu surplus can have toxic effects on plants and several animals (especially sheep). In contrast, chronic Cu toxicity due to nutrition is hardly documented in humans.

9.7.3.1 Cu Contents, Minerals and Forms in Soils

The mean Cu content in the continental crust is 35 mg kg^{-1}, and in various rocks 4–90 mg kg^{-1}. In igneous rocks and Cu-rich shale, copper is found as sulfide (e.g. Cu_2S, $CuFeS_2$), and after oxidation also as malachite [$Cu_2(OH)_2CO_3$], among others. In addition, it can sometimes be bound instead of Mg^{2+} and Fe^{2+} in silicates. The Cu contents of hardly polluted soils generally lie between 2 and 40 mg kg^{-1}; in polluted soils, values of up to >1000 mg Cu kg^{-1} were measured. The formation of malachite was observed in strongly polluted soils containing carbonates.

Investigations on the **binding form** of copper in A horizons of soils in temperate humid regions demonstrate that 25–75 % of the copper is bound in organic compounds, 15–70 % on Mn and Fe oxides, and 1–10 % is bound on silicates. At pH values <6, the organically bound fraction generally represents the largest fraction. The fractions bound on oxides sometimes dominate at neutral soil pH. Also in subsoil horizons, copper is predominantly bound to oxides (up to 80 % of the total Cu) or is contained in the lattice of silicates (up to 40 % of the total Cu). The significance of iron oxides for Cu binding is also reflected by the fact that 8 to 10 times more Cu can accumulate in concretions of Gleysols and Stagnosols than in the remaining soil mass. Cu sulfides (CuS, CuS_2) can be found in soils and sediments under **anoxic conditions**.

The majority of the copper fixed on Mn and Fe oxides and organic matter is very firmly bound and in a form that is difficult to desorb. For this reason, the portion of the **exchangeable** Cu^{2+} in the total Cu is generally low (<1 %) at pH values >5. However, in strongly to extremely acidic soil pH values, as are often observed in acidic forest soils, the percentage of this fraction in the total Cu can rise to 20 %. The **Cu solution concentration** in agricultural soils is <0.03–0.3 mg L^{-1} and can rise up to 0.8 mg L^{-1} in extremely acidic forest soils. In these cases, the solution concentration is mainly determined by pH-dependant adsorption and desorption processes, as well as by complexing processes depending on the content of soluble organic and inorganic complexing ligands. With the presence of HCO_3^- ions and organic ligands and pH values >6, ca. 80 % and more of the copper in the soil solution is in the form of carbonate complexes ($CuCO_3^0$) and organometallic complexes (DOCu). **Soluble organic ligands**, which are mainly liberated during the microbial **decomposition of litter** and from vegetation residues or excreted by living roots, are capable of mobilizing adsorbed copper and therefore cause a considerable increase in the Cu solution concentration. At pH values <5, the DOCu fraction in the total dissolved Cu can rise to 95 %. Inversely, the presence or input of high molecular **insoluble organic substance**s, e.g. of peat, can lead to strong Cu fixation and therefore Cu deficiency in plants.

At low contents or with the absence of soluble organic complexing ligands (e.g. in subsoils), mainly Cu^{2+} and $CuSO_4^0$ are observed as inorganic Cu species at acidic soil pH. Although Cu^+ ions can be formed under strongly reducing conditions, they are unstable in terrestrial soils. At weakly acidic to alkaline pH values, $CuCO_3^0$ and hydroxo Cu complexes [$CuOH^+$, $Cu(OH)_2^0$ etc.] are found in the soil solution. Soluble phosphato Cu complexes can also be formed in intensively fertilized soils with high phosphate contents. Furthermore, phosphate increases Cu

adsorption and therefore causes a lowering of the Cu solution concentration and uptake by plants. Because of the different behavior of organic and inorganic Cu species, the Cu concentration in the soil solution under humid conditions is usually relatively little affected by the pH.

9.7.3.2 Cu Supply to Plants, Cu Removal and Leaching, Cu Fertilization

In the pH range above 5, Cu uptake by plants on uncontaminated arable soils of temperate humid climates is also generally not or hardly affected by the soil pH. Even on soils containing $CaCO_3$, Cu deficiency is very rare because sufficient copper is generally available in the form of soluble carbonato- or organometallic complexes.

The **Cu contents of plants** usually range between 2 and 30 mg kg^{-1} of DM. Yield losses can be expected at Cu contents <1.5 mg kg^{-1} of DM in the youngest fully developed cereal leaf blades. Critical contents of 2–5 mg kg^{-1} of DM in the leaf were determined for other plants. With respect to the health of cattle, Cu contents in the feed of 5–6 mg kg^{-1} are considered to be sufficient; lower Cu contents in the feed of grazing cattle can cause hypocuprosis.

Under central European conditions, the removal of Cu by harvesting generally represents about 50 (wheat grain) to 155 (sugar beet with leaves) g Cu ha^{-1} (Table 9.16). **Cu leaching in agricultural soils** of Central Europe was measured to be 10–90 g ha^{-1} a^{-1}, and in acidic forest soils up to 110 g ha^{-1} a^{-1} (see Table 9.10). Before the implementation of air quality control measures, Cu inputs with precipitation were sometimes considerable (up to more than 300 g ha^{-1} a^{-1}), so that soils in urban agglomerations had a **positive Cu balance** for many decades, which resulted in a good Cu supply in the soil. In regions with very low atmospheric Cu inputs, e.g. in some areas of Scotland, Ireland, Denmark and other countries, in contrast, only have a suboptimal Cu supply for the crops and the Cu contents in the animal feed are too low.

Under humid climate conditions, **Cu deficiency** occurs mostly on sandy soils developed from parent rocks with low Cu contents and on peat soils, and rarely on silty, loamy, and clayey soils. Wheat, oats and alfalfa are particularly sensitive to Cu deficiency. Cu deficiency can be remediated by means of foliar fertilization with Cu chelates. For soil fertilization, 3–6 kg Cu ha^{-1} in the form of Cu sulfate or finely ground Cu alloys are recommended for all soil types, which is sufficient for 5–8 years. Regular spreading of liquid swine manure (4–20 g Cu m^{-3}) is also suitable.

In Anglo-Saxonian regions, the Cu supply in soils is often determined using DTPA and EDTA as extraction agents (Sect. 9.7.1.2). The specifications for an optimal supply in the soil vary in different countries. In Germany and the Netherlands, the Cu supply of soils is determined through extraction with 0.43 M nitric acid at room temperature [Westerhoff method; abbreviated Cu (HNO_3)]. In arable soils, Cu(HNO_3) contents of 4 mg kg^{-1} are considered to be sufficient for all crops. The CAT method (Sect. 9.6.6.2) is also recently being used: here, the Cu contents for sandy and loamy to clayey soils lie between 0.8 and 2.0 or 1.2–4.0 mg Cu kg^{-1} for the desired optimal supply category C.

On Cu-contaminated soils, there may also be **toxic Cu effects** on plants. In some cases, decades of use of pesticides containing Cu (35–40 kg Cu ha^{-1} a^{-1}) in hop and wine growing in Central Europe have caused Cu accumulation in soils reaching 600 mg Cu kg^{-1}. The spreading of large amounts of liquid swine manure, which often has high Cu contents due to the use of Cu-enriched compound feeds (up to ca. 20 mg L^{-1}), has resulted in Cu contamination of the soil in some areas with intensive industrial livestock farming. Cu surplus can lead to Fe, Zn and Mo deficiency in plants and therefore considerable yield losses. Cu toxicity was observed in different plants at contents above ca. 20–35 mg Cu kg^{-1} of DM (leaves). In nutrient solutions, some plants already exhibit toxic effects at >0.1 mg Cu L^{-1}. Microbial activity can already be reduced at 0.1 mg Cu L^{-1} in soil solution. For this reason, threshold values for the total Cu contents in sewage sludge and in soils were also defined for the spreading of sewage sludge in different

countries. In Germany, sewage sludge can only be spread if the total Cu content of the soil is less than 60 mg kg^{-1}.

In contaminated soils, the **solubility** and **availability** of copper increase considerably at pH values <5. On Cu-rich, strongly acidic soils, toxic effects of copper can therefore be reduced if the soil pH is raised to values around 6. Increased Ca fertilization, e.g. as gypsum, can also compensate Cu toxicity. High inputs of phosphate can also sometimes reduce Cu uptake by plants and cause lower Cu contents in the roots.

9.7.4 Zinc

Zinc is an indispensable trace element for plants, animals and human beings. It is mostly absorbed by plants from the soil solution as Zn^{2+} and probably also as $Zn(OH)^{+}$, as well as in the form of dissolved organic Zn complexes. It activates various enzymes (phosphatases, proteinases) for chlorophyll formation, among others, and is involved in the synthesis of growth substances. Deficiency symptoms include light yellow interveinal chloroses especially in younger leaves, and later brown necrotic spots, reduced plant growth, and rosette-like appearance of the leaves (e.g. in apple). At very high contents in the soil, however, zinc can have a toxic effect on plants and microorganisms. In human beings, chronic zinc toxicity resulting from high dietary intake of zinc has not been observed.

9.7.4.1 Zn Contents, Minerals and Forms in Soils

The mean Zn contents in different rocks range between 15 and 100 mg kg^{-1}; the average content in the continental crust is ca. 70 mg kg^{-1} (Table 9.16). Sandstone generally contains low amounts of zinc, and mudstone, in contrast, has higher amounts. Some slates can contain up to 300 mg Zn kg^{-1} and more. In igneous rocks, metamorphic rocks, and in ore deposits, zinc is found as sulfide (ZnS) and sometimes also together with other heavy metals as a mixed sulfide. $ZnCO_3$ can be formed as a weathering product of sulfides. In addition, zinc is bound in considerable fractions in silicates, mostly as a minor constituent and substitute for Mg^{2+} and Fe^{2+}.

The total Zn contents in soils that are not or only slightly contaminated often fluctuate between 10 and 80 mg kg^{-1}. In topsoils developed from sand, glacial loam and loess in Central Europe, the mean background levels are ca. 15, 50 and 55 mg kg^{-1} (Table 9.16). Contaminated soils can reach contents of up to 5000 mg kg^{-1}. In such strongly contaminated soils, Zn minerals can be formed, such as $ZnFe_2O_4$ (franklinite) and Zn phosphates [e.g. $Zn_3(PO_4)_2 \cdot 4H_2O$], and at pH values >7 also Zn silicates such as Zn_2SiO_4 (willemite) and Zn carbonates [$ZnCO_3$, $Zn_5(OH)_6(CO_3)_2$]. Under reducing conditions, e.g. in paddy soils, very poorly soluble Zn sulfide (ZnS) can also be precipitated, which converts the zinc into a form that is not plant-available.

In temperate humid climate regions, in A horizons that are not or only slightly contaminated and have a moderately to weakly acidic soil pH, 40–60 % of the total Zn is bound in organic compounds. A rise in the pH values >7 leads to a strong increase in the affinity of Zn towards Mn and Fe oxides. The oxide-bound fraction then reaches 40–70 %, and in contaminated soils, up to 85 % of the total Zn. Through diffusion processes, zinc, as well as Mn, Co, Ni, Cu and other heavy metals, can enter the inside of oxide particles and be so strongly bound or trapped that they can only be mobilized again after the oxides have been dissolved. Zn diffusion takes place both in poorly crystallized oxides (e.g. ferrihydrite) and well-crystallized oxides (e.g. goethite), and in different clay minerals (especially smectite). At pH values <5, the affinity of Zn towards humic substances and Mn, Fe oxides is strongly reduced, however, it remains relatively high towards clay minerals. The fraction of the total Zn bound by **clay minerals** and other silicates reaches high proportions especially in Zn-poor acidified topsoils and in subsoils (30–85 %). The **exchangeable zinc** contents are very low at pH values >6. With decreasing pH, the proportion of this fraction in the total replenishable Zn (=EDTA extractable Zn) strongly increases, at pH 5 to 10–30 %

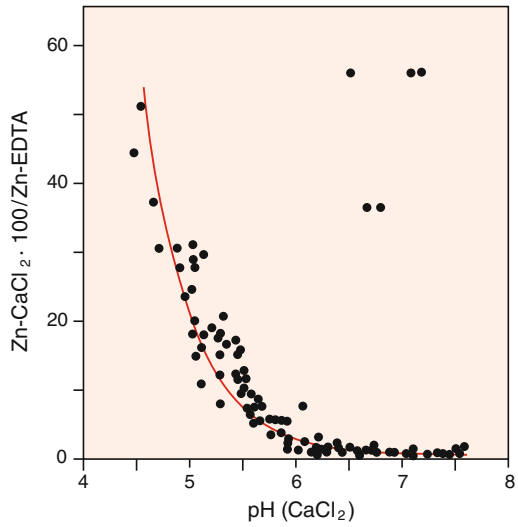

Fig. 9.20 Total replenishable Zn as function of soil pH

(Fig. 9.20) and at pH 3 (forest stands) sometime up to more than 50 %.

The Zn contents in the **soil solution** increase with decreasing pH and increasing contents of exchangeable and replenishable Zn. In agricultural soils that are not or only slightly polluted (pH 5–7.5), Zn contents range between 0.001 and 0.8 mg L^{-1}, in extremely acidic forest soils up to 4 mg L^{-1}, and in strongly polluted soils Zn concentrations may reach 15 mg L^{-1}. The majority of the zinc in humic topsoils is found as organometallic complexes in the soil solution (DOZn: 50–90 %). Zn^{2+}, $Zn(OH)^{+}$, $ZnCO_3^0$ and other Zn species are also found at pH values >6.5. Especially $Zn(OH)^{+}$ ions, whose proportion increases with rising pH, can be strongly adsorbed and fixed by oxides (specific adsorption). At low contents of organic complexing ligands (e.g. in the subsoil) and pH values <5, the majority of the dissolved zinc consists of Zn^{2+} ions. $ZnSO_4^0$ and $ZnHPO_4^0$ can also be found at higher sulfate and phosphate contents in the soil solution.

9.7.4.2 Zn Supply to Plants, Zn Removal and Leaching, Zn Fertilization

The Zn concentration in the soil solution has a significant influence on the Zn supply to plants. Because of increasing Zn^{2+} solubility with decreasing pH (Fig. 9.20), the Zn supply to plants in central European soils with pH values <6 is generally ensured. The Zn contents of plants generally lie between 10 and 100 mg kg^{-1} of DM. Yield losses in cereals (oats, wheat) can occur at a Zn content <25 mg kg^{-1} DM at the beginning of shoot development, however, deficiency symptoms are only observed at contents <15 mg kg^{-1} DM.

Through one harvest, the plants can extract ca. 450 (cereal grain) to 1050 g Zn ha^{-1} (sugar beet with leaves, Table 9.16) from the soil. **Zn leaching** from arable land in Central Europe varies between 10 and 360 g ha^{-1} a^{-1} and increases with decreasing pH. Losses with seepage water of up to 2400 g ha^{-1} a^{-1} were measured in acidic forest soils (Table 9.10). In contrast, atmospheric Zn inputs in Central Europe are relatively low. Therefore, the Zn balance of soils in Central Europe is mostly negative.

Zn deficiency with clear deficiency symptoms is relatively rare in Central Europe, mostly restricted to soils **containing carbonates**. However, Zn deficiency is relatively frequent worldwide in semi-humid to arid regions on alkaline soils with high contents of fine-grained $CaCO_3$. In these cases, the Zn availability is mainly reduced by high pH values. High phosphate concentrations in the soil can cause increased Zn binding and therefore lower Zn^{2+} concentrations in the soil solution, as well as reduced Zn uptake. Especially maize and beans as well as apple and citrus have high Zn requirements. Zn deficiency is also relatively frequently observed in rice plants. Causes for this can include Zn immobilization under reducing conditions by sulfides and/or clay minerals as well as ion competition for uptake by roots at high Fe^{2+}, Mn^{2+}, and rarely also Cu^{2+} contents. In cases of Zn deficiency under central European conditions, fertilization with 5–10 kg Zn ha^{-1} as Zn sulfate is sufficient for about 3 years. The spreading of liquid swine manure (15–70 mg Zn L^{-1}) can also improve the Zn supply in soils. Another option is foliar fertilization with Zn chelates.

In Anglo-Saxonian areas and other countries, the **Zn supply** in the soil is often determined through extraction with DTPA or EDTA. In doing so, the Zn contents for an optimal supply

in the soil and for the cultivated plants are adapted to the respective local conditions. In Germany, mainly the CAT method is used (Sect. 9.6.6.2): Ideal contents (soil test category C) are 1–3 mg Zn kg^{-1} of soil. Extraction of the water-soluble and exchangeable Zn fraction (mobile Zn) with 0.1 M $CaCI_2$ or with 1 M NH_4NO_3 has also proven to be suitable. Furthermore, EDTA is also used as an extraction agent. Particularly in permanent crops, leaf analysis and visual assessment of deficiency symptoms are also suitable evaluation criteria.

On soils that are strongly contaminated with zinc, there may also be **toxic Zn effects** in different plants above contents in the plant material of about 200–400 mg Zn kg^{-1} of DM. Up to 400 mg Zn kg^{-1} of DM were measured in grass plants. In pot trials with additions of soluble Zn salts, the Zn content of various plants increased to >1000 mg kg^{-1} of DM. The threshold concentration in nutrient solutions for the onset of Zn toxicity in various plants is about 2 mg Zn L^{-1}. Temporary harmful effects on microorganism activity are observed above ca. 1 mg Zn L^{-1}.

Zinc is one of the most commonly used heavy metals in industrial production processes. The soils of many regions of Europe with centuries of ore mining are highly contaminated with zinc (up to 5000 mg kg^{-1}). There is also often strong Zn pollution in the soils of areas surrounding steel mill operations and industrial plants working with zinc ore. In addition, there are also other sources of Zn contamination of soils, such as the spreading of sewage sludge. The remediation of soils contaminated with Zn requires liming up to pH values ≥7. At this pH, the proportion of dissolved and exchangeable zinc is low (cf. Fig. 9.20). Furthermore, the spreading of iron oxides can cause additional Zn fixation. Zn uptake by plants can also be lowered by high phosphate fertilization.

Threshold values for the total Zn contents in soils were defined in different countries for the spreading of sewage sludge. In Germany, the spreading of sewage sludge is only legally permitted on soils with a total content <200 mg Zn kg^{-1} and pH values >6. For sandy soils (<5 % clay) and/or soils with pH 5–6, the threshold was set at 150 mg kg^{-1} for the total Zn content. However, this value is set too high for soils with pH 5.0–5.5, because the Zn availability in this pH range strongly increases (Fig. 9.20). To test for Zn phytotoxicity, a trigger value of 4 mg kg^{-1} $Zn(NH_4(NO_3)$ was suggested for the water-soluble and exchangeable Zn [extracted with 1 M $NH_4(NO_3)$].

9.7.5 Boron

Boron is an essential trace element for plants; however, it is not yet proven to be vital for animals and human beings. It is mainly absorbed by plants as $B(OH)_3^0$ from the soil solution. Boron is a component in the cell walls of plants and is therefore required for cell division and plant growth. It is also involved in nucleic acid synthesis and carbohydrate metabolism. B deficiency causes deformation and paling of the youngest leaves as well as chlorosis to necrosis with brown to black coloration and dying off of the apical tip or terminal bud, and in beets, heart rot leading to multiple branching (multiple crowns). At higher concentrations, there are phytotoxic effects with necrosis at the edges and tips of leaves.

The mean B contents in different rocks vary between 2 and 100 mg kg^{-1}; the average content in the continental crust is about 10 mg B kg^{-1} (Table 9.16). Igneous rocks usually have low B contents (2–15 mg B kg^{-1}) and sedimentary rocks usually have much higher B contents (up to more than 200 mg B kg^{-1}), especially clay-rich sediments of marine origins. In igneous rocks, boron is mainly bound in micas and in the form of weathering-resistant borosilicate tourmaline (B content ca. 10 %). In sedimentary rocks, boron is mainly found in illites and smectites. Because of the high B contents in seawater (on average 4.6 mg L^{-1}), especially marine clay minerals are rich in boron. In natural boron deposits that have formed in arid regions, boron is found in the form of Na, Mg or Ca borates, e.g. as borax ($Na_2B_4O_7 \times 10H_2O$, B content ca. 11 %).

With the weathering of rocks, boron is mostly liberated as boric acid H_3BO_3 [better: $B(OH)_3$],

which is a very weak acid and is readily water-soluble, just like its salts. The **B contents** of soils in humid climate regions usually range between 5 and 80 mg kg^{-1}, whereby topsoils generally have higher B contents than the subsoil, and sand-rich soils typically have lower contents (5–20 mg kg^{-1}) than clay- and humus-rich soils (30–80 mg kg^{-1}). Saline soils in arid regions can exhibit much higher B contents. Furthermore, widespread wastewater irrigation and spreading of sewage sludge in the past caused boron contamination in some soils. The binding forms of boron in soils are mostly characterized by adsorption on Fe and Al oxides as well as on clay minerals, and through binding on organic substances. In addition, boron is found in small fractions in the soil solution.

In the **soil solution** at pH <7, boron is almost only found as undissociated $B(OH)_3^0$. At pH >7, rising pH values cause increased formation of B $(OH)_4^-$ ions. At higher B concentrations, e.g. in the soil solution of saline soils, polyborate ions [$B_3O_3(OH)_4^-$, $B_3O_3(OH)_5^{2-}$] can be formed, and probably also with soil desiccation through polymerization on exchange surfaces. Under temperate humid climate conditions, the B concentration in the soil solution (or in the saturation extract) often lies between 0.02 and 0.25 mg L^{-1}, and is usually <0.02 mg L^{-1} in the groundwater. Up to 18 mg L^{-1} were measured in soils developed from B-rich rocks. The B content of the soil solution is significantly determined by adsorption and desorption processes.

B adsorption takes place as $B(OH)_4^-$ and increases strongly in soils from pH 6–8.5. It reaches peak values at pH 8.5–10. At such elevated pH level, $B(OH)_4^-$ is mainly adsorbed on the surfaces of **Fe and Al oxides** as well as on the edge surfaces of **clay minerals** as ligand exchange against OH groups. Among the clay minerals, especially illite and vermiculite have a high B adsorption capacity, and smectite and kaolinite have much lower B adsorption capacities. B fixation on **organic matter** probably mostly occurs on alcoholic and phenolic OH groups, and among others, on poly- and disaccharides, whereby the $B(OH)_3^0$ present at pH values <7 is presumably partly fixed. $B(OH)_3^0$ adsorption is very low at pH values in the moderately to strongly acidic range, so that strong B leaching and depletion can occur with high amounts of precipitation, especially on sandy soils.

Depending on the plant species and the B supply, the **B content of plants** often ranges between 2 and 100 mg kg^{-1} of DM. B requirements vary greatly among different plants. Plants with particularly high B requirements are sugar beet, rape and other cruciferous plants. For example, sugar beet requires 35–100 mg B kg^{-1} of DM in the leaves, and already exhibits deficiency symptoms <20 mg kg^{-1}. In contrast, cereals and other grasses have low B requirements. Wheat and barley are generally satisfied with 5–10 mg B kg^{-1} of DM in the shoots during the shooting phase; deficiency symptoms are observed <3.5 mg B kg^{-1}. Cereals, especially spring barley, react sensitively to elevated B contents in the soil. The optimal range for the B supply is very narrow, so that boron can very easily be over- or underdosed.

With a good harvest of cereals, the **B removal** by plants is ca. 150–200 g B ha^{-1}, and in sugar beet including the leaves, ca. 450 g B ha^{-1}. In Central Europe, **B leaching** reaches values of 10–200 g ha^{-1} a^{-1} with **B inputs** from the precipitation of ca. 10–80 g ha^{-1} a^{-1} (the latter in coastal areas). Therefore, the B balance is negative. **B deficiency** is widespread around the world on acidic soils of humid climate regions because of the low adsorbability of $B(OH)_3^0$ and resulting strong B leaching. Especially in hot and dry years, B deficiency occurs on sandy soils that are low in B, as well as on B-fixing clay-rich soils. But also on alkaline soils of arid regions, B deficiency is commonly observed because of strong $B(OH)_4^-$ adsorption and fixation. **B fertilization** for plants with high B requirements (e.g. 0.5–2 kg B ha^{-1} for rape, beet) can be accomplished using either compound fertilizers containing B or borax (see above), which is hydrolyzed in soils to form boric acid. The dosage here must be very precise, because subsequent B-sensitive crops, such as cereals, can be easily damaged.

While **B toxicity** is rarely observed on plants of humid climate regions (and then usually because of excess B fertilization), it is of great significance in arid and semiarid regions because

of salt accumulation or the use of irrigation water with high B contents. For this reason, the water used to irrigate sensitive plants (citrus, wheat, etc.) should not contain more than 0.3–1 mg B L^{-1}, 1–2 mg L^{-1} for semi-tolerant plants (maize, legumes, etc.), and 2–4 mg L^{-1} for tolerant plants (lettuce, cabbage, sugar beet, etc.).

The B concentration in the soil saturation extract can be used to determine the **B availability** in soils. The most widely used method is extraction with boiling water (5 min; soil: water = 1:2; Berger-Truog method). According to this, an ideal B supply (soil test category C) in Central Europe is provided in sandy soils with 0.2–0.4 mg kg^{-1} of boron, and in loamy and clayey soils, with 0.3–0.8 mg kg^{-1}. The content of hot water-soluble boron in soils of humid regions is usually <1, and in arid regions, up to several hundred mg kg^{-1}. In recent years in Germany, the B supply in soils is also determined using the CAT method (Sect. 9.6.6.2). According to this method, the range of optimal supply (C) for sandy to silty soils lies between 0.2 and 0.4 (pH <5.5) and 0.25–0.50 (pH >5.5) mg B kg^{-1}, and in loamy to clayey soils between 0.25–0.80 (pH <6.0) and 0.40–1.20 (pH >6.0) mg kg^{-1}.

9.7.6 Molybdenum

Molybdenum is a necessary micronutrient for plants, animals and human beings. It is contained in enzymes as Mo (IV) and Mo (V) (oxidoreductase), e.g. in nitrogenase, a key enzyme for N fixation by microorganisms, and in nitrite reductase, a decisive enzyme for the nitrate metabolism of plants. It is mainly taken up by plants as molybdate (MoO_4^{2-}) from the soil solution. Mo deficiency causes the development of pale green to yellow spots mainly on younger leaves, symptoms resembling those of N deficiency in some crops, as well as necrosis at the edges of leaves. In Brassicas, mainly deformation of the leaves with a reduced blade is observed (whiptail symptom, death of the edges of the small heart leaves in cauliflower). Particularly ruminants can exhibit toxic Mo effects at high Mo concentrations in feedstuffs.

The mean Mo content in the continental crust is 1.5 mg kg^{-1}, and in various rocks 0.2–1.8 mg kg^{-1}. Mo is usually found as a lattice component in silicates (e.g. in biotite). Sandstone and sandy unconsolidated sediments generally have low molybdenum contents. In bituminous schists and clay-rich alluvial sediments with organic matter, molybdenum can accumulate as a sulfide (MoS_2) with contents of 20–2000 mg kg^{-1}. Coal and coal ash also have higher Mo contents (3–5 mg kg^{-1}). Weathering liberates molybdenum in anionic form as molybdate (MoO_4^{2-}).

In **soils**, the Mo content mostly lies between 0.2 and 5 mg kg^{-1} and is generally higher in the topsoil than in the subsoil. Especially soils developed from sandy parent materials are low in Mo. Higher Mo contents are found in some alluvial soils of temperate climate regions, and in soils rich in iron oxides of tropical and subtropical regions. Several Ferralsols in Hawaii contain 15–30 mg Mo kg^{-1}. Soils developed from parent rocks containing MoS_2 can exhibit very high Mo contents (20–2000 mg kg^{-1}). The **binding forms** of molybdenum found in soils are mainly determined by the soil pH and redox conditions. Under strongly **reducing** conditions, 4-valent molybdenum can react with sulfide to form MoS_2. Under **oxidizing** conditions, it is found in a 6-valent form as molybdate, and is, beside small water-soluble fractions, mostly bound on Fe and Al oxides and on the organic matter. At very high Mo contents and acidic soil pH, the formation of $Fe_2(MoO_4)_3 \cdot 8H_20$ (ferrimolybdite) is possible, or $PbMoO_4$ (wulfenite) with the presence of high Pb contents.

The adsorption of molybdate ions mainly takes place on iron oxides in exchange for OH^- ions, and increases continuously with decreasing pH from pH 8.0 to 4.5. Therefore, the strongest Mo fixation is also observed at pH <4.5, associated with very low Mo availability. The adsorbed ions are initially fixed to the oxide surface, but then diffuse into the oxide particle and are occluded there. Within a few years, this leads to a reduction in the Mo availability after

fertilization with water-soluble molybdates. To a lesser extent, organic matter (probably OH groups of organic Al and Fe complexes) and clay minerals can also act as sorbents. Mo adsorption decreases with increasing pH, so that the Mo availability increases up to alkaline pH values.

Under **aerobic** conditions, molybdenum is only found in the **soil solution** as an anion. Above pH 5–6, MoO_4^{2-} ions dominate. At very strongly acidic pH values, $HMoO_4^-$ ions and undissociated $H_2MoO_4^0$ are also formed. Furthermore, polymolybdate ions such as $Mo_7O_{24}^{6-}$, $Mo_8O_{26}^{4-}$ etc. can be formed below pH 5. The soil solution and the soil saturation extract usually contain 2–10 μg Mo L^{-1}, and 0.1–5 μg Mo L^{-1} in the groundwater.

The Mo requirements of **plants** are lower than the requirements for other micronutrient elements. Mo contents in the plant material usually range between 0.2 and 6 mg kg^{-1} of DM, and up to >10 mg kg^{-1} in legumes, several Brassicas and sugar beet leaves. Mo deficiency can occur at contents <0.1–0.5 mg Mo kg^{-1} of DM. **Mo removal** by plants is low at 3–10 g ha^{-1} a^{-1} (Table 9.16), and losses by Mo leaching is usually negligible for the Mo balance. **Mo deficiency** is observed especially on sandy soils that are low in Mo (e.g. Podzols), bog soils and horticultural substrates consisting of bog peat. Also in strongly acidified forest soils, Mo deficiency is considered as one of the causes of forest damage. In subtropical and tropical regions (Australia, New Zealand, Florida etc.), it is particularly widespread on soils rich in Fe oxides (e.g. Ferralsols) and acidic soil pH values. This is often caused by strong Mo adsorption and fixation at low pH values, especially by iron oxides. A rise in the pH values of acidic soils by liming increases the Mo availability. Similarly, due to the microbial formation of organic anions, phosphate fertilization and additions of fresh organic matter often lead to molybdate desorption and improved Mo availability. Plants with high Mo requirements include several Brassicas (e.g. cauliflower), sugar beet and legumes, the cultivation of which can require Mo fertilization (50–400 g Mo ha^{-1}) through spreading of Na molybdate ($Na_2MoO_4 \cdot 2H_2O$). **Mo toxicity** is rarely observed in plants, even at >100 mg Mo kg^{-1} in the plant material. In contrast, contents of 5–10 mg kg^{-1} in feedstuffs can already be toxic for ruminants.

Determination of the Mo availability in soils using chemical methods has shown little success until now. For this reason, there are no test methods calibrated for the plant requirements in many countries. In Central Europe, sometimes extraction with boiling water is used, like for boron. The values obtained using this method and the respective soil pH can then be used to calculate the so-called Mo soil value [=pH value + (10 mg Mo kg^{-1} of soil)]. Optimal Mo supply (soil test category C) in soils is provided at Mo soil values of 6.4–7.1 in sandy soils, 6.8–7.8 in loamy soils, and 7.2–8.2 in clayey soils. Mo contents <4 μg L^{-1} in the soil saturation extract also indicate a poor Mo supply in the soil.

9.7.7 Chlorine

Chlorine is an essential element for all life forms. It is absorbed by plants as chloride (Cl^-) from the soil solution and mainly influences the cation–anion equilibrium of plants and their water balance. Cl deficiency practically does not exist under field conditions. At higher concentrations, chloride has toxic effects.

The average Cl content of **rocks** in the continental crust is 0.03 %. Igneous rocks usually contain 50–500 mg Cl kg^{-1}, sedimentary rocks up to several g kg^{-1}, and clay-rich marine sediments up to 3 %. Rock salt deposits, as are found e.g. in the subsoil of the Netherlands, Northern Germany, Denmark and Poland where deposits from the Lopingian (late Permian) can reach thicknesses exceeding 1000 m, mainly consist of NaCl. Together with alkaline and alkaline earth metal ions, the chloride liberated by rock weathering forms readily soluble salts (solubility ca. 200–500 g L^{-1}), which are very rapidly leached under humid climate conditions and transported to the oceans by the rivers, so that they accumulated in seawater during the course of geological eras. As an ocean-borne element, chloride is added to soils through precipitation and therefore often accumulates in arid regions.

In **soils**, chlorides are practically not adsorbed at pH values >5. Particularly in soils rich in iron oxides, the Cl^- adsorption increases with decreasing pH values <5. The Cl^- contents of soils in humid climate regions are usually low (2–200 mg kg^{-1}). For this reason, the Cl^- concentration of the seepage water at unfertilized sites usually only ranges between 2 and 40, but reaches often 40–80 mg L^{-1} at fertilized sites. However, higher Cl^- contents can also be observed in the groundwater under humid conditions (e.g. near the coast, also in the North German Lowlands 40–200 mg L^{-1}, the drinking water threshold value in Europe is 250 mg L^{-1}). Salt marsh soils also have high Cl^- contents (up to 2 %). In soils of arid regions, both natural sources and irrigation can lead to Cl^- accumulation, causing salt damage to the vegetation (Sect. 10.2.5).

The Cl content of **plants** usually lies between 0.2 and 2.0 % in the DM; it is much higher than the physiological requirements (mostly <0.04 %). For this reason, Cl is also called a micronutrient element. The Cl content of plants is mainly determined by the Cl^- supply in the soil solution as well as the absorption rate by different plants. With a suitable supply, Cl-philic plants like barley, sugar beet, rape etc. absorb a relatively high amount of chloride (up to >2 % in the DM). Cl-sensitive plants like potato, beans, fruits etc. already suffer at contents >0.35 % in the DM. Under central European conditions, the plant requirements of ca. 4–8 kg Cl^- ha^{-1} a^{-1} are covered by **Cl^- inputs** with precipitation (2–25, on average 8 kg Cl ha^{-1} a^{-1}) and with K fertilizers containing Cl^-. **Cl^- leaching** is approximately equal to the inputs through fertilizers and precipitation.

9.8 Beneficial Elements

Si, Na (Sect. 9.6.7), and Co are beneficial elements for all plants, promoting plant growth and resistance. Other elements like Se are also beneficial for some plants. However, Si, Na, Co, Se and other elements are essential for animals and human beings. For this reason, soils must also have a sufficient supply of these elements to be able to produce high-quality plant food.

9.8.1 Silicium

Silicium represents an essential element for rice and other swamp grasses. In contrast, the vital necessity of Si for most other plants has not been clearly established. Nevertheless, silicium is a beneficial element for many plants, promoting growth and resistance at higher concentrations. In cereals and other grasses, for example, it causes increased stalk stability and elasticity, because it is embedded in supporting tissue in amorphous form as bio-opal ($SiO_2 \cdot nH_2O$) and as polyphenol-Si complex. Quartz (SiO_2) was also detected in older plant parts. Furthermore, it promotes the resistance of cereals towards fungal disease and insects. It is mainly absorbed by plants as $Si(OH)_4^0$ from the soil solution. There are no known toxic effects caused by high Si contents.

After oxygen, silicium is the second most common element in the Earth's crust with an average content of 28 %. In **rocks** and **soils**, it is mainly found in the form of silicates and oxides. Silicic acid, H_4SiO_4 [better $Si(OH)_4$] is formed with the weathering of silicates and is a very weak acid, which is found at pH values <8 undissociated in the soil solution as $Si(OH)_4^0$. It mostly exhibits a high affinity for Fe and Al oxides, where it is strongly adsorbed at neutral to alkaline pH values. $Si(OH)_4$ can also be bound by organic substances, especially by aliphatic, aromatic and heterocyclic groups. The Si content in the soil solution is mainly determined by weathering and adsorption and desorption processes.

The Si concentration in **soil solutions** varies in central European A horizons in a range between 1 and 60, commonly 4–25 mg Si L^{-1}. In B and C horizons, ca. 2–3 mg Si L^{-1} were measured. The latter corresponds to the solubility of quartz. The higher contents of dissolved Si in the A horizons can probably be attributed to the presence of bioopal and of soluble Si-organic

complexes. Bio-opals liberated by litter decomposition have a Si solubility of ca. 20 mg L^{-1}, and ca. 60 mg L^{-1} for amorphous silicic acid. The content of water-soluble Si also increases in extremely acidic as well as in the moderately to strongly alkaline pH-range, and with increasing temperature. Due to the pH effect and higher contents of organic substances in the soil solution, very strongly acidified topsoils of forest stands often exhibit higher Si contents in the soil solution. This can also be attributed to increased silicate weathering at pH <3–4, which results in augmented liberation of $Si(OH)_4^0$ and transformation to opal ($SiO_2 \cdot nH_2O$).

The **Si content of plants** is determined both by the Si concentration in the soil solution and by the Si absorption capacity of the different plants. Si-accumulating plants such as rice contain 10–15 % Si in the DM, and Si-excluding plants like most dicotyledons contain <0.5 %. Cereals and other grasses lie in between, with slightly elevated Si contents (1–3 %). Therefore, elevated bio-opal contents in soils can be an indication of prehistoric steppe vegetation (grassland). The **Si availability** is also affected by the soil's phosphate content. Because silicic acid and phosphate compete for the same adsorption sites, P fertilization leads to higher Si availability. Inversely, P mobilization was observed in the alkaline pH-range after additions of silicic acid to the soil. On very strongly acidified forest soils with elevated Si availability, spruce exhibited increased Si uptake with the transpiration flow and deposition in the needles. One year-old spruce needles have up to 0.8 % Si in the DM, and four year-old needles up to 3.6 %. The Si was mainly embedded in the central cylinder of the needles and caused obstruction of the conducting channels for water and assimilate transport, leading to indirect damage by **Si**. In some soils (e.g. Durisols) in the humid tropics and subtropics, as well as in arid and semiarid climates, translocated Si can also lead to irreversible cementation of the soil particles (formation of durinods and duripans, see also silcretes) and therefore to poor rootability and strongly restricted land use (Sect. 7.5.1.4).

9.8.2 Cobalt

Cobalt is mainly a component of vitamin B_{12} and its derivates (cobalamin), an essential element for animals and human beings. In contrast, it is not required for higher plants. It is, however, an essential component of various enzymes for N fixation by microorganisms and therefore an indispensable constituent of the natural N cycle. For this reason, a good Co supply in the soil is also required for optimal N fixation by legumes.

The mean Co content in the continental crust is 18 mg kg^{-1}. Especially rocks with high contents of Fe- and Mn-rich minerals, like basic and ultrabasic rocks (50–150 mg Co kg^{-1}), generally exhibit high Co contents, and in contrast, sandstones and sands usually only have <1 mg kg^{-1}. Depending on the parent rock, **soils** usually contain 1–40, commonly 5–15 mg Co kg^{-1} (Table 9.16). In addition to fixation in Fe/Mn-rich silicates (e.g. biotite), Co is mainly found in Fe and particularly Mn oxides. It therefore often accumulates in oxide-rich horizons. In doing so, it is mainly adsorbed as Co^{2+} and sometimes also as Co^{3+} on the surfaces of oxides, occluded inside the oxides or bound as a component of the oxide lattice. At pH >6, the Co adsorption by oxides is very high; at lower pH values, the **Co^{2+} solubility** and therefore the Co availability increase significantly. The Co contents in soil solutions or soil saturation extracts generally range between 0.3 and 80 μg L^{-1}. At pH values <5, Co^{2+} ions dominate in the soil solution. With rising pH, the fraction chelated by soluble organic substances increases and reaches more than 90 % at pH values >6.

The Co contents of **plants** usually lie between 0.02 and 0.5 mg kg^{-1}, and are generally higher in legumes than in grasses. Co contents in the feed of at least 0.08 mg kg^{-1} are required to prevent **Co deficiency in ruminants**. Under temperate humid climate conditions, Co deficiency in the feed occurs mainly on acidic, Co-depleted soils developed from granite and sand or sandstone (Podzols, acidic Umbrisols). Worldwide, however, it is also found on soils with pH ≥7 as well as on oxide-rich soils due to Co fixation. Therefore, Co deficiency

in feed is also widespread in different regions of the USA, Australia and Scotland. To remediate Co deficiency on pastures, e.g. fertilization with 2 kg $CoSO_4 \cdot 7H_2O$ ha^{-1} is recommended, which is generally sufficient for five years. At high contents of Mn and Fe oxides in the soil, more frequent fertilization may be required due to Co fixation.

9.8.3 Selenium

Selenium is a beneficial element for some plants; however, it is essential for animals and human beings. Excess selenium has toxic effects on all life forms. The range between deficiency and toxic effects in animals and human beings is very narrow.

The average content in the continental crust is 0.09 mg Se kg^{-1}. Among the different rocks, the average Se content in clay rocks is 0.5 mg kg^{-1}, and in igneous rocks 0.09 (basalt, gabbro) to 0.04 mg kg^{-1} (granite). Rocks with ores containing Se, e.g. Cu_2Se, can have contents ranging between 100 and 1000 mg Se kg^{-1}. Coal also sometimes exhibits relatively high Se contents (up to 8 mg kg^{-1}). The Se contents of soils generally range between 0.02 and 2.0 mg kg^{-1}, and are usually less than 1 mg kg^{-1} under cool to temperate humid climate conditions. Se contamination of soils is possible mainly through volcanic exhalations and through the combustion of coal and spreading of coal ash.

The **oxidation levels** and **binding forms** of selenium in soils, like with sulfur that is chemically very similar, are strongly determined by the redox conditions and pH values. Like sulfur, selenium can exhibit oxidation level +6 (selenate: SeO_4^{2-}), +4 (selenite: e.g. SeO_3^{2-}), 0 (elemental selenium: Se^0) and −2 (e.g. H_2Se). Under strongly **oxidizing** conditions, e.g. in low-humus, dry soils of arid and semiarid regions, mainly selenate (SeO_4^{2-}) is found. Under moderately oxidizing conditions, as they are often observed in humic soils of humid climate regions, selenite (SeO_3^{2-}, $HSeO_3^-$) dominates. Like sulfates, selenates are not absorbed much by the solid particles of the soil, in contrast, selenites are much more strongly adsorbed. Selenite adsorption mainly takes place on Fe and Al oxides and increases above pH 6.0 to strongly acidic pH values. Organic substances, e.g. amino acids (selenomethionine) and proteins, are also significant for Se binding in soils. **Reducing** conditions can lead to the formation of elemental selenium (Se^0) and selenides (e.g. FeSe, H_2Se), as well as volatile dimethyl selenium [$(CH_3)_2Se$].

Plants mostly absorb selenium from the soil solution as selenate and selenite. The **Se availability** in soils is therefore determined by the soluble selenate and selenite contents. With acidic soil pH values, moderately oxidizing conditions (with predominance of selenite), and high Fe and Al oxide contents, the Se availability is low due to strong selenite adsorption. High Se availability dominates in soils with alkaline pH and strongly oxidizing conditions (with predominance of selenate) due to low Se adsorption.

The Se contents of plants generally vary between 0.01 and 1 mg kg^{-1} of DM. **Grazing cattle** requires 0.1–0.3 mg kg^{-1} of DM in the **pasture** growth. In countries with **Se-poor soils** (often <0.1 mg kg^{-1}), **Se deficiency** causes high livestock losses, e.g. in some regions of Scandinavia, New Zealand and the USA. Se feed supplements or Se fertilization can prevent Se deficiency. Also in human beings, the Se nutrition in Central Europe and other countries is sometimes considered to be insufficient.

In several regions of the USA, England, Ireland and other countries with Se-rich soils (total Se content >10 to several hundred mg kg^{-1}) and high fractions of available Se compounds, mostly because of neutral to alkaline soil pH values, **Se toxicity** was observed in grazing cattle at Se contents in the feed of >5–10 mg kg^{-1} of DM. Several plants such as *Astragalus* (a legume), among others, have a high Se-accumulating capacity (Se-accumulator plants) and can contain up to >4000 mg Se kg^{-1} of DM on Se-rich soils. The uptake of such Se accumulator plants by grazing cattle together with the other pasture plants can then lead to Se toxicity.

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10 Threats to the Soil Functions

Soils, as a part of ecosystems, fulfill a series of functions for human beings and the environment. These include habitat, utilization, transformer, filtering, buffering, and archive functions (see Chap. 1). They are potentially endangered by human activities. On the one hand, these include chemical contaminations such as industrial emissions, spreading of sludges, dredged material and physical soil degradation including soil erosion, soil compaction or excavations.

Because of their **filtering, buffering and transformer functions**, soils represent a natural purification system capable of absorbing and binding emitted contaminants, and depending on the type of contaminant and the soil properties, of removing them to variable extents from the matter cycle of the ecosphere. A considerable portion of gaseous and particulate pollutants and harmful substances that are liberated into the atmosphere are washed into the soils with precipitation. However, after the purifying passage through intact soils, the seepage water generally turns into clean groundwater that is suitable for use as drinking water. Pollutants entering water bodies with wastewater also accumulate in subhydric soils at the bottom of lakes, rivers and oceans. Wastewater irrigation results in an accumulation of contaminants in the treated terrestrial soils. The large amounts of incoming wastes from various sources that are deposited on the soil surface are subject to progressive decomposition and leaching into the soils under the influence of precipitation.

Figure 10.1 shows a schematic representation of the behavior of pollutants in the soil. Suspended particles of pollutants and harmful substances are mechanically bound in the soil through **filtration**. Even the finest particles can be filtered out of the seepage water in clay-rich soils. The **filtering capacity** of a soil is characterized by the quantity of water (rain water, bank infiltrate) that can pass through the respective soil per unit of time. The filtering capacity is mainly determined by the diameter of soil pores and their continuity (Sect. 6.4.3). It decreases strongly when the water-conducting pores are filled with the filtered substances. The filtering capacity is generally high in gravel- and sand-rich soils, and low in silt- and clay-rich soils.

Through the **buffer action of soils**, gaseous and especially dissolved contaminants are bound on sorbents or are chemically precipitated after reacting with soil inherent substances, and are therefore largely immobilized (Fig. 10.1). Depending on the type and quantity of the contaminant as well as the soil properties, however, there is always a variable fraction of the contaminant remaining in or returning to the solution phase if the soil properties change, e.g. the pH value (dynamic equilibrium). Dissolved contaminants can enter the food chain both through uptake by plants and contamination of drinking water through leaching into the groundwater (Fig. 10.1). As a result, especially the dissolved fractions of a contaminant and those that can be transferred into the solution phase are of

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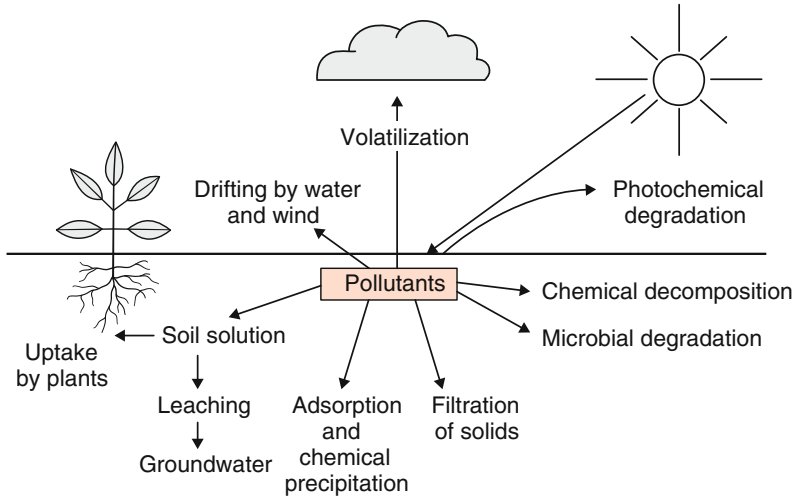


Fig. 10.1 Behavior of pollutants in the soil (after Brümmer 1978)

ecological relevance. The buffer capacity is generally high in soils with high organic matter and clay as well as Fe, Al and Mn oxide contents, and low in quartz-rich sandy soils. In addition to the texture and organic matter content, the soil reaction (pH value) and the redox potential have a great influence on the mobility of contaminants (Sect. 10.2.4).

The behavior of organic waste and contaminants in soils is mainly determined by the microbial activity, which affects the **transformer function** of soils. For example, solid organic substances can be transformed or decomposed by microbial activity to form gaseous (e.g. CO_2), dissolved or other solid substances (e.g. humus constituents). In the same way, dissolved organic substances can be transformed into solid and/or gaseous substances. The **microbial transformation of organic pollutants** therefore results in substances with different aggregate states and different chemical compositions (metabolites), which are usually less toxic than the initial substance. In isolated cases, however, metabolites can be formed that have a higher toxicity and/or other behavioral characteristics than the initial substances. In addition to organic substances, inorganic substances (e.g. nitrogen compounds; see Sect. 9.6.1) can also be subject to microbial transformation.

Furthermore, organic pollutants that are deposited at the soil surface can be also transformed by **photochemical processes** (Fig. 10.1). **Erosion** and **drifting** of contaminated topsoil material by water and wind can lead to redistribution and increasing dispersion of contaminants in the pedosphere. Contaminants with high **vapor pressures**, e.g. mercury and various organic compounds such as ethylene, which can escape from contaminated soils into the air, can also reenter the soil with precipitation at a different site after drifting (Fig. 10.1).

Sooner or later, most pollutants produced by humans generally cause soils to no longer be able to fulfill their habitat and utilization functions. In Germany, trigger and action values were defined to protect humans, crop plants and the groundwater (Sect. 10.5). If these values are exceeded, the soils must be remediated at high costs. The methods used for this purpose often lead to complete destruction of the soil (Sect. 10.6).

10.1 Threats to the Soil Functions Through Chemical Contaminations

Chemical soil contaminations arise through the input of pollutants. These are substances and preparations that cause adverse impacts on soil functions due to their properties, amount or concentration. These also include naturally

occurring substances such as heavy metals, and chemicals that are not formed in biological systems [grouped under the collective term xenobiotics, e.g. polychlorinated biphenyls (PCB)]. Contaminants are defined as substances and preparations (mixtures or solutions consisting of two or more substances) that were introduced to the environment through human activities, but are not necessarily harmful.

Whether a substance or preparation is harmful or not essentially depends on the acting dose (or the concentration in the soil) and its exposure time (Sect. 10.5). Many inorganic elements such as B, Mn, Cu, Zn and Mo are indispensable in trace amounts for the nutrition of plants and soil organisms, and are therefore called essential substances (Sect. 9.7). However, already a relatively small excess of these elements can have a toxic effect (Fig. 10.2). These and other trace elements that are contained in plant material, such as Co, Se, J etc., are required at least for animal and human nutrition. Other elements such as Cd, Hg and Pb probably do not have any nutritional physiological function. At low concentrations, they do not affect the growth and yields of plants. When specific threshold concentrations are exceeded, however, these elements cause harmful effects (Fig. 10.2). All inorganic and organic pollutants, with few exceptions (e.g. carcinogenicity), have a similar effect.

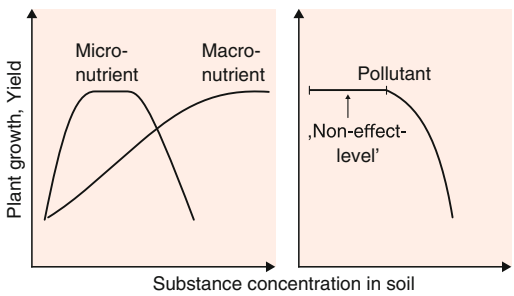


Fig. 10.2 Effect of the concentration of micro- and macronutrients as well as pollutants in the soil on plant growth and yield (schematic representation)

10.1.1 Entry Paths of Pollutants in Soils

Pollutants enter soils through atmospheric deposition or direct inputs. Atmospheric deposition is defined as substance flows from the atmosphere onto the soil surface. They enter the troposphere (bottom layer of the atmosphere) through combustion and production processes from various anthropogenic sources (power plants, iron works, motor vehicles, domestic fuel). Here, they strive to achieve equilibrium between the air phases and are then found in gaseous or dissolved form, or bound on particles.

Atmospheric deposition can be divided into **direct** and **indirect deposition,** as well as according to the type of deposition into **dry (gases, dust), moist (fog)** and **wet (rain, snow)** deposition. The form in which the pollutants enter the soil (dissolved, particle-bound, gaseous) depends on the substance properties (vapor pressure, solubility etc.). The elimination of contaminants from the atmosphere is not completely reversible. A portion of the deposited substances can return into the atmosphere through vaporization. With persistent substances, a cycle is established over longer periods of time, representing an indirect emission source. This was observed for polychlorinated biphenyls (PCB), among others, which are no longer produced or used today, yet perpetual inputs are still observed.

Dry **deposition** is defined as the input of contaminants through solid particles (>10 μm) and through gravity and adsorption or diffusion of gases, particulate matter and aerosols on surfaces (e.g. needles). Losses and deposition of substances through fog, dew and frost are separately designated as **moist deposition**. For technical reasons relating to the measurement, they are seldom recorded separately from the dry deposition. Particle and droplet size determine the deposition mechanisms of contaminants in soils or on plant surfaces. Due to their mass, particles >1–10 μm are sedimented downwards.

While very small particles <0.2 µm are mainly deposited on acceptor surfaces through diffusion, in between particle sizes adhere there when they are transported with air currents. Gaseous substances behave like very small particles, whereby the mechanism is called **gas deposition** and plays a significant role particularly in plants.

Wet **deposition** (wet only) is the input of dissolved and particulate-bound substances through aqueous precipitation like rain, snow, and hail. In this way, substances can reach acceptor surfaces from an air layer with a thickness of several kilometers. The output of gaseous substances in liquid particles, including their deposition, is called "**gas scavenging**".

Direct input of contaminants in soils occurs through leakage, improper handling of chemicals in production processes as well as through their utilization with waste dumping, spreading of dredged material, plant treatment agents, sludges and other fertilizers (e.g. Cd in phosphate fertilizers) as well as the input of contaminated sediments during floods.

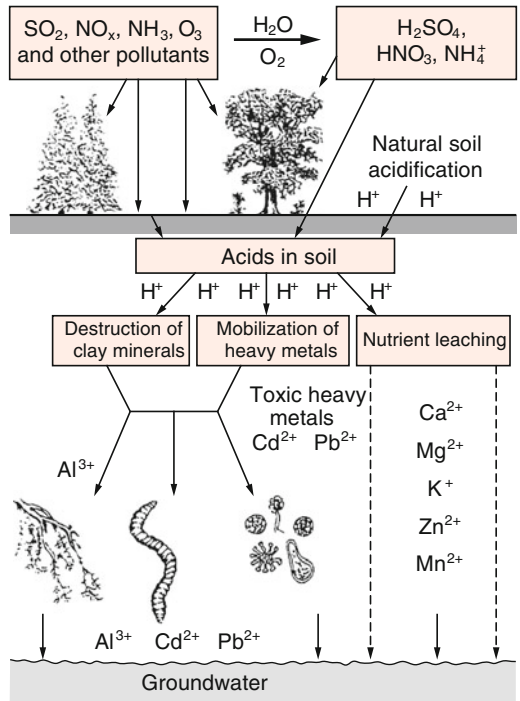


Fig. 10.3 Direct and indirect effects of emitted pollutants on forests and soils (after Veerhoff and Brümmer 1992)

10.2 Inorganic Substances

10.2.1 Sulfur Dioxide and Nitrogen Compounds—Forest Decline

Sulfur and nitrogen are indispensable nutrient elements for plants, animals and human beings. Toxic effects due to elevated sulfur and nitrogen contents in plant food and feed have not been observed to date (Sects. 9.6.1 and 9.6.3). However, strongly excessive N inputs can lead to nutrient imbalances in plants and cause growth disharmonies. Both elements, when present in higher concentrations in the form of SO_2 and NO_x as well as acids, cause damage to plants and, especially on forest sites, also lead to strong acidification and degradation of the soil (Fig. 10.3). At the same time, nitrogen compounds (NO_x, NH_y) can also promote the N availability in forest stands.

As a result of high energy consumption, the combustion of coal, petroleum and natural gas releases large amounts of sulfur dioxide into the atmosphere, a large portion of which enter the soil with precipitation. In addition to SO_2, considerable amounts of nitrogen oxides, fluorides, fluorine and chlorinated hydrocarbons are released into the atmosphere.

After reacting with the water contained in the atmosphere, the emitted gases are transformed into strong acids (H_2SO_4). A portion of these acids is neutralized by other air pollutants (e.g. NH_3) and soil particulate matter. However, since the beginning of industrialization until 1988, the existing acid surplus in Central Europe has led to a lowering of the pH values in the rainwater from on average 5.7 (without SO_2 and NO_x emission at equilibrium with the CO_2 in the atmosphere) to ca. 4.1; extreme low values down to pH <3 have also sometimes been measured. Especially rainwater associated with fog is often extremely acidic. Because SO_2 and NO_x are subject to

considerable long-distance transport, the pH value of precipitation is significantly lowered even at greater distances from the central European urban agglomerations all the way to Scandinavia. There has been improvement in the past few years. Because of reduced SO_2 and NO_x emissions, the pH values in the rainwater have risen by ca. 0.5 units.

In rural areas with lots of animal husbandry, NH_4–N input is also significant, which greatly contributes to soil acidification after uptake of NH_4^+ by plant roots in exchange for protons or after oxidation of NH_4^+ to HNO_3.

The input of sulfur and nitrogen as well as other substances from the air takes place in the form of **wet** (rain, snow), **moist** (fog, smog) and **dry** (gas, particulate matter) **deposition**. In addition to inputs with precipitation, especially SO_2 and other S compounds, as well as NO_x and other N compounds to a lesser extent, are directly adsorbed by the vegetation and soils (Sect. 9.6.3) and are filtered out of the air (dry deposition). Particularly with SO_2, dry deposition is high and can account for more than 50 % of the total S deposition. Interception by vegetation is mainly significant for sulfur inputs. For example, significantly higher sulfur inputs were measured in forest regions than in the open field.

The strong increase in forest decline observed in the last 30 years in the northern hemisphere and especially in Central Europe is directly or indirectly attributed to the high emissions of SO_2, NO_x and other harmful substances. The toxic effects of SO_2 and NO_x can trigger direct damage to needles and leaves of trees (brown to reddish necrosis).

Ozone (O_3) and other toxic photooxidants are formed through atmospheric chemical reactions with the participation of NO_2 and emitted organic substances. The extent of O_3 formation is linked to the intensity of the sunlight and therefore reaches peak values on sunny days, especially at midday and at high elevations. In central European cities, short-term contents of more than 200 μg O_3 m^{-3} were measured, and in mountain regions, up to 300 μg O_3 m^{-3}. The annual mean values in Germany are 10–90 μg m^{-3}. Repeated short-term influence of ozone at concentrations of 100–200 μg m^{-3} can already cause damage to forest trees (formation of brown interveinal chlorosis). Damage was already observed with the combined effect of O_3, SO_2 and NO_x at concentrations below the damage threshold for the individual gases.

Furthermore, precipitation with pH values <3, particularly with fog and dewdrops, can cause direct acid damage as well as strong nutrient leaching on needles and leaves.

The direct effect of harmful gases and acids on the assimilation organs of trees can reduce photosynthesis, lead to a modified physiology of metabolic processes, and disturbed mass transport in the roots. In turn, this can inhibit the formation of mycorrhiza and of the root system of trees.

Indirect effects of SO_2 and NO_x emissions on the growth of forest trees are triggered by acid inputs in soils. In addition to the natural processes of soil acidification in temperate to cool-humid climate regions taking place since many years, as well as land use forms (timber, litter and sod removal, wood pasture use) that promote soil degradation (nutrient depletion, acidification through the formation of mor humus), the elevated acid inputs from the atmosphere taking place mainly in the last 40 years and more have led to strong acidification of the upper soil horizons. In many regions of Germany, pH reductions of more than one pH unit, e.g. from pH($CaCl_2$) 4.5 to 3.3, were measured in the topsoils of forest stands within this period. Today, pH($CaCl_2$) values of 2.8–3.8 are measured in the O and A horizons of many forest soils. Severe acidification is observed especially in soils with a low buffering capacity developed from sandy parent rocks with a low base saturation. In mineral soils, pH values <3 represent the boundary threshold for plant growth.

Although the strong acids entering soils are largely buffered (Sect. 5.6.4), it leads to serious negative changes in the soil properties. At pH values below 5.0–4.5, there is increasing **dissolution** of Al oxides and **destruction** of clay minerals and other silicates. This causes irreversible soil degradation. Furthermore, it also causes the liberation of Al^{3+} ions from the lattice

of silicates (Fig. 10.3). In humic horizons, the majority of Al ions is then fixed by humic substances through complex formation and is transformed into a non-toxic form. In addition, Al ions can be incorporated into the interlayers of expanded clay minerals. This causes a transformation of clay minerals into Al-chlorites with a much lower CEC. In low-humus subsoil horizons, after reaction with the sulfate from acidic depositions, the liberated aluminum can then also be bound as hydroxy-Al-sulfate (e.g. jurbanite: $AlOHSO_4$, see Sect. 9.6.3). In addition, there is adsorption of Al^{3+} and hydroxy-Al ions ($AlOH^{2+}$, $Al(OH)_2^+$, $Al_x(OH)_y^{(3x-y)}$) on the surfaces of clay minerals. As a result of the high exchange strength of Al ions, there is increased displacement and leaching of nutrient cations from the exchange media. Overall, the Al fraction on the exchange media and the Al concentration in the soil solution increase with increasing acidification. Furthermore, in extremely acidic soils ($pH(CaCl_2) < 3$), weakly crystallized Fe oxides (ferrihydrite) begin to dissolve, which leads to a **liberation of Fe^{3+} ions**.

In very strongly to extremely acidic forest soils, 80 to almost 100 % of the exchangeable cations can consist of Al^{3+} ions, and to a lesser extent, H^+ and partly also Fe^{3+} and Mn^{2+} ions. This results in pronounced nutrient deficiency and toxic effects of Al^{3+} and also Mn^{2+} ions on forest trees. On many sites, both are considered to be an important cause for the observed forest decline, especially in exposed highland areas.

Al concentrations in the soil solution of 10–20 mg L^{-1} can trigger **toxic Al effects** on the roots, especially on the fine roots, of forest trees and their mycorrhiza system. Agricultural crops react much more sensitively to Al toxicity, where significant root damage and growth inhibition can already occur at concentrations of 0.1–0.5 mg Al L^{-1}. In these cases, aluminum is usually present in the soil solution in the form of various species. In addition to monomers and polymers, Al ions can be present in the soil solution as soluble Al-organic complexes as well as very stable Al complexes with fluorides and phosphates. In this case, Al complexes, especially with the participation of organic substances, have a relatively low toxicity. The activity (=effective concentration) of the Al^{3+} ions in the soil solution generally exhibits the closest correlation with plant damage.

Furthermore, the extent of Al toxicity also depends on the contents of available **plant nutrients** in the soil, especially Mg and Ca. Therefore, the Ca/Al and Mg/Al ratios in the soil solution and on the exchange media are also a good measurement for possible Al toxicity as well as for the degree of Mg supply to the forest trees. For example, damage to spruce roots is possible at Ca/Al ratios (in mol) <1 in the soil solutions, and is apparently inevitable at ratios <0.1. The needles of damaged spruce trees exhibit insufficient Mg supply at Mg/Al ratios of the exchangeable soil fraction ≤0.05. Mg deficiency is particularly widespread in spruce, initially leading to yellow chlorosis (yellowing of the needle tips), and later to necrosis on older needles and ultimately to dying off of the trees. Investigations on spruce stands by the German forest soil condition monitoring demonstrated that with available Mg reserves in the main rooting zone below 100 kg ha^{-1}, the average needle contents drop below the guideline values required for a stable supply mentioned in the literature. These are of 1 mg g^{-1} m_D in the 1st needle generation and 0.7 mg g^{-1} m_D in the 3rd needle generation. If the Mg fraction fixed in the humus layer represents more than 50 % of the total existing Mg reserves in the main rooting zone, the Mg supply deteriorates noticeably, and the fraction of discolored needles strongly increases.

In addition to the aerial plant parts, the **tree damage** triggered by nutrient deficiency and Al toxicity mainly affects the trees' fine roots (Fig. 10.3). Dying off of the fine roots strongly reduces the nutrient and water uptake by plant roots. This results in reduced frost, drought and disease resistance. For this reason, a strong increase in damage on trees can be observed after strong cold snaps and longer dry periods as well as with disease infestation.

The **soil flora** and **fauna** are also damaged by Al toxicity (Fig. 10.3). At pH values <3.5–4, Lumbricidae are generally hardly found in forest

soils. The number of species and individuals of many other soil animals are also strongly reduced. Among the microorganisms, the bacteria, which exhibit the highest decomposing capacity, are hardly active, so that organic layers and unfavorable humus forms develop in forests in conjunction with nutrient-poor needle litter.

Like with aluminum, there is also increased mobilization of **heavy metals** with increasing acidification in soils (Fig. 10.4). This also results in elevated heavy metal availability, and with higher heavy metal concentrations, probably also intensification of the Al toxicity.

Increasing Al and heavy metal mobilization is accompanied by increasing dislocation and leaching of these elements, so that the **groundwater** and **surface waters** in the catchment area of forest regions are also subject to increasing Al and heavy metal pollution (Fig. 10.3).

Because of the widespread forest decline, an increase in erosion processes and hillside slumping is observed in low mountain ranges and in the Alps. In some areas, the restricted protective function of the forests causes serious soil and landscape damage.

Anthropogenic acidification of forest soils through to Al toxicity and elevated heavy metal mobility result in additional damaging factors in the complex structure of the so-called new forest decline that was intensively observed and investigated in the 1980s and 90s. These include e.g. nutritional disturbances due to trace element deficiencies (e.g. boron and molybdenum deficiency), as well as epidemics of pathogenic microorganisms due to increased nitrogen deposition. Because of the complexity of the highly variable spatial and temporal combinations of damaging factors and their different feedback mechanisms, precise regionally differentiated diagnosis of specific causes of damage is often difficult. For this reason, the environmental monitoring of forests program was developed to record and monitor the state of the forests in Germany, providing area-representative information on the extent and development of forest decline, and an intense investigation of the cause-effect relationships in forest ecosystems.

In addition to measures for reducing emissions, the remediation of forest and soil damage also requires measures for reducing Al toxicity and nutrient deficiency. On many forest stands, liming (e.g. with ca. 3000 kg ha^{-1} of dolomitic lime) as well as Mg and sometimes also K fertilization (e.g. 5–1000 kg ha^{-1} kieserite or potash magnesia) can result in a revitalization of damaged trees, or at least an improvement of the soil condition. It is generally recommended to repeat liming and fertilization, depending on the site

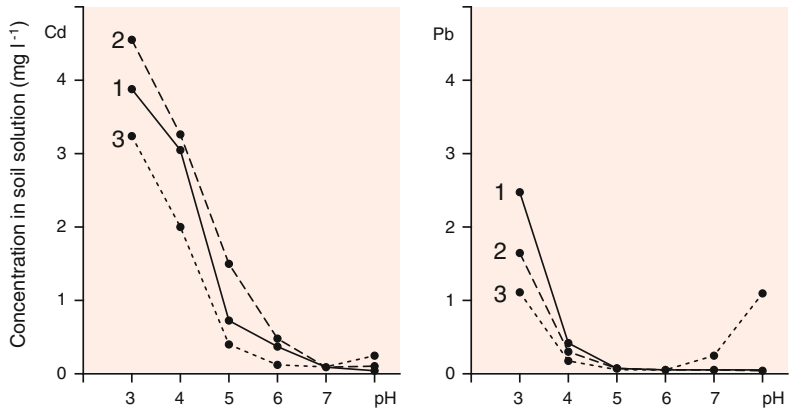


Fig. 10.4 Cadmium and lead concentration in the equilibrium solution of different soil samples from Ap horizons depending on the established pH (soil samples were put in equilibrium with 15 mg Cd kg^{-1} and 100 mg Pb kg^{-1} before the pH adjustment). Soils (soil texture; humus content): 1. Calcaric fluvic Gleysol (sandy loam; 2.6 %) 2. Luvisol (sandy loam; 2.8 %) 3. Podzol (sand; 4.4 %) (after Herms and Brümmer 1980)

and extent of soil acidification, at 3- to 5-year intervals, with the goal of achieving pH values of more than 4–4.5 in the topsoil on the long term. However, with the implementation of rehabilitative or prophylactic liming measures, caution must be exercised particularly on primary poor sites (e.g. Pleistocene cover sand in the North German lowlands). The stimulation of mineralization through liming can lead to nutrient losses from the humus layer, which are not stored by the forest vegetation. Site-specific expert opinions should ensure that suitable treatments are performed according to the regional site and requirement conditions.

Nitrogen was one of the growth-limiting factors in forests for a long time. For this reason, it was kept in constant circulation. The losses were low and a large part of the nitrogen quantities were fixed in the plants and in the humus. Increased input of nitrogen compounds from industrial livestock farming (NH_y) and especially from motor vehicle and industrial emissions (NO_x) has significantly changed this situation. Today, the nitrogen inputs in forest ecosystems are considerably greater than the consumption (see below). This results in increased leaching of calcium and magnesium and an accumulation of nitrogen, and leads to **nutrient imbalances (Mg/N and Ca/Mg ratios)**. Despite the deficiency of various nutrients, nitrogen acts as a growth-stimulating fertilizer. Analyses of forest condition have demonstrated increased tree growth. Shoot growth is more strongly promoted than root growth. As a result of this, there is a higher risk of snow breakage, storm damage and drought stress. Furthermore, the high nitrogen supply in combination with nutrient deficiency reduces the tree's resistance towards frost as well as fungal and insect infestations, and increase the risk of drinking water contamination through nitrate leaching.

Significant traces of high nitrogen inputs were detected on forest sites in the North German lowlands. The poor, classic nitrogen-limited sites are particularly affected. The formerly widespread mor humus under pine and spruce as a morphological characteristic of the humus state is only still observed on a few sites. Grass root sods with efficient N users (e.g. wavy hair-grass) are common. They promote the decomposition of the humus layers, compete for water with the tree vegetation, and impede the natural forest rejuvenation. The C/N ratio was also narrowed by anthropogenic nitrogen inputs to a widespread level of 23–28, without changing the morphological structures of the common humus forms moder and mor-type moder on sandy sites.

The **investigation of forest decline** increasingly involves inventory-supported evaluation methods, which take both the acid input and the total nitrogen deposition into account, and include information on the condition of the tree crowns as well as data from climate and deposition monitoring networks. Short-term acute effects of air pollutants are evaluated using the **critical levels** concept, and long-term effects of immissions using the **critical loads** method. For example, critical levels for ozone are defined as a cumulative dose, the so-called AOT 40 value (=accumulated exposure over a threshold: 40 ppm). All values exceeding the hourly average of 40 ppm (corresponds to 80 $\mu g\ m^{-3}$) are added up. The sum for forest regions should not exceed 10,000 ppm h^{-1}. Only the time periods of highest sensitivity for the receptors (from April to September for forest regions) are taken into account.

Critical loads are load limits for the input of air pollutants. They are given as the atmospheric loads that can be deposited in the ecosystem per unit of area and time without causing damage according to the current state of knowledge. In Germany, the development of methods and models for the determination and mapping of ecological load limits is documented in a constantly updated method handbook. A simple mass balance approach is usually used for the calculation of the critical loads for acid inputs. The acid inputs are compared to the acid buffering processes in forest ecosystems. The liberation of base cations through mineral weathering is considered a buffering process (acid neutralization capacity (ANC) Sect. 5.6.4). To prevent soil acidification on the long term, the actual acid input must not exceed the critical load, which includes the base reserves of the soil to buffer the

H ion surplus. To be able to compare the deposited acid inputs to the buffer capacity of the soil, the added substance amounts are not given in kg ha^{-1} a^{-1}, but rather in acid equivalents (measurement unit mol_c ha^{-1} a^{-1}).

In Germany, critical loads for acid inputs were determined based on 1:1,000,000 soil maps (BÜK 1000). On 80 % of the forested area, the critical load on sites with base-poor parent rocks (sands, schist in the low mountain ranges) are below 2000 mol_c ha^{-1} a^{-1}. Regions with base-rich soils [Swabian Alps, Kalkalpen (Limestone Alps)] are characterized by critical loads >2000 mol_c ha^{-1} a^{-1}. Maximum values are of 6000 mol_c ha^{-1} a^{-1}. Although the nitrogen and sulfur depositions in the last years have been greatly reduced, in the year 2000 they exceeded the critical loads for acid input on the majority of German forest soils. Particularly high surpluses were observed on the sensitive North German sandy soils due to pollutant emissions from industrial and agricultural operations.

For the calculation of the critical loads for eutrophying nitrogen inputs, the inputs (nitrogen deposition) are compared to the processes that fix nitrogen or remove it from the forest ecosystem (e.g. nitrogen losses with timber harvest and seepage water, denitrification). Depending on the humus reserves and soil texture, critical loads for eutrophying nitrogen in forest ecosystem vary between 5 and 20 kg N ha^{-1} a^{-1}. Regions with industrial livestock farming exhibit particularly high surpluses.

10.2.2 Fluorine

Fluorine is apparently not a required element for plants. For animals and human beings, however, it is considered to be beneficial, because when there is a sufficient supply, it is built into the dental enamel and decreases the risk of cavities. Excess fluorine has a toxic effect on all organisms, causing tooth and bone damage (fluorosis) in human beings and animals.

The **fluorine content** of soils often ranges between 20 and 400 mg F kg^{-1}. However, there can be great differences depending on the composition of the parent material. The most common fluorine mineral is CaF_2 (fluorite). Phosphates (fluorapatite) also contain fluorine. Especially micas (400–5800 mg F kg^{-1}) and clay minerals (bentonite up to 7400 mg F kg^{-1}) have high F contents. For this reason, clay-rich soils generally contain lots of fluorine (up to 4000 mg kg^{-1}). The F concentration in the soil solution is therefore probably partly determined by the fluorine content of the micas. The fluorine content often increases with depth due to weathering and translocation processes. Because of the great natural variations, the total concentration of fluorine in geologically heterogeneous parent material is neither a suitable indicator for fluorine contamination of the soil, nor is it suitable for the delimitation of guideline or threshold values for tolerable fluorine contents in contaminated soils.

Potential **fluorine emission sources** are especially the aluminum producers, stone and earth industry, waste incinerating plants as well as conventional power plants with coal, petroleum or natural gas combustion. The annual fluorine input with open field precipitation in the form of hydrogen fluoride (HF), fluorides or fluorine bound to dust particles was estimated to be between 0.3 and 1.6 kg F ha^{-1}; inputs of up to 3 kg F ha^{-1} a^{-1} were measured in forest stands, and up to 20 kg F ha^{-1} a^{-1} close to some industrial plants. The spreading of phosphate fertilizers, which usually have F contents between 1.5 and 4 % (Thomas phosphate <0.15 %), leads to an addition of 7.5–20 kg of F ha^{-1} to the soil with a fertilization of 500 kg ha^{-1}.

According to investigations in Switzerland in the surroundings of iron works emitting fluorine, the total contents in the soil decrease with increasing distance from the source (0.5 to 8.8 km) from 2700 to 616 mg F kg^{-1}, and therefore decrease 4.4-fold. The contents of water-extractable fluorine decrease in the same way (soil: water = 1: 50) from 292 to 10 mg kg^{-1}, and the fluorine contents in the soil solution from 8.2 to 0.3 mg L^{-1}. The contents of the soluble fluorine fractions therefore exhibit differences in the fluorine contamination of soils

much more clearly. The fluorine content of spruce needles also decreases with the distance (by 29-fold) in close correlation with the content of the soluble fluorine fractions.

F^-- ions are relatively strongly bound in soils. Here, F adsorption in exchange against OH groups from Al and Fe oxides and clay minerals is particularly significant. Binding onto the organic matter is less strong. F adsorption increases with increasing soil acidity up to ca. pH 4. Poorly soluble CaF_2 can be formed in soils with high pH values.

The **binding capacity** for fluoride is low in sandy soils and high in clayey soils. Therefore, the solubility, availability, and leaching of fluorine is high in sandy soils and low in clayey soils. In Germany, the fluorine content in the seepage water lies between 0.004 and 0.22 mg F L^{-1} (mean value 0.1 mg L^{-1}). The annual **leaching** ranges between 20 and 400 g F ha^{-1}.

As shown by the results from model trials, F-contaminations cause considerably increased translocation of aluminum, organic matter and heavy metals especially in acidic soils. Fluorides form highly stable soluble complexes with aluminum (and other metals) and can therefore liberate aluminum from humic substances and increase the solubility of organic substances. In this way, elevated fluorine deposition probably accelerates podzolization processes. Furthermore, fluorine input reduces phosphate availability due to the incorporation of fluorine in Ca phosphates. The mobilization of heavy metals in fluorine-contaminated soils is attributed to the formation of soluble organic substances.

Elevated fluorine contents in soils are detrimental to **soil microorganisms** and their decomposing capacity. The microbial biomass and the dehydrogenase activity were considerably inhibited at a concentration of 100 mg F_{H_2O} kg^{-1} of soil, and the arylsulfatase activity already at 20 mg F_{H_2O} kg^{-1}. The water-extractable, available fluorine fractions must be used for the evaluation of ecotoxicological effects, and not the total fluorine contents. Soils with naturally high F contents generally only contain little soluble fluorine.

The fluorine content of plants generally lies between 1 and 20 mg kg^{-1} m_D. Tea plants can exhibit extremely high contents up to 400 mg F kg^{-1}. The removal through one harvest represents 5–80 g F ha^{-1}.

In the area surrounding some industrial plants, F contents of up to 300 mg kg^{-1} were detected in the dry mass of pasture grasses. Contents of up to 2000 mg kg^{-1} were measured in other plants.

Hydrogen fluoride (HF) and fluorides are deposited on the surfaces of leaves through interception, and partly penetrate into the plant tissues. In very sensitive plants, a HF concentration of 1 μg F m^{-3} of air already lead to necrosis on the edges and tips of leaves, and in less sensitive plants, with 4.2 μg F m^{-3} and an exposure time of 30 min. Fluorine, SO_2 and drought damage on plants all have the same appearance. Fluorine damage can be detected through fluorine analysis of the plant material.

10.2.3 Cyanides

Cyanides are salts of hydrocyanic acid (hydrogen cyanide, HCN). All water-soluble cyanides are highly toxic (e.g. potassium cyanide). Iron cyanide complexes are intense blue in color (Prussian blue), lending their name to these compounds (Greek kyaneos = steel blue).

Microorganisms and plants can synthesize HCN (cyanogenesis). Plant cyanogenesis involves the enzymatic cleavage of compounds containing cyanide (cyanogenic glycosides) to form cyanohydrins, which rapidly disintegrate to form HCN. Microbial cyanogenesis mainly involves basidiomycetes, ascomycetes and heterotrophic bacteria.

For industrial purposes, HCN is produced from methane and ammonia and is used as an intermediate for the production of plastics, paints, pharmaceuticals as well as for the production of cyanides and cyanogen (C_2N_2). Simple cyanide salts serve for the extraction of silver and gold as well as for ore dressing. They are also used for electroplating and for flotation. Road salt often contains sodium ferrocyanide.

Color pigments based on iron-cyan complexes are used in the paper industry. They enter the waste sludge produced during paper treatment, which was also used as a soil conditioner. Cyanides are also produced with coke and iron making, and are found in the wastewater and solid wastes. HCN is formed with the gasification of black coal through reactions of ammonia with carbon. Cyanides and complex cyanides are therefore particularly widespread in the production residues of former gas plant sites and coking plants. They are used in metal refining for hardening metals.

Cyanides are not found in rocks. No cyanide was detected in 87 % of **uncontaminated soil** samples from Michigan (USA). The remaining samples contained less than 1.2 mg CN kg^{-1}. In subsoils of North Rhine-Westphalia (Germany), the CN concentrations were below 0.5 mg kg^{-1}. The highest cyanide contaminations were observed in soils of coking plant sites. The concentrations vary across wide ranges and in extreme cases, can reach up to 63 g CN kg^{-1}. Up to 1150 mg CN kg^{-1} were detected in soils of a former sewage irrigation fields.

Alkali and alkaline earth cyanides are readily soluble in the soil. Metal-cyanide complexes are formed in the presence of heavy metal ions. In contaminated soils of former gas plants and coking plants, cyanide is mainly found in the compound Prussian blue ($Fe_4[Fe(CN)_6]_3$). The solubility of this compound strongly depends on the pH, as shown by the following reaction:

$$Fe_4[Fe(CN)_6]_3 + 12H_2O \rightarrow 4Fe(OH)_3 + 3[Fe(CN)_6]^{4-} + 12H^+$$

Elevated cyanide concentrations are found in the soil solution at pH values >5.

Cyanide ions and metal-cyanide complexes are negatively charged and are hardly sorbed in soils of temperate climates, which barely carry any positive charges. However, CN^- ions can be bound on humic substances. In acidic environments, where cyanide is only found in the form of HCN, binding takes place via hydrogen bonds, and in neutral to alkaline environments via charge-transfer complexes. It can therefore be assumed that CN^- is practically not held back in humus-poor subsoils.

Dissolved iron-cyanide complexes are mainly bound to iron and aluminum oxides (sesquioxides). The sorption is promoted by a low soil pH. With decreasing pH, the number of positive charges on the sesquioxide surfaces increases due to protonation of the functional groups. Iron-cyanide complexes are attracted by electrostatic forces (outer-sphere complexes) and accumulate on the oxide surfaces. In doing so, Fe oxides bind more strongly than aluminum oxides. The complexes become part of the oxide surface with the formation of inner-sphere complexes. In the acidic range, there are surface precipitations where phases similar to Prussian blue are formed. As a matter of principle, ferrocyanide is more strongly bound than ferricyanide. Long-term trials have shown that ferrocyanide is oxidized to form ferricyanide. Iron-cyanide complexes can also bind to humic substances. It is assumed that the complexes react with functional groups (e.g. quinone groups) of the organic matter.

Under strongly reducing conditions, the dissolution of manganese and iron oxides can lead to higher Mn^{2+} and Fe^{2+} concentrations in soils. These ions precipitate iron cyanide(II) complexes. The precipitates are $Fe_2^{II}[Fe(CN)_6]$ (Prussian white) and $Mn_2^{II}[Fe(CN)_6]$.

In darkness, the **disintegration of iron-cyanide** complexes is extremely slow. They disintegrate rapidly in the visible range (up to 480 nm) and with UV light. Free CN^- ions are formed in the process. In principle, free cyanide can escape from the soil in the form of HCN. Due to the high vapor pressure of HCN, its good water solubility and low binding in soils (see below), the gas can diffuse to the soil surface and escape into the atmosphere.

Fungi and bacteria can use free cyanide as a source of carbon and nitrogen. **Decomposition** takes place both under aerobic and anoxic conditions. In doing so, CO_2 and NH_4^+ are liberated. On the short term, formic acid, thiocyanate and formamide can be formed as intermediates. Due to their good bioavailability, simple cyanides hardly accumulate in soils. Iron-cyanide

complexes are only decomposed very slowly by microbes, so that this process can hardly be used for remediation.

Simple cyanides are mainly found as HCN in human and animal bodies and have higher biomembrane mobility than its dissociated species CN^-. In the body, HCN is rapidly adsorbed as CN^- on the iron(III) cytochrome oxidase localized in the mitochondria and thus inhibits the oxygen transfer from hemoglobin to the tissues. This results in a rapid stop of all aerobic respiration processes. The LD_{50} for human beings lies between 1.1 and 1.5 mg CN kg^{-1} of body weight for NaCN and KCN.

Complex-bound cyanides exhibit highly variable **toxicities**, because the CN ion is bound in the complex as a ligand. Complexes with Ca, Zn, Ag, and Ni are more toxic than those with Fe. Daily intakes of up to 2 g iron cyanide(II) salts are harmless for adults. Trigger values are defined in the Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV) for the paths soil–human being and soil–groundwater.

Plants are more resistant towards low CN concentrations than human beings and animals. They have CN detoxication enzymes and have an alternative path in the mitochondrial electron transport chain. Plant trials with ^{15}N-marked ferrocyanide suggest that the anion is transported and metabolized in plants.

10.2.4 Heavy Metals

Metals that follow light metals with a density >3.5–5 (in a native state) are called heavy metals. They include both micro nutrients that are required for the metabolism of human beings, animals, plants and microorganisms such as iron, manganese, chromium, copper, cobalt, nickel and zinc, and elements that do not have any physiological significance (lead, cadmium, mercury, thallium). In terms of the chemical contamination of soils, heavy metals are of special significance because they already have toxic effects at low concentrations. In contrast to many organic pollutants, they occur naturally in rocks and soils, and are not microbially or chemically decomposable. Manganese and iron are not included here, which are found in soils at concentrations up to several thousand mg kg^{-1} and do not exhibit any toxic effects at these contents, as well as the trace nutrients cobalt, molybdenum and selenium, which are of no significance in terms of their inputs. However, due to its high density, the toxicity of its compounds, and partly similar chemical reactions, arsenic as a metalloid (semi-metal) is included with the heavy metals and is addressed in this chapter.

10.2.4.1 Sources and Entry Paths

Heavy metals are natural constituents of minerals. Lead, cadmium, chromium, cobalt, nickel, thallium and zinc occur as trace constituents in isomorphic positions of the primary elements silicium and aluminum. Heavy metal contents in rocks normally lie in the mg kg^{-1} range (Table 9.15). Considerably higher contents are found in ultrabasic extrusive igneous rocks (150 mg Co kg^{-1}, 1600 mg Cr kg^{-1}, 2000 mg Ni kg^{-1}) and in serpentine rocks (up to 8000 mg Ni kg^{-1}). Ores (arsenopyrite, galena, sphalerite) consist of up to 100 % heavy metals (e.g. native copper and mercury).

Heavy metals enter soils naturally through the weathering of rocks and ores. In Germany, the liberation from primary minerals lies between 0.1 g ha^{-1} a^{-1} (cadmium) and 3.5 g ha^{-1} a^{-1} (copper, see also Table 10.1). Their percent fraction in the total inputs of agricultural soils is of 0.2 % (zinc) to 2.3 % (cadmium). Other sources of heavy metals are continental dust immissions as well as gas emissions from seawater and volcanoes. Compared to the loads from anthropogenic sources, the natural sources are usually insignificant. Hg emissions from volcanoes and oceans are an exception. Current estimations indicate that anthropogenic and natural sources contribute equally to Hg emissions. However, the latter do not lead to locally elevated contents in soils.

Anthropogenic sources of heavy metals are emissions from industrial plants, incinerators, and motor vehicles. Recycling of wastes containing metals, wastewater irrigation, fertilizer and pesticide applications lead to direct inputs of

Table 10.1 Heavy metal inputs in (g ha^{-1} a^{-1}) from various sources

Elements	Atmospheric inputs		Direct inputs				
	Rural areas/ forest sites	Industrial/ urban areas	Weathering	Sewage sludge[a]	Compost[a]	Farmyard fertilizer[b,c]	Mineral fertilizer[b,d]
As	3	n.d.	n.d.	0.12	n.d.	n.d.	n.d.
Cd	1.5–3	≤ 35	0.1	2.21	4.7	0.33–0.61	0.15–2.98
Cr	3	n.d.	2.0	61	253	6.11–33.8	15.3–464
Cu	11–13[e]	1526	3.5	520	577	73.1–454	2.89–9.5
Ni	5–35	n.d.	0.8	43.5	163	8.93–13.6	1.50–6.63
Hg	0.2–0.8	2	n.d.	1.17	1.6	0.02–0.13	0.00–0.3
Pb	31–310	270–14,000	0.8	76	464	5.14–16.7	0.24–4.93
Zn	70–618	Up to 4000	2.3	1253	2037	467–1077	36.9–54.3

[a]Calculated values from maximum load rates according to the German Sewage Sludge and Biowaste Ordinance (1.5 and 10 Mg ha^{-1} a^{-1}) and average contents according to Table 10.13
[b]Heavy metal inputs by fertilization with 50 kg P_2O_5 ha^{-1} a^{-1}
[c]Farmyard fertilizer = cattle liquid manure, liquid swine manure, poultry manure, solid manure from swine and cattle
[d]Mineral fertilizer = triple superphophate, raw phosphate, min. NPK, NP, PK fertilizer, Thomaskali
[e]Wet only data from 2000; n.d. = no data/not determined

heavy metals in soils. Especially atmospheric inputs from industry and incinerators have caused a dramatic increase in metal concentrations in the environment worldwide.

Industrial plants and the smokestacks of large-scale firing plants (power plants and cement plants, waste incinerating plants) represent punctual sources, while smaller emission sources such as domestic fuel are considered to be diffuse sources. With industrial emissions, the highest metal accumulations are found in the direct vicinity of the emission sources. Linear structures are found along traffic routes.

Heavy metals are transported bound on particles as well as in vapor and gas form. The process temperatures at which the heavy metals are liberated determine the initial particle size at the time of emission. Volatile elements such as arsenic and mercury are vaporized at relatively low temperatures and condense highly enriched in small particles and aerosols. Atmospheric deposition of heavy metals is characterized by large spatial and temporal variability. It depends particularly on the geographic location (distance from the emission sources) as well as on macro- and microclimatic conditions (wind direction, precipitation volume and type, season).

Table 10.2 shows a list of the origins of anthropogenic heavy metal pollution. Input rates in soils from various sources are shown in Table 10.1. Metalworking **industries** count among the main emission sources of arsenic (copper and nickel production), lead, cadmium (non-ferrous metal working plants), chromium (leather, steel, building material, and paint manufacturing, corrosion protection), copper, nickel, mercury and zinc. **Power plants** and **large-scale firing plants** mainly emit cadmium and lead. **Cement plants** count among the primary thallium emission sources. The metal is liberated from iron sulfides with the firing of the cement clinker and accumulates in the cement dust. These contained up to 50 mg Tl g^{-1}.

Up until the introduction of lead-free gasoline, motor vehicles were the main emission source of lead. The combustion of gasoline containing Pb leads to the production of PbBrCl, an aerosol with a particle size <0.1 μm that can be transported to distances of up to 1000 km. However, most of the Pb emitted by traffic accumulated up to 30 m beside the roads. Cd emissions from motor vehicle traffic originate from tire abrasion (20–90 mg Cd kg^{-1} of tire material) and combustion residues from diesel oil; they lead to soil

Table 10.2 Origins of anthropogenic heavy metal pollution in soils

	As	Cd	Cr	Cu	Hg	Ni	Pb	Tl	Zn
Power plant emissions	+	X	+	+	+	+	X		+
Domestic fuel emissions	+	+	+	+	+	+	+		+
Industrial emissions	+	X	+	X	X	+	X	X	X
Vehicle emissions		+					X		+
Sewage sludges	+	X	X	X	X	X	X		X
Biowaste	+	X	X	X	X	X	X		X
Excavated sludges	X	X	+	X	X	X	X		X
Waste water irrigation		X	X	X	+		X		X
Pesticides	*			+	+				
Farmyard fertilizers				X					+
Mineral fertilizers	+	X		+					

* Only very small amounts; + Measurable but only rarely significant amounts; X Significant amounts to be regulated

contamination in the immediate area of influence of roads (up to 10 m beside main artery roads). One quarter of the atmospheric Zn emissions also come from traffic. Emission sources are tire abrasion, fuels and galvanized car bodies.

Sewage sludges, biowastes and **dredged materials** are potential sources of heavy metal inputs. Legal ordinances for sewage sludges and biowastes were issued in Germany to reduce the heavy metal loads (see Sects. 10.5 and 11.7.4). They regulate the spreading of sludges and biowastes on agricultural, forestry or horticultural soils. The loads listed in Table 10.1 were calculated under the assumption of maximum spreading rates and the average heavy metal contents in composts or sludges according to Table 10.13. Based on the total agricultural land area in Germany, the metal inputs through composts and sludges are insignificant compared to other sources such as farmyard fertilizers (0.01 % (Cd, Cr, Cu, Zn)–0.05 % (Pb) for composts, 2.73 % (Cr)–6.91 % (Zn) for sewage sludges).

Wastewater irrigation has led to an accumulation of lead, cadmium, chromium, copper and zinc in sewage irrigation fields. Soil contamination on intensive filtering areas can reach several thousand mg kg^{-1} (see Table 10.3).

Farmyard fertilizers (liquid manure, manure, fowl excrements) mainly lead to copper and zinc inputs in agricultural soils. Extremely high contents are found in liquid swine manure (268 mg Cu kg^{-1} m_D, 744 mg Zn kg^{-1} m_D) and swine manure (454 mg Cu kg^{-1} m_D, 1077 mg Zn kg^{-1} m_D). The calculable load rates taking a fertilization of 50 kg P_2O_5 ha^{-1} a^{-1} as a basis therefore correspond to those with biowaste and sewage sludge applications (Table 10.1).

Cadmium and chromium enter the soil through **mineral fertilization**. High cadmium contents are found in raw phosphates. Depending on their source, their Cd content ranges between 2 and 80 mg kg^{-1}. Currently, only phosphates with contents considerably lower than 40 mg kg^{-1} are used for the manufacturing of fertilizers. Depending on the management system, fertilizer-related Cd inputs lie between 1 and 11 g ha^{-1} a^{-1}. Extremely high Cr contents are found in ground basic slag (2500 mg kg^{-1}) and NPK fertilizer (up to 6100 mg kg^{-1}).

Mercury, copper and arsenic were used as **pesticides** and wood preservatives (kyanization = impregnation of wood with $HgCl_2$). The use of metal compounds for crop protection has long been prohibited in Germany with the exception of copper. Soils under hop and vine cultivation exhibit particularly high Cu contents (Table 10.3).

10.2.4.2 Contents in Soils

Because soils naturally contain heavy metals, knowledge of the geogenic background contents

Table 10.3 Heavy metal contents in soils

Metal	Background values in (mg kg^{-1})	Substrate/land use	Precautionary values (mg kg^{-1})			Contaminated soils (mg kg^{-1})
	90th percentile		Sand	Silt/loam	Clay	
Arsenic	4–22	Sands/arable topsoil Periglacial layers over limestone/forest topsoil	n.d.	n.d.	n.d.	≤2500
Lead	35–130	Sandy loess/arable topsoil	40	70	100	50–1850 cities
		Periglacial layers over clay rock/forest topsoil				≤3600 sewage irrigation fields
						22,000 mineral deposits
						≤30,000 lead works
Cadmium	0.6–1.5	Sands/arable topsoil	0.4	1	1.5	3 roadside soils
		Periglacial layers over				
		limestone/forest topsoil				0.5–5 cities
						≤70 sewage irrigation fields
Chrome	26–1400	Sands/forest topsoil	30	60	100	
		Ultrabasic igneous rocks and metamorphic rocks/no use differentiation				
Copper	7–140	Sands/forest topsoil	20	40	60	67 garden plots
		Ultrabasic igneous rocks and metamorphic rocks/no use differentiation				149–421 hop cultivation
						80–2000 copper mills
Mercury	0.1–0.5	Sands, sandy loess/arable topsoil	0.1	0.5	1	1–10 chloralkali production
		Periglacial layers over basic igneous rocks, ultrabasic igneous rocks, metamorphic				5–10 sewage sludge spreading
		rocks, marine muds and Sedimentation/Deposits from rivers in the tidal range/grassland				
Nickel	9–650	Sands/arable topsoil	15	50	70	≤26,000
		Ultrabasic igneous rocks and metamorphic rocks/no use differentiation				
Thallium	0.005–1.8	Sands/arable topsoil	n.d.	n.d.	n.d.	5.5
		Granite/forest topsoil				cement mill
Zinc	33–240	Sands/forest topsoil	60	150	200	1800 orchards
		Periglacial layers over limestone/forest topsoil low in loess				Up to 180,000 tailings piles, metal industry

or background values is required to assess contamination situations. The geogenic background content comprises the mineral content resulting from the parent rock (lithogenetic fraction), possible ore mineralization (chalcogenic fraction), and the redistribution of substances in the soil due to pedogenic processes. The geogenic background contents differ only little from those of the parent rock. Carbonate and sulfate weathering soils as well as soils developed from sulfidic parent material and soils developed under tropical weathering conditions represent exceptions. The soil contents here lie above those of the rocks, because the weathering products from the dissolution of the minerals are leached out faster than the heavy metals.

The **background contents** of a soil consist of the geogenic background content and the ubiquitous substance distribution resulting from diffuse atmospheric inputs in soils. **Background** levels are representative values for generally prevalent background contents of a substance or a substance group in soils. The German Working Group of the Federal States on Soils (LABO) compiled substrate- and use-dependent background contents of heavy metals for rural areas as well as for individual Federal States (Table 10.3).

The background levels were compared to precautionary values according to the German Federal Soil Protection and Contaminated Sites Ordinance as well as selected contents of contaminated soils. Precautionary values were graduated as a function of the soil texture based on toxicological/ecotoxicological investigations. This takes account of the various sorption capacities of soils. According to current knowledge, concerns regarding soil degradation can be ruled out below the precautionary values. The background levels for several elements can exceed the precautionary values (soils developed from ultrabasic rocks, ore deposits). However, they are considered to be harmless, as long as the liberation of the contaminants does not lead to adverse effects on the soil functions.

Harmful substance contents in contaminated soils can fluctuate across a wide range. The values listed in Table 10.3 provide indications on contamination in urban regions as well as extreme values due to individual emission sources.

10.2.4.3 Binding Forms, Solubility and Translocability

Depending on their origins (lithogenic, pedogenic, anthropogenic), heavy metals are found in specific binding forms in soils . Metals of of lithogenic origin occur in carbonatic, silcatic and sulfidic binding forms. Pedogenic heavy metals were liberated and redistributed through pedogenic processes (weathering, humification, lessivage etc.). They are mainly bound to clay minerals, organic substances and pedogenic oxides and sulfides. Anthropogenic heavy metals entering the soil through atmospheric immissions are mostly bound to oxides or sulfates. In composts, sewage sludges or wastewaters, in contrast, they are sorbed or occluded on organic or also inorganic constituents.

Due to their strong binding in the crystal lattice, lithogenic heavy metals are not very mobile. As a result of this, there is often no accumulation observed in plants despite elevated metal contents in the soil.

Especially for heavy metals from anthropogenic sources, the fractions in the solid or solution phase are mainly determined by physical-chemical interactions between metals and solids of the soil matrix (organic matter, clay minerals, oxides etc.). Furthermore, the soil reaction (pH value), redox potential, organic and inorganic complexing ligands and also microorganisms affect the mobility and speciation of metals in the soil solution. Most heavy metals occur as hydrated ions (e.g. Cu^{2+}, Cd^{2+}), inorganic ion pairs ($NiSO_4^0$, $CdSO_4^0$), inorganic (e.g. $CdCl^+$) or dissolved organic matter (DOM) in the solution (Table 10.4).

The behavior of metals in soils can usually be described with adsorption and desorption reactions of defined metal compounds as well as with precipitation and dissolution reactions in the case of strong soil contamination.

In aerobic environments, mainly **nonspecific** and **specific** adsorption and desorption processes determine the **metal** sorption. In weakly acidic

Table 10.4 Concentrations of dissolved heavy metals (Me_d) and hydrated metal ions $(Me^{2+})_t$ as well as their most common species in an acidic and in an alkaline soil (after Sposito 1981)

Metal	Me_d	Me^{2+}	Most common species
	(mol L^{-1})		
Acidic soil			
Ni (II)	$10^{-5,8}$	$10^{-5,9}$	Ni^{2+}, $NiSO_4^0$, org. complexes
Cu (II)	$10^{-5,7}$	$10^{-6,3}$	Org. complexes, Cu^{2+}, $CuSO_4^0$
Zn (II)	$10^{-6,6}$	$10^{-6,8}$	Zn^{2+}, $ZnSO_4^0$
Cd (II)	$10^{-8,3}$	$10^{-8,4}$	Cd^{2+}, $CdSO_4^0$, $CdCl^+$
Pb (II)	$10^{-7,3}$	$10^{-7,7}$	Pb^{2+}, org. complexes, $PbSO_4^0$, $PbHCO_3^+$
Alkaline soil			
Ni (II)	$10^{-8,0}$	$10^{-9,0}$	$NiCO_3^0$, $NiCO_3^+$, $NiB(OH)_4^+$
Cu (II)	$10^{-6,0}$	$10^{-8,1}$	Org. complexes, $CuCO_3^0$, $CuB(OH)_4^+$
Zn (II)	$10^{-8,5}$	$10^{-9,0}$	$ZnHCO_3$, Zn^{2+}, $ZnSO_4^0$, $ZnCO_3^0$
Cd (II)	$10^{-10,1}$	$10^{-10,5}$	Cd^{2+}, $CdSO_4^0$, $CdCl^+$
Pb (II)	$10^{-7,7}$	$10^{-9,6}$	$PbCO_3^0$, $PbHCO_3^+$, $Pb(CO_3)_2^{2+}$

to alkaline environments, heavy metals are mainly specifically bound. The specific sorption of heavy metals is based on the formation of inner-sphere complexes of metal hydroxides ($MeOH^+$) in the solid soil phase (pedogenic oxides). In doing so, the formation of hydroxo complexes is surface-induced already at pH values lower than those calculated from complex stability constants. The specific adsorption on pedogenic oxides increases with increasing stability of the heavy metal-hydroxo complexes in the sequence Cd < Ni < Co < Zn < Cu < Pb ≪ Hg. With nonspecific sorption, the metal cations are electrostatically bound to cation exchanger surfaces. They are then found in an alkali and alkaline earth metal ion exchangeable, plant-available form.

In addition to **binding on exchanger surfaces**, there is also a very slow diffusion of cadmium, nickel, zinc and other heavy metals into the crystal lattice of Fe and Mn oxides and clay minerals in soils. In this way, the heavy metals can be irreversibly fixed.

Adsorption and desorption processes (Sect. 5.5) of metals in soils can be simply described using adsorption isotherms. The Freundlich adsorption isotherm has proven to be particularly suitable for this purpose. The sorption coefficients K_F of the heavy metals increase in the following sequence: Cd < Ni < Cu < Zn < Cr < Pb. Topsoils exhibit 2.4-times higher K_F values than subsoils. The pH value, cation exchange capacity, total heavy metal content and contents of organic matter, clay, fine silt and other pedogenic oxides correlate with the K_F values of soils.

Many investigations document the central influence of the pH value on the heavy metal adsorption. The solubility of metals increases with decreasing pH values. The solubility of cadmium increases strongly at pH values below 6.5, and that of lead at pH values below pH 4.0 (Fig. 10.4). This is because the metals are nonspecifically bound at lower soil pH values.

In addition to the soil pH, the redox conditions affect the solubility of heavy metals. Under reducing conditions, many metals are insoluble, because they are precipitated as heavy metal sulfides (e.g. lead as PbS).

The chloride concentrations, and to a limited extent, also the sulfate concentrations in the soil solution increase the solubility. This effect is caused by the formation of stable, water-soluble chloro-Hg and chloro-Cd complexes.

Organic matter often decreases the solubility in acidic soils, and in contrast, increases the solubility in neutral to alkaline soils (cf.

Fig. 10.4). Especially copper, zinc, mercury and lead are organically bound in acidic A horizons. In contrast, the mobilization of lead and cadmium by organic matter at pH values >7 is due to the formation of soluble organic complexes. Under reducing conditions, microbially formed organic ligands already mobilized cadmium, lead, copper and zinc at weakly acidic soil pH values.

Arsenic, chromium and mercury have a slightly more complex behavior in soils than most other heavy metals. Depending on the redox conditions, **chromium** is found in tri- and hexavalent form. Cr(III) is strongly bound on Fe oxides, but also forms poorly soluble hydroxides. In well-aerated soils, chromium is also found in the form of oxyanion complexes ($Cr(VI)O_4^{2-}$, $HCrO^{4-}$). In contrast to Cr(III) compounds, Cr (VI) is classified as being highly toxic.

$H_2AsO_4^-$ is usually the most important **arsenic** species in the soil solution, while H_3AsO_3 is only found at low pH values and low redox potentials. In addition, arsenate and arsenite can also be found in the soil solution. Arsenic sulfides can be precipitated under reducing conditions. Microorganisms are capable of converting arsenic into volatile compounds such as dimethylarsinic and arsine through methylation or reduction. However, these processes hardly contribute to removal from soils. The most important sorbents are iron oxides. Furthermore, arsenic is sorbed by clay minerals, manganese oxides and the soil organic matter. In soils low in Fe oxides, aluminum and calcium compounds represent the most important sorbents.

The As concentrations in the soil solution depend on the existing As species, the type and contents of As sorbents, the pH values, and the concentrations of anions competing for sorption sites. In doing so, the pH value plays a decisive role for the As solubility. In contrast to other heavy metals, the solubility of As increases with increasing pH (Fig. 10.5). Above pH 7, there is a massive liberation of As. This pH effect could be caused by the increasing negative charge of competing organic anions, the deprotonation of the sorbents, as well as the increasing negative charge of anionic arsenic itself (arsenate and arsenite).

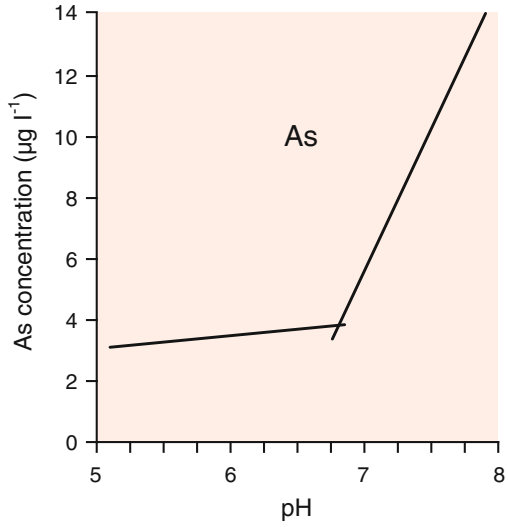


Fig. 10.5 Concentrations of As as related to pH of the soil solution of a Cambisol developed from a mixed shale-gneiss moraine (after Tyler and Olson 2001)

The behavior of mercury is determined by the disproportionation reaction:

$$2Hg^{+} = Hg^{2+} + Hg^{0}$$

Microorganisms have a significant influence on the transitions between the individual oxidation levels. Hg ions and Hg vapor are mainly specifically adsorbed by mineral and organic adsorbents. Organic matter immobilizes mercury particularly strongly. In doing so, the metal forms covalent bonds with HS as well as –S–S– groups. In this form, it is largely protected from vaporization, leaching and uptake by plants.

The binding forms and solubility of heavy metals must be determined to assess the ecological significance of their accumulation in soils. For this purpose, commonly used extraction agents were tested and optimized to develop a sequential extraction method (see Table 10.5). Total heavy metal contents are routinely determined using aqua regia extraction. The extracted fractions fluctuate between 50 and 100 % depending on the element and mineral composition of the soil. In contrast, quantities from anthropogenic sources are completely dissolved.

Table 10.5 Sequential extraction (after Zeien and Brümmer 1989)

Fraction	Tentative assignment to geochemical fractions	Extraction agent
1	Mobile fraction/H_2O soluble, exchangeable (nonspecifically sorbed) readily soluble organometallic complexes	1 M NH_4NO_3
2	Readily soluble fraction Specifically adsorbed metals, forms occluded near the surface and bound to $CaCO_3$ as well as organo-metal complexes with low binding strength	1 M NH_4OAc (pH 6.0)
3	Metals bound to Mn oxides	0.1 M NH_2OH-HCl + 1 M NH_4OAc (pH 6.0 or 5.5)
4	Metals bound to organic matter	0.25 M NH_4-EDTA (pH 4.6)
5	Metals bound to poorly crystalline Fe oxides	0.2 M NH_4-oxalate (pH 3.25)
6	Metals bound to crystalline Fe oxides	0.1 M ascorbic acid in 0.2 M oxalate buffer (pH 3.25)
7	Residual fraction; metals in silicates	Conc. $HClO_4$/conc. HNO_3 or Conc. HF/conc. $HClO_4$

10.2.4.4 Translocation, Losses

Translocation of metals significantly depends on the soil properties (pH, eH, CEC, texture, humus and pedogenic oxide contents). For heavy metals, it has been demonstrated that their binding on aggregate surfaces is less strong than inside the aggregates. Particularly metals from atmospheric inputs are bound in aggregated soils on the aggregate surfaces in readily extractable forms. Here, they can be easily dissolved and translocated.

Especially dissolved and nonspecifically bound metals can be easily translocated. Cadmium and thallium count among the metals that are soluble to a greater extent. Still, there is considerable retardation in the translocation of these elements in soils compared to water transport. Lead, copper, mercury, and zinc can be considered as having low mobility. Nevertheless, they are still found in the groundwater. Possible causes for this are the formation of soluble organic complexes or particle-bound transport in macro-pores.

Estimations on heavy metal losses are available for arable land (Table 10.6). On uncontaminated sites, 0.28 (Cd, Hg) to 38 g ha^{-1} a^{-1} (Zn) are leached with the seepage water. In forest ecosystems, losses are much higher (up to 20 g Cd or 1500 g Zn ha^{-1} a^{-1}) because of the low pH. Losses through harvest removal amount to 0.67 (Cd) to 173 (Zn) g ha^{-1} a^{-1}.

In addition to the vertical translocation in the soil, heavy metal losses from agricultural ecosystems through erosion can be considerable and usually represent the predominant loss quantities (Table 10.6). Because soil is transported at the same time, this process leads to small changes in the soil concentrations at the most. Due to the low solubility of the metals, the solute load with surface waters is very low.

Table 10.6 Average heavy metal losses from agricultural ecosystems (g ha^{-1} a^{-1}) (after Wilcke and Döhler 1995; Bannick et al. 2001)

	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Seepage water conc. µg L^{-1}	0.14	4.6	4	0.14	8.9	0.28	10
Soil seepage water[a]	0.28	9.2	8	0.28	17.8	0.56	38
Water Erosion	2	147	81	n.d.	96	189	338
Harvest[b]	0.67	5.27	34	n.d.	10.3	5.92	173

[a]Seepage water amount at 200 mm
[b]Mean for the crop types wheat, rye, barley, oats, grain maize, potato, and sugar beet

Compared to the input rates (Table 10.1), the losses are much lower, with the exception of those possible through water erosion. As a result, especially in contamination regions, heavy metals have accumulated so much in soils that soil deterioration has occurred.

10.2.4.5 Heavy Metal Uptake and Effects on Plants

Heavy metals can accumulate in or on aerial plant parts through deposition from the air or can be absorbed through the roots from the soil solution. For metals with low mobility, e.g. lead, heavy metal accumulations through the air path only play a role near emission sources. The extent to which plants absorb heavy metals from the soil and are disturbed in their growth or accumulate concentrations that may be questionable for food depends on their solubility in the soil as well as the translocation in the plant.

Table 10.7 shows normal heavy metal contents and contents that are critical for plant growth as well as common ranges for the soil-plant transfer coefficients (TF_{SP}). The transfer coefficient is calculated from the total heavy metal contents in the plant and soil according to:

$$TF_{SP} = \text{mg metal/kg of plant dry mass: mg metal/kg of soil}$$

Depending on the observed plant species and the soil substrate, the transfer coefficients vary across wide ranges. The coefficients for individual metals also differ from one another, sometimes even by a factor of 1000. Due to their strong binding in the soil, elements such as arsenic, lead, chromium and mercury are only absorbed by plants in small amounts, so that entry into the food chain only becomes of concern at very high contamination levels in the soil. Critical contents for plant growth are also only reached in isolated cases.

In contrast, with transfer coefficients of 0.03 to 10, cadmium, thallium and zinc are classified as being mobile or readily plant-available. However, with the exception of zinc, plant damage is hardly ever observed even on contaminated soils, since normal plant concentrations strongly deviate from those considered being critical for plant growth.

When the threshold and guideline values are exceeded in plants for feed and food, health risks for animals and human beings must be expected. Looking at the metal contents of plants that are considered to be critical for feed (Table 10.7, column 5), it can be seen that the concentrations of cadmium and thallium are considerably lower than the phytotoxic relevant concentrations. This means that Cd- and Tl-contaminated plants do not exhibit symptoms of damage and do not differ in appearance from healthy plants. For lead, copper, mercury, nickel and zinc, although the intervals between phyto- and zootoxic damage thresholds in the plants are close together (cf. columns 4 and 5 in Table 10.7), concrete problems have only been observed with copper in ruminants until now.

Table 10.7 Soil-plant transfer coefficients, normal and critical concentrations of heavy metals in plants (given in mg kg^{-1} m_D)

Metal	Transfer coefficient	Normal in plants	Critical for plant growth	Critical for feed
Arsenic	<0.5	<0.1–5	10–20	>50
Lead	<0.5	1–5	10–20	10–30
Cadmium	0.03–10	<0.1–1	5–10	0.5–1
Chromium	<0.5	0.1–1	1–2	50–3000
Copper	0.01–2	3–15	15–20	30–100
Nickel	0.01–2	<0.1–5	20–30	50–60
Mercury	<0.05	<0.1–0.5	0.5–1	>1
Thallium	0.03–10	0.5–5	20–30	1–5
Zinc	0.03–10	15–150	150–200	300–1000

Investigations on heavy metal availability in polluted soils have shown that different plant species absorb heavy metals to various extents from the soil. They may also be differences between the varieties of a species as well as between different plant parts. Leafy vegetables such as spinach, head lettuce, chard, and endives accumulate heavy metals much more than grasses (cereals) and beans, and dicotyledonous plants generally more than monocotyledonous. With leafy vegetables, there is also an increased risk of contamination through deposition of dusts containing heavy metals on the shoots.

The metal contents are often high in roots and leaves, and low in the stems, fruit and seeds (Fig. 10.6). Especially lead, chromium and mercury accumulate in the roots and are hardly transported into the aerial plant parts. The plant-internal retention of heavy metals on their way into the fruit and seeds therefore prevents input of heavy metals from the soil in animal feed and food.

Some plants are capable of accumulating heavy metals beyond the normal extent. They are called hyperaccumulator plants. The criterion for classification is the metal content in the leaves. They are >0.01 mg kg^{-1} m_D for cadmium, >0.1 mg kg^{-1} m_D for copper, lead and nickel, and >1.0 mg kg^{-1} m_D for zinc and manganese. Hyperaccumulator plants were found on soils with "naturally" high heavy metal contents in the vicinity of ore deposits. They belong to, amongst others, the genera *Thlaspi* and *Alyssum* (Zn accumulators). It has often been attempted to make use of these plants for the remediation of soils contaminated with heavy metals (phytoremediation) . However, because of the low formation of biomass, the removal rates of these plants were very low.

To protect human beings and animals, the German Federal Soil Protection and Contaminated Sites Ordinance issued examination and action values for the soil–plant path. They were subdivided into values for protecting plant quality and growth impairment on agricultural fields and plant quality on grassland.

10.2.4.6 Effects on Soil Organisms

Several heavy metals, including copper, zinc, iron and manganese, are essential micronutrients for soil microorganisms. Concentrations of 1–100 µg g^{-1} of biomass are sufficient. Positive effects on nitrogen-fixing bacteria were achieved with cobalt. Vanadium and nickel are also essential.

If heavy metals are present in elevated concentrations, they can disrupt the microbial populations (Sect. 4.4.2). Both reductions of the microbial biomass and activity inhibition were observed. Virtually all of the parameters

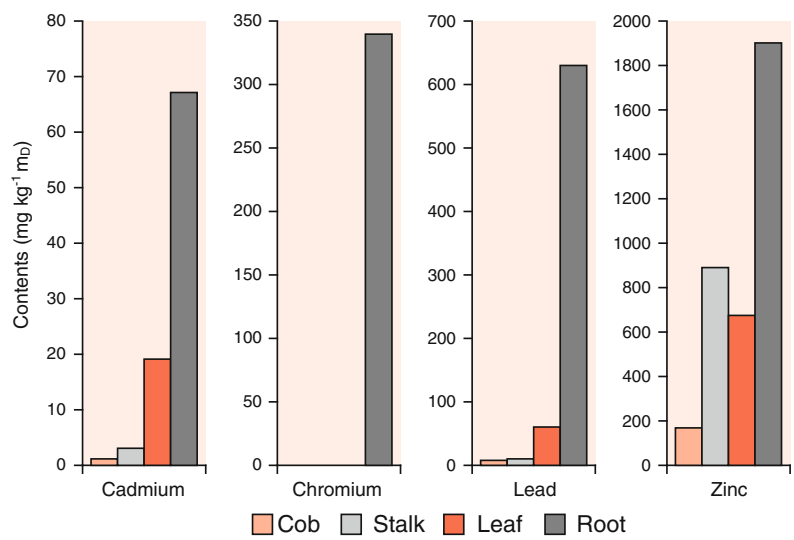


Fig. 10.6 Cadmium, chromium, lead and zinc contents in different plant parts of *Zea mais* grown on a highly contaminated sewage farm soil

characterizing microbial activity (enzyme activity, mineralization) were reduced by heavy metals. As a result of this, significant transformation processes such as decomposition and transformation of organic matter or the mineralization of nitrogen were disrupted. Furthermore, heavy metals change the species spectrum in favor of resistant species. Many investigations have shown that there is a reduction in the bacteria and actinomycete populations in favor of fungi. In contrast, others have shown that fungi also react sensitively to heavy metals. The resistance of the microorganisms is based on their capacity to reduce the toxicity of the metals through binding or precipitation on the cell surfaces, biomethylation (e.g. As), biosynthesis of intracellular polymers or oxidation. The time required for the development of heavy metal resistance is highly variable. In some investigations, heavy metal-tolerant bacteria communities were formed within a few days, and in others, it took several years.

Effects of heavy metals on soil microorganisms and microbial processes are affected by the physicochemical properties of the soils. The toxicity of heavy metals itself is specific and decreases in the following sequence: Hg > Cr, Co, Cd, Cu > Ni, Pb, Zn.

The effects of Cd, Cr, Cu, Hg, Ni, Pb and Zn observed in different soils on the soil respiration, ammonification and nitrification are shown in Fig. 10.7. There is a wide range between the highest concentrations that cause no inhibition ("no-effect level") and the concentrations at which reductions in activity were always observed. This can be explained through the modifying effect of abiotic and biotic soil properties as well as with the data collection (laboratory test vs. open field trials). Because microorganisms only absorb dissolved metal species, the effect thresholds in strongly sorbing soils are higher than in weakly sorbing soils. Positive correlations were often observed between effective concentrations (e.g. EC_{50} see Fig. 10.16) and organic matter contents and the cation exchange capacity. In terms of the binding form of the metals, it is assumed that hydrated

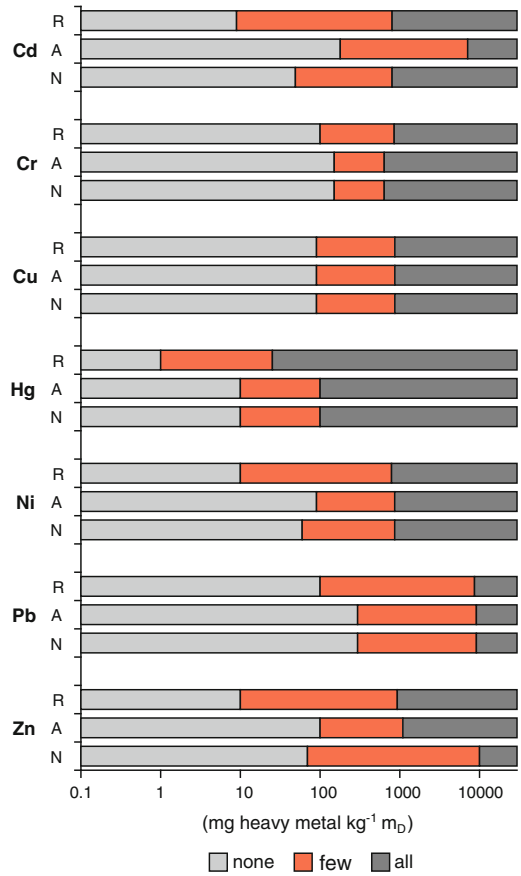


Fig. 10.7 Effect of heavy metals on the basal respiration (R), ammonification (A) and nitrification (N) in different soils (supplemented after Doelman 1986)

metal ions have a more toxic effect than heavy metal complexes.

Although the solubility of heavy metals plays a decisive role for the availability, some investigations have shown that the EC_{50} values decreased with increasing pH value and decreasing metal solubility (Fig. 10.8). This effect, observed with zinc, amongst others, was explained by H^+/Zn^{++} competition on the cell membrane. The soil pH apparently had an opposite effect on the Zn solubility and toxicity.

The effects of heavy metals on soil microorganisms and the processes they accomplish have been often investigated in laboratory experiments. These trials involve adding increasing amounts of heavy metal salts to the soil, and their

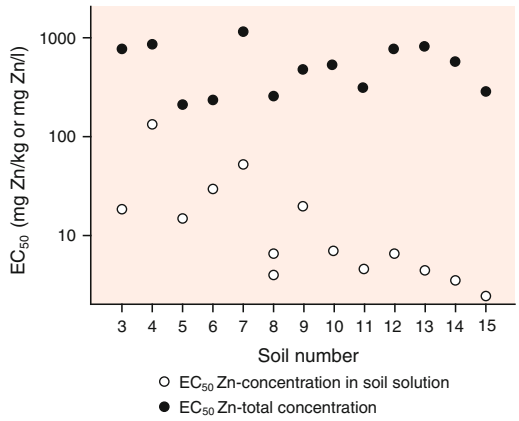


Fig. 10.8 EC_{50} values (medians) of the potential nitrification rate in 15 soils spiked with $ZnCl_2$. The soils are plotted from left to right with increasing pH value (after Smolders et al. 2004)

effects are compared to an uncontaminated control. Field investigations are based on artificial (field experiments) or "natural" contaminated sites (soils in the direct vicinity of emission sources). For the latter, samples are taken at increasing distances from the emission sources. Compared to laboratory and field experiments, naturally contaminated soils have the disadvantage that the soils are often contaminated with a mixture of several heavy metals (e.g. brass works (Cu + Zn), sewage sludge application), and the effects of individual metals cannot be determined. Comparative soil analyses on samples from soils under hot-dip galvanized pylons and soils artificially contaminated with $ZnCl_2$ have demonstrated that the effect thresholds can vary by powers of ten (Fig. 10.9). These differences were explained by the extreme differences in the zinc concentrations in the soil solutions, among other things. The transferability of laboratory test results to field conditions was put into question. Other investigations indicated that fresh (addition of heavy metal salt) and aged (addition of metal-contaminated soil) contaminations on the same soil with approximately the same soil solution concentration led to the same effects.

Soil fauna can incorporate heavy metals through the soil air, soil solution or through direct uptake. While insects, spiders or millipedes, which all have a "hard" body surface (cuticle containing chitin), absorb the metals primarily through their food (i.e. absorption takes place in the intestine), soft-bodied animals (e.g. earthworms or Enchytraeidae) mainly absorb metals through their skin. In this way, earthworms accumulate the most cadmium and zinc. Bioaccumulation factors (BAF = concentration animal/concentration soil) for these metals reach a maximum of 40 (Zn) and 12 (Cd). The BAF decreases significantly with increasing metal concentration in the soil. The contents of other toxic elements such as lead, mercury and copper in the biomass of animals is much lower than the soil contents, which can be caused by species-specific storage or extraction measures in addition to population-specific adaptation reactions.

Table 10.8 shows the effect thresholds for heavy metals on the soil fauna. Many investigations have been performed on the effects on earthworms, annelids (Enchytraeidae), nematodes

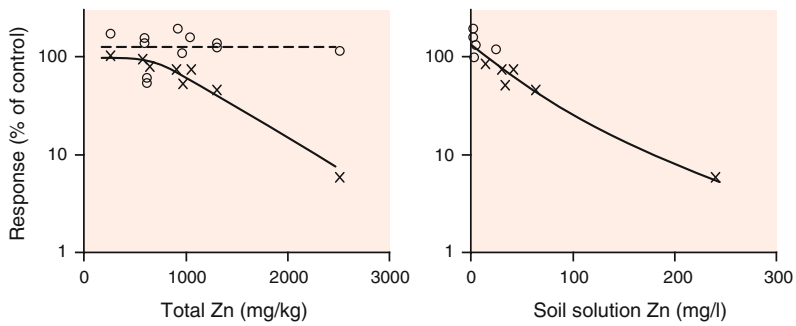


Fig. 10.9 Potential nitrification rates in Zn-contaminated soils along a contamination gradient under a pylon (o) and laboratory spiked reference soils (x) (after Smolders et al. 2004)

and collembola. These organisms often differ in their sensitivity towards a metal by several orders of magnitude, whereby even relatively closely related species (e.g. earthworms and Enchytraeidae) can exhibit quite different reactions.

Compost worms (*Eisenia fetida*) were used for chemical testing, because this species is easy to breed. Based on the prescriptions of the International Organization for Standardization (ISO) and the OECD, these toxicity tests are often performed using artificial soil consisting of a mixture of peat, kaolinite and sea sand (ratio: 1: 2: 7). In acute tests, where the mortality of the animals after 14 days of exposure is measured, the earthworms react much less sensitively than in reproduction tests with a duration of 56 days. For this reason, it is recommended to perform chronic reproduction tests not only for earthworms but also for other soil animals such as collembolas.

The values given in Table 10.8 were obtained using natural soils and indicate the lower effect thresholds for the metals. It is remarkable here that in addition to the "standard test species" listed in the OECD or ISO guidelines, such as the compost worm *Eisenia fetida* or the collembola *Folsomia candida,* high sensitivity was often also observed in species that were sampled directly in the field (e.g. the earthworms *Lumbricus terrestris* or *Aporrectodea caliginosa*). This leads to the conclusion that the values listed in Table 10.8 only ensure the protection of the soil ecosystem to a limited extent, because testing of other species would very probably show even more sensitive reactions. This is consistent with the observation that regional extinction of soil fauna (the earthworm genus *Scherotheca* sp. found in Southern France) was attributed to the effect of the heavy metals lead and copper originating from human activities (mines).

On the other hand, it must be noted that the effect thresholds determined through laboratory tests are often based on experiments using metal salts that were "freshly" added to the soil. Under

Table 10.8 Effect thresholds for different heavy metals on the soil fauna

Metal	Species	Parameter	Content in the soil (mg kg^{-1})	Inhibition/reduction (%)
Arsenic	*Lumbricus terrestris*	Mortality	117	50
	Eisenia fetida	Reproduction	70	30
Lead	*Lumbricus rubellus*	Mortality	3000	50
	Caenorhabditis elegans	Mortality	1305	4
Cadmium	*Aporrectodea caliginosa*	Reproduction	1.86	10
	Folsomia candida	Reproduction	12	10
Chromium	*Octochaetus pattoni*	Reproduction	2	40
	Eisenia fetida	Reproduction	100	52
Copper	*Eisenia fetida*	Reproduction	16.8	10
	Aporrectodea caliginosa	Growth	69.8	10
Nickel	*Eisenia fetida*	Reproduction	85	10
	Nematodes	Population density	100	18
Mercury	*Octochaetus pattoni*	Reproduction	0.5	35
	Eisenia fetida	Mortality	13	26
Zinc	*Eisenia fetida*	Reproduction	136	50
	Folsomia candida	Reproduction	185	50

real conditions in the field, however, the metals are usually found in an "aged" form, i.e. they were exposed to the effects of climate and soil properties for a long time. In many cases, this aging leads to reduced bioavailability of the metals and therefore to lower toxicity. On the other hand, under real conditions, where a heavy metal is only present alone in the soil in exceptional cases, there may be interactions between different contaminants (in addition to metals, also organic chemicals such as PAH), which in turn may lead to higher toxicity. Because of this complexity, the assessment of the effects of heavy metals in the field should be performed using a number of tests with different species under the real conditions of the site to be evaluated.

10.2.5 Salts

The harmful effects of soluble salts on plant growth can be attributed to specific and osmotic effects. Specific effects can occur already at low concentrations of an ion in the soil solution if the toxicity threshold has been exceeded. In addition, the excess soluble cations and anions can reduce the uptake of nutrients by plants to such an extent that salt damage through nutrient deficiency occurs. This can sometimes be corrected by compensation fertilization. Osmotic effects only occur at high total salt concentrations. Individual plant species react to this in different ways. For example, barley and sugar beet are relatively salt-tolerant, and peas, beans, red clover and azalea are salt-sensitive; furthermore, young plants are sometimes more sensitive than older plants.

The electrical conductivity (EC) in the soil saturation extract is usually determined as a measurement for the **ecologically effective salt content of soils,** and is given in mS cm^{-1}. With sensitive plants (peas, beans), salt damage can already be observed at an EC of 2 mS cm^{-1} or an osmotic pressure of 72 kPa. Most crops suffer damage at >4 mS cm^{-1} (>144 kPa), corresponding to a salt content of >3 g L^{-1} of saturation extract.

High natural salt contents are found in mudflats and wet beaches, **Gleyic Salic Tidalic Fluvisols** as well as in **saline soils** of arid regions (Sects. 7.5.15.17 and 7.5.19.3), which have adapted halophilic vegetation.

High salt concentrations can also occur in the spring in the plow layer, if there were high additions of readily soluble salts with fertilization (chlorides, nitrates) and low amounts of precipitation. After a low-precipitation autumn and winter, 8 from 100 soil samples from the plow layer in loess soils exhibited a salt concentration in the saturation extract of 2.5–3.9 g L^{-1} (mainly chlorides), and a calculated osmotic pressure of 180–380 kPa. However, because the water content of soils during the vegetation period is usually much lower than in the saturation extract, a higher osmotic pressure is obtained for the soil solution under natural conditions, which can lead to growth damage in plants.

In arid regions, salt damage is especially found in irrigated farming. Even low-salt irrigation water can lead to elevated salt concentrations in the rooting zone of crops, if it is not periodically counteracted by excess water inputs. However, this requires sufficiently deep groundwater levels. Furthermore, the soils must have sufficient permeability. Sandy soils are usually more suitable than loamy to clayey soils (see also Sect. 7.2.4.5).

Another example for salt damage are the soil changes occurring in temperate climates during the winter due to de-icing salt application (mainly NaCl) and the associated vegetation damage at the roadsides. Salt symptoms observed at roadside vegetations include retarded leaf shoots, leaf necrosis, premature fall of leaves, and in extreme cases, dying off of plants.

The salt application also leads to considerable impacts on the soils up to 5–10 m beside the roadside ("roadside soils"). The addition of NaCl in soils causes an exchange of mainly Ca and Mg ions by Na ions, so that the Na saturation of roadside soils often reaches values of 10–20 %. This leads to soil alkalization and a rise in the pH values into the alkaline range, and salt alkali soils are formed. In the humid climate of Central

Europe, there is considerable leaching of readily soluble NaCl from the spring through to autumn, as well as leaching of nutrient cations liberated by Na exchange (especially Ca, Mg and K). Due to the high Na occupancy of the exchange media, roadside soils have a tendency towards surface sealing and high densities, and are characterized by unfavorable air and water balances as well as reduced nutrient uptake. However, because roadside soils often consist of artificial applications or anthropogenic covering layers and are compacted during road construction, it is difficult to attribute compaction to the effect of Na ions. Bulk densities of urban roadside soils exhibit a high variation range (very low to very high). Mean values lie in the range between 1.4 and 1.75 g cm^{-3}.

10.2.6 Radionuclides

Radionuclides are natural constituents of minerals and therefore of rocks and soils. Furthermore, because they also are found in the atmosphere, both from natural and artificial sources, they can enter soils and accumulate there. The radiation emitted during radioactive decay can cause damage to plants, animals and human beings.

The capacity of certain nuclides (nuclear types) to transform themselves without any external influence is called **radioactivity**. Only 264 of the about 2800 different nuclides known to date, which are isotopes of the 115 chemical elements, are stable; all of the others transform themselves at different rates, sometimes through multiple radioactive changes, into stable isotopes. The energy liberated during decay is released as short-wave electromagnetic radiation (γ rays) and/or as corpuscular radiation in the form of particles (α, β^+, β^- or neutron rays). The various types of rays/radiation have very different behaviors in terms of their penetration ($\gamma \gg \beta > \alpha$) and their biological effects (α and β^- rays are more damaging than β^+ and γ rays). Today, the term ionizing radiation is used as a generic term for the different types of rays.

The rate of transformation is characterized by the **half-life** ($T_{1/2}$), which represents a specific parameter for each isotope. The $T_{1/2}$ fluctuates across very wide ranges from the femtosecond range (e.g. ^{8}Be: 2×10^{-16} s) up to geological periods (e.g. ^{128}Te: 7.2×10^{24} a). With sufficient contents in soils and rocks, various radionuclides with different half-lives can be used for radiometric **dating**. In soil science, the ^{14}C method is of special significance; it enables dating for periods of time from several hundred up to about 40,000 years. Geological periods are dated using e.g. the potassium-argon or the rubidium-strontium method.

Several natural radionuclides have the longest half-lives, existing since the formation of Earth and therefore called **primordial**; these include the elements of the three radioactive series of ^{238}U, ^{235}U and ^{232}Th with a total of 47 nuclides as well as 25 other long-lived nuclides, among which the potassium isotope ^{40}K has special significance due to its omnipresence in soils and its comparatively high specific activity. Other natural radionuclides were and are produced through bombardment with high-energy cosmic radiation (e.g. ^{3}H, ^{14}C). Table 10.9 shows several parameters for naturally occurring radionuclides.

In addition to these, there are also artificially produced radionuclides from nuclear reactions, which can principally be created from any element. Many of these substances are used in various fields of research and technology as well as for radiation therapy; others are liberated from nuclear weapon detonations or from the operation of nuclear plants. A common trait of all of these substances is that the ionizing radiation they emit triggers cellular changes in organisms and therefore also in the human body, which in turn can cause cancer or genetic damage.

Since 1986, the international SI unit **Becquerel** (Bq = number of nuclear decays per second) is used to characterize the activity of a radioactive source. In addition, the **equivalent dose** is used to estimate the effect of ionizing radiation on living cells; it is measured in the unit sievert (Sv). The equivalent dose is the product of the energy dose delivered by the ionizing

Table 10.9 Parameters for selected primordial and cosmogenic radionuclides as well as radioactive series of ^{235}U, ^{238}U and ^{232}Th (excluding some branchings with nuclides that only occur in very small traces)

Radio-nuclide	Half-life (years)	Fraction of the radionuclide in the element content (%)	Mean specific activity in the earth's crust (Bq kg^{-1})
^{40}K	1.26×10^{9}	0.018	603
^{50}V	6×10^{15}	0.25	1×10^{-5}
^{87}Rb	4.8×10^{10}	27.85	70
^{113}Cd	1.3×10^{15}	12.26	7×10^{-7}
^{115}In	6×10^{14}	95.77	2×10^{-5}
^{138}La	1.12×10^{11}	0.089	0.02
^{142}Ce	5×10^{16}	11.07	1×10^{-5}
^{147}Sm	1.05×10^{11}	15.07	0.7
^{176}Lu	2.2×10^{10}	2.6	0.04
^{187}Re	4.3×10^{10}	62.93	1×10^{-3}
^{192}Pt	1×10^{15}	0.78	3×10^{-6}
^{3}H	12.3	10^{-16}	n.d.
^{14}C	5736	10^{-12}	330

Uranium-actinium radioactive series:

^{235}U ($7.13 \cdot 10^{8}$ a) → ^{231}Th (25.6 h) → ^{231}Pa ($3.43 \cdot 10^{4}$ a) → ^{227}Ac (21.773 a) → ^{227}Th (18.17 d) → ^{223}Ra (11.7 d) → ^{219}Rn (↑) (4.0 s) → ^{215}Po ($1.8 \cdot 10^{-3}$ s) → ^{211}Pb (36.1 m) → ^{211}Bi (2.15 m) → ^{207}Tl (4.78 m) → ^{207}Pb (∞)

Uranium-radium radioactive series:

^{238}U ($4.51 \cdot 10^{9}$ a) → ^{234}Th (24.10 d) → ^{234}Pa (1.18 m) → ^{234}U ($2.48 \cdot 10^{5}$ a) → ^{230}Th ($8.0 \cdot 10^{4}$ a) ^{226}Ra (1600 a) → ^{222}Rn (↑) (3.823 d) → ^{218}Po (3.05 m) → ^{214}Pb (26.8 m) → ^{214}Bi (19.7 m) ^{214}Po ($1.64 \cdot 10^{-4}$ s) → ^{210}Pb (21 a) → ^{210}Bi (5.0 d) → ^{210}Po (138.40 d) → ^{206}Pb (∞)

Thorium radioactive series:

^{232}Th ($1.39 \cdot 10^{10}$ a) → ^{228}Ra (6.7 a) → ^{228}Ac (6.13 h) → ^{228}Th (1.91a) → ^{224}Ra (3.64 d) → ^{220}Rn (↑) (55.6 s) → ^{216}Po (0.16 s) → ^{212}Pb (10.64 h) → ^{212}Bi (60.6 m) → ^{212}Po ($3 \cdot 10^{-7}$ s) → ^{208}Pb (∞)

radiation (gray, Gy; absorbed radiation energy per mass) and the radiation weighting factor W_R, which quantifies the different biological effectiveness of different types of radiation in the individual human organs (e.g. $W_R = 20$ for α rays and ≤1 for β and γ rays).

10.2.6.1 Geogenic Radioactivity of Soils and Rocks

Soils essentially inherit their inventory of radionuclides from the respective parent rock. Rocks contain a multitude of radioactive substances in different concentrations and with great regional variation. In terms of quantity, the above-mentioned nuclides of natural origins represent the greatest fraction (Table 10.9). Table 10.10 shows the contents of selected radionuclides in rocks and in soils. A higher natural radioactivity is characteristic for K-rich, and therefore feldspar-, mica- and/or illite-rich rocks; for this reason, the radioactivity is higher in acidic igneous rocks than in alkaline/rocks, higher in illite-rich clays and clay rocks than in smectite- or kaolinite-rich rocks, and higher in silicate-rich sands or sandstones than in those rich in quartz. Likewise, phosphate-rich rocks and soils can exhibit above-average radiation. Specific activities of 1800 Bq kg^{-1} for ^{226}Ra, 20 Bq kg^{-1} for ^{232}Th and 700 Bq kg^{-1} for ^{40}K were mentioned for raw phosphates from Morocco. Because illites dominate the clay fraction in many soils in Germany, the natural

Table 10.10 Specific activities of natural radionuclides in rocks and soils (given in Bq kg^{-1})

Rock/soil	^{40}K	^{226}Ra	^{232}Th
Sandstones	461	35	4
Claystones	876	n.d.	41
Schist (Franconia)	1000	3000	60
Carbonates	97	<10	5
Acidic igneous rocks	997	37	52
Basic igneous rocks	187	10	8
Soils developed from loess	n.d.	41	54
Soils developed from granite	~1100	65–75	38–72
Soils developed from quartzite	~300	54–56	63–70
Soils developed from phyllite	n.d.	40–70	50–80

radioactivity is often higher the higher the clay contents in the soil.

Rocks and soils are the primary source for the radioactive noble gas radon. In all three radioactive series, the radionuclides pass through the atomic number 86 (=radon), whereby three isotopes are produced (^{219}Rn: $T_{1/2}$ 3.96 s; ^{220}Rn: $T_{1/2}$ 55.6 s; ^{222}Rn: $T_{1/2}$ 3.82 d). As an inert noble gas, radon does not react with the solid soil components; it escapes into the atmosphere through air-filled pores, where it is finally transformed into stable Pb isotopes (Table 10.9), which re-enter neighboring soils through aerosols with precipitation. ^{222}Rn is the dominant component of natural radiation exposure in human beings after inhalation. With Rn activities in the soil air often reaching several thousand to more than a million Bq m^{-3}, small leaks in buildings towards the natural foundation can lead to elevated Rn concentrations in houses. Especially depending on the geological conditions, there are large regional differences in the Rn contents of the soil air. High values are found e.g. in the granite regions of eastern Bavaria, the Black Forest and Erzgebirge, while low values are found in the North German lowlands. According to preliminary estimates, about 9 % of the surface area of Germany has Rn activities of more than 100 kBq m^{-3} of soil air. At these contents, the Rn guideline values for living spaces are often exceeded in older houses (recommendation of the European Commission: 200 Bq m^{-3} as a planning level for new buildings, 400 Bq m^{-3} as an action level for existing buildings).

On a local to regional scale, the mining and processing of rocks containing uranium is the cause for elevated radiation in soils and watercourses. Here, the residues from ore dressing (tailings), which contain most of the radium contained in the ore, represent the greatest hazard. In the area surrounding intensively exploited natural mineral deposits, considerable environmental impacts were documented in some cases (especially in Australia, Canada, USA, Kazakhstan, Niger). In Germany, there are natural mineral deposits in the Erzgebirge, Black Forest and in north-east Bavaria. The public eye has been and still is focused on an area of about 1200 km^2 suspected of radioactivity, which was left behind by the former Soviet-German Wismut AG in the triangle between the cities of Gera–Zwickau–Chemnitz.

10.2.6.2 Inputs, Soil Radiation, Radiation Exposure

In addition to the geogenic radionuclide inventory of soils, there is another input of natural radioactive substances through cosmogenic nuclides such as ^{3}H and ^{14}C, which enter the soil through precipitation or uptake by plants, amongst others. Natural forest and steppe fires as well as the combustion of coal and other fossil fuels lead to the liberation of natural radioactive substances, e.g. isotopes of potassium, carbon, uranium and thorium, and they reach the

pedosphere through the air path. Finally, potassium and phosphate fertilizers also add radionuclides to soils.

However, all of the entry paths for natural radionuclides listed here are of minor significance compared to the amounts from rock sources. For example, in the vicinity of coal-fired power plants, no significant rise in the contents of ^{232}Th, ^{226}Ra, ^{137}Co and ^{40}K was observed in soils. An addition of phosphate of 45 kg P ha^{-1} resulted in a specific activity of 26.5 Bq m^{-2} for K, Th and U, which corresponded to an increase in radiation of 0.03 % compared to the natural radioactivity in the corresponding plow layer (85,850 Bq m^{-2}). Similarly, a potassium input of 85 kg K ha^{-1} with typical K reserves in the plow layer of about 90,000 kg ha^{-1} led to a rise in the K content and therefore in the ^{40}K activity of less than 0.1 %.

In addition to the naturally occurring radionuclides, artificial radionuclides have entered the environment and therefore also soils due to surface nuclear weapon detonations (1945–1981; mostly between 1951 and 1962) and the operation of nuclear facilities since about the middle of the 20th century. Because of their very rapid disintegration, most of the resulting nuclides are insignificant on the medium to long term. In contrast, ^{137}Cs ($T_{1/2}$ 30.2 a) and ^{90}Sr ($T_{1/2}$ 28.5 a) can till be detected several decades after their production.

The soils in the immediate surroundings of nuclear weapon tests were particularly strongly contaminated (up to 50 % of the total activity within a radius of 100 km). Finer radioactive suspended loads and aerosols were lifted to elevations of 50 km and resulted in a global increase in ^{3}H, ^{137}Cs and ^{90}Sr inputs with precipitation. Accidents in nuclear power plants have also led to the emission of large amounts of radioactive substances. Among the numerous accidents, those of Windscale in England (1957) and Tschernobyl in the Ukraine (1986) are of special significance. In Windscale, ca. 7.4×10^{14} Bq ^{131}J, 4.4×10^{13} Bq ^{137}Cs, 1.2×10^{13} Bq ^{106}Ru and 1.2×10^{15} Bq ^{133}Xe were released. With the reactor accident of Tschernobyl in April of 1986, 2.6×10^{17} Bq ^{131}J and 2.8×10^{16} Bq ^{137}Cs were liberated and distributed mainly over Europe. In Germany, depending on the wind conditions, distribution of the precipitation and elevation, the inputs in soils fluctuated between about 20,000 and 280,000 Bq m^{-2}. Parts of the Bavarian Forest, the foothills of the Alps and Swabia suffered particularly high contamination. For the northern hemisphere in the first year after the disaster, an effective dose of 200,000 Sv (up to the year 2036: 600,000 Sv) was calculated for the total population. About 70 % of the effective dose is attributed to ^{137}Cs, 20 % to ^{134}Cs and 6 % to ^{131}J.

The ionizing radiation emitted in soils with the decay of radioactive substances is called **earth radiation** (sometimes also terrestrial radiation). Because of the different radionuclide contents of rocks and soils, the earth radiation varies on a regional basis within specific boundaries. The radiation values partly reflect the soil texture distribution, because especially illitic clay minerals have higher radioactivity, and quartz-rich sandy substrates have lower radioactivity. For this reason, the lowest values are measured in the sandur landscapes of northern Germany (Brandenburg: 0.18 mSv a^{-1}, Berlin: 0.19 mSv a^{-1}, Mecklenburg-Western Pomerania: 0.22 mSv a^{-1}), while the highest earth radiation is found in Bavaria (0.42 mSv a^{-1}), Rhineland-Palatinate (0.42 mSv a^{-1}) and in Saarland (0.49 mSv a^{-1}). For the year 1999, the German Federal Office for Radiation Protection published a nation-wide mean value of 0.40 mSv a^{-1}.

The earth radiation, together with the cosmic radiation (on average 0.3 mSv a^{-1}) as well as the absorption of radioactive substances through inhalation (1.4 mSv a^{-1}) and ingestion (0.3 mSv a^{-1}), represent the **natural radiation exposure**, the sum of which amounted to 2.4 mSv a^{-1} in the year 1999 (Fig. 10.10). The radon absorbed through inhalation and its short-lived secondary products therefore represent the main contribution to the radiation levels from natural sources. More than 99 % of the mean effective dose through **artificial radiation** (2 mSv a^{-1}) is caused by the use of ionizing radiation in medical science, especially through diagnostic radiology. The contributions from

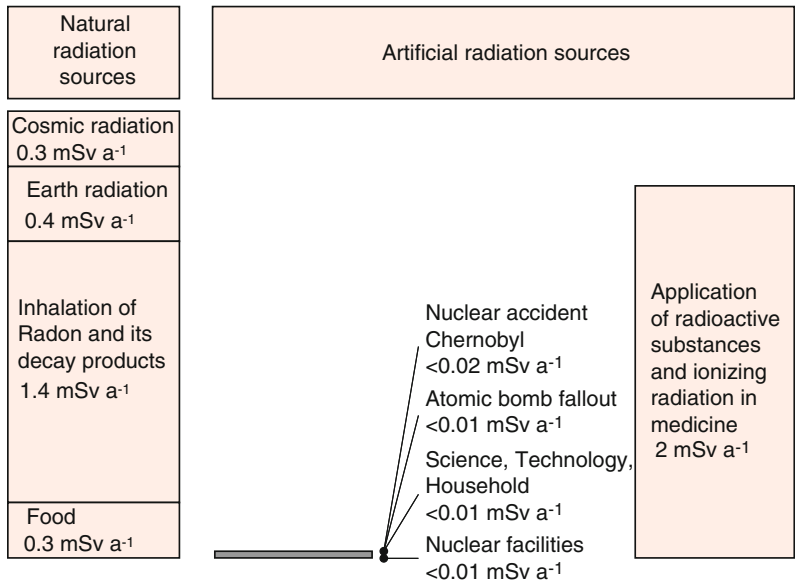


Fig. 10.10 Distribution of the mean effective dose through ionizing radiation from natural and artificial radiation sources in the year 1999 in Germany (after the German Federal Environmental Agency 2001)

nuclear facilities in Germany as well as from nuclear weapon detonations from 1945 to 1981 are very low (<0.01 mSv a^{-1}).

The mean radiation exposure triggered by the accident in Tschernobyl went down from 0.11 mSv a^{-1} in the year 1986 to less than 0.02 mSv a^{-1} in the year 1999. It is almost exclusively caused by earth radiation from the deposited ^{137}Cs. However, compared to the average natural earth radiation, the radiation from the ^{137}Cs attributed to Tschernobyl hardly plays a role. Still, the local dose in several parts of southern and eastern Germany can be one power of ten higher due to locally and temporally limited strong rainfall during the passing of the radioactive clouds in 1986.

10.2.6.3 Behavior in Soils

Because the physical-chemical properties of an element are strongly determined by the nuclear charge, the different isotopes of an element usually have largely the same behavior.

Natural rock-borne radionuclides are liberated during mineral weathering in the same way as the stable isotopes, and depending on the pH, redox conditions and mineral contents of the surrounding matrix, they assume soil-native binding forms. In principle, the same is true for artificially produced nuclides, which are added to soils in highly variable forms, from solid particles to dissolved ions. Depending on the binding form of the immited nuclides, the transition to soil-specific binding forms takes place over highly variable periods of time.

The radionuclides bound in minerals are potentially less toxic than those adsorbed on the colloid surfaces and dissolved fractions, because on the one hand, they are less mobile and available, and on the other, the radiation intensity decreases with the square of the distance. In the following representation of selected radionuclides, ^{40}K is not included despite its significance for terrestrial radiation (Table 10.9), because K was discussed in detail elsewhere as a nutrient element (Sect. 9.6.4).

10.2.6.4 Uranium

The uranium found in soils and rocks consists of three radioisotopes. ^{238}U (99.28 %; $T_{1/2}$: 4.47×10^9 a) is in equilibrium with ^{234}U (0.0056 %; $T_{1/2}$: 2.45×10^5 a), which belongs to the radium radioactive series like the parent nuclide ^{238}U. ^{235}U (0.72 %; $T_{1/2}$: 7.04×10^8 a) is the parent isotope of the uranium–actinium radioactive series (Table 10.9). Because of its large ionic radius (U^{4+}: 0.105 nm, U^{6+}:

0.080 nm), uranium is a geochemically incompatible element and is only found in contents of a few mg kg^{-1} in rock-forming minerals, whereby it is not evenly distributed, but rather is found concentrated along cracks and particle boundaries. Natural mineral deposits that are worthy of mining contain U in the form of uraninite (UO_2, pitchblende), coffinite ($USiO_4$) or accessory minerals such as apatite, zircon and monazite, which have U contents of up to more than 1 g kg^{-1}. The U contents in soils are often in the range between 0.8 and 11 mg kg^{-1}, corresponding to 20–280 Bq kg^{-1}.

Among the possible oxidation levels (+3 to +6), only the valences +4 and +6 dominate in nature. The predominantly tetravalent uranium in primary minerals is rapidly oxidized to form U^{6+} through weathering under aerobic conditions, which forms uranyl complexes in aqueous solutions and also represents the predominant species in soils. The sorption of uranyl complexes exhibits strong pH dependence. Model tests with clay minerals delivered a sorption maximum at pH 6–6.5, which was closely linked to the occurrence of uranyl-hydroxo complexes. In addition to clay minerals, mainly humic substances as well as Fe oxides are effective uranyl sorbents. Under anoxic conditions, U^{4+} is stable and is classified as being very immobile because it forms poorly soluble compounds such as UO_2 or phosphate and sulfide compounds. Altogether, the U mobility and translocation in soils is considered to be low. U inputs, which mainly originate from phosphate fertilization, therefore mostly cause an accumulation of U in the topsoil; elevated contents in subsoils are generally not observed.

10.2.6.5 Cesium

The alkali metal Cs is found in soils and rocks, in addition to the natural isotope ^{133}Cs, in the form of various artificial radioisotopes, whereby ^{134}Cs ($T_{1/2}$: 2.06 a) and especially ^{137}Cs ($T_{1/2}$: 30.17 a) are of particular significance. An important source for the latter isotope was the surface nuclear weapon tests (liberated activity until 1962: 10^{18} Bq), where the fallout until the mid-1980s often left activities of 5–10 Bq kg^{-1} in the topsoils of the FRG. This inventory, almost only ^{137}Cs due to the more rapid decay of ^{134}Cs, was raised on average by a factor of 8 with the reactor accident of Tschernobyl in 1986 (liberated activity with ^{137}Cs: 2.8×10^{16} Bq). Due to the higher inputs (interception) and stronger retardation of cesium in the humus layer, forest soils usually exhibit higher contents than arable soils.

The process of Cs fixation essentially consists of the migration of dissolved or exchangeable bound Cs ions into the interlayers of expanded 2:1 clay minerals (Cs fixation). Cs that is bound in this way can hardly be exchanged against Na and Ca ions; however, the Cs in the clay mineral interlayers competes with K and NH_4 ions for these specific binding sites. Accordingly, an elevated supply of K also leads to a reduced fixation of Cs. In general, the fixation of cesium entering soils increases with increasing clay contents and pH values as well as with decreasing supply of dissolved and exchangeable K. As a result of the selective fixation, the solubility of cesium is considered to be low. Nevertheless, the K_D values published in the literature vary across wide ranges depending on the pH value and mineral contents of soils. In predominantly acidic, sandy soils, K_D values between 60 and 300 were determined, while in neutral to alkaline, loamy soils, the K_D values vary across an interval of 1000 up to more than 100,000. With longer residence times, Cs is increasingly transformed into more stable binding forms. Thus, 36 years after an application of ^{137}Cs, >95 % of the cesium could only be extracted with 9 M HNO_3 or was in a non-extractable form.

The translocation rate of Cs is greater in sandy-gravelly substrates than in loamy-clayey soils, and decreases with time because of increasing fixation. After the Tschernobyl accident, a translocation of 0.5–1.0 cm a^{-1} was measured for various soils in the first years for ^{137}Cs; the rate later sank down to 0.1–0.6 cm a^{-1}. For this reason, 15 years after the input, 70 % of the Cs from the Tschernobyl fallout is still found in the Ah horizons or almost completely in the Ap horizons of soils. If the basic conditions for preferential flow are fulfilled, e.g. in clay-rich substrates with considerable swelling and

shrinking dynamics, stronger translocation can also be observed in such soils.

10.2.6.6 Strontium

The alkaline earth metal Sr is found in soils and rocks in the form of natural (^{84}Sr–^{88}Sr) and artificial isotopes (^{79}Sr–^{98}Sr, $T_{1/2}$: 0.4 s–29 a). ^{90}Sr ($T_{1/2}$: 29 a) inputs in the environment occurred in larger amounts through surface nuclear weapon tests (liberated activity: 0.6×10^{18} Bq). With the reactor accident in Tschernobyl, the amounts of emitted low-volatility ^{90}Sr were low compared to Cs, because the temperatures of the reactor fire were lower than with the nuclear weapon explosions.

The behavior of Sr in soils is similar to that of Ca. In contrast to Cs, it is not specifically adsorbed and is subject to the normal laws of ion exchange. Humic substances, clay minerals as well as pedogenic oxides act as sorbents, where Sr is desorbed from their surfaces again if there is a corresponding supply of other cations. The pH value is the most important determining parameter for the different sorption and solubility in various soils. For the adsorption constant K according to Freundlich (K_F), K_F values of 0.6–21 were determined at soil pH values of 3.1–7.2. Even after longer residence times, Sr is not more strongly fixed. 36 years after an application of ^{90}Sr, 63–75 % of the remaining activity could still be attributed to a readily exchangeable fraction (extraction with NH_4 acetate); the strongly fixed and extractable with 9 M HNO_3 fraction is limited to percent fractions <10 %. The relatively low binding strength of strontium translates into high mobility. Thus, more than 50 % of the ^{90}Sr from nuclear weapon tests was translocated to depths of more than 1 m already at the beginning of the 1980s. The mobility of Sr is therefore much higher than that of Cs in most soils. Organic soils represent a certain exception, where Cs is relatively mobile, while Sr is comparatively strongly immobilized by humic substances. The binding form of the immited strontium has a noticeable influence on the solubility and mobility. With the Tschernobyl reactor accident, ^{90}Sr was added to soils mainly in particulate form in the direct surroundings of the power plant, and only 10–15 % was extractable with NH_4 acetate; in soils of White Russia and Norway, because of the input in ionic form, >70 % of the strontium was extractable with NH_4 acetate.

10.2.6.7 Transition into Plants

Radionuclides can be absorbed by plants in the same way as the stable isotopes of nutrients and harmful substances, both through the leaves and through the roots. The foliar path gains in importance when the supply through dry and wet deposition of radionuclides takes place over a longer period in small amounts (like during the periods of surface nuclear weapon testing) or short-term in greater amounts (like after the Tschernobyl accident). However, uptake through the plant roots is dominant overall.

The transfer of radionuclides from the soil into plants, and therefore the entry into the food chain, is often characterized by the soil–plant transfer factor (TF_{SP}); it represents the quotient of the radiation activity of the radionuclide in the plant and soil. Such transfer factors, which have been determined for many plant species and different soils, help to assess the radioactivity absorbed by the plants from the soil.

However, the transfer factors determined in numerous research projects have proven to be a highly variable parameter, which can fluctuate by up to four powers of ten for a radionuclide in a specific plant species depending on the soil properties, climate conditions and the experimental design. Even in comparative studies, the transfer factor fluctuated by more than 100-fold when using different soils. This great variability is significantly determined by the factors that also regulate the solubility and mobility of radionuclides. Soil properties that promote binding of elements in cationic form, e.g. a high exchange medium supply and high pH values, therefore lead to low solution contents of the radionuclides and a corresponding limited transition to the plant roots. Negative relationships between the sorption intensity and the uptake of radionuclides by plants have been found in many trials. Nevertheless, a reliable prediction of the soil–plant transfer from sorption parameters is not possible, because a

whole series of other factors have a parallel effect. Here, interactions between different ions in the soil solution play a central role. Thus, an increasing supply of K ions in the soil solution is capable of significantly reducing the uptake of Cs by perennial ryegrass (*Lolium perenne* L.). However, this mechanism is only effective up to K solution concentrations of about 1 mM; at higher K concentrations, Cs desorption triggered by K ions causes increased Cs transfer into plants.

Despite their variability, transfer factors are used in prognostic models to estimate long-term doses of radioactivity resulting from the ingestion of contaminated food. To do so, the TF_{SP} values published by the German Federal Ministry or the Interior (BMI) in 1979 in the "General Algorithms for Radiation Exposure" (^{90}Sr: 0.20; ^{137}Cs: 0.05) are often used e.g. for ^{90}Sr and ^{137}Cs. The corresponding factors are to be considered as realistic upper limits, aiming to prevent stronger exposure of human beings to radionuclides when assessing the risk potentials. However, experimentally determined values can deviate considerably. Trials with a Luvisol and a Podzol and different vegetables (only plant parts intended for consumption) delivered TF_{SP} values for ^{90}Sr of 0.01 (radish) to 0.80 (spinach) as well as for ^{137}Cs of 0.0001 (radish) to 0.021 (spinach). However, in view of this, predictions on the uptake of radionuclides by plants are associated with great uncertainty depending on the plant species and soil properties.

10.3 Organic Pollutants

Global chemical production has increased from a million tons in the year 1930 to 400 million tons today. For more than 80 % of the chemicals used today, knowledge is not sufficient to make a risk assessment for these substances. A considerable fraction of organic chemicals enter the environment in many different ways, so that organic pollutants from anthropogenic sources were detected in terrestrial and aquatic ecosystems. Because of their filtering and buffering capacity, soils are a sink for most organic pollutants. Only volatile and readily decomposable substances hardly accumulate in soils.

10.3.1 Classification, Use, Inputs and Contents in Soils

Based on their chemical properties, environmental behavior and use, organic pollutants are divided into different substance classes. In terms of the chemical properties, a distinction is made between aromatic, aliphatic or chlorinated hydrocarbons, amongst others.

In terms of the use, a distinction can be made between pesticides, solvents, surfactants, plasticizers, and pharmaceuticals , amongst others. Pesticides comprise substances from various substance classes. Chlorinated aromatic hydrocarbons (e.g. DDT, HCB), antibiotics and heavy metal salts (e.g. Cu compounds) were used in the past and are still used today as pesticides. Only organic pesticides will be discussed in this chapter.

Persistent organic pollutants (POP) are defined as chemicals that are decomposed only very slowly and accumulate in organisms (bioaccumulation), have toxic and ecotoxic effects, and are transported over great distances. In principle, a distinction is made on the one hand between commercial synthetically produced POPs such as pesticides (DDT, HCB etc.) and PCBs, and on the other, POPs such as dioxins and furans that were unintentionally produced through various thermal processes. Because of their properties, POPs represent a global environmental problem that can only be solved on an international level. Various international environmental agreements have been made in the past (e.g. Stockholm Convention in 2004) to counteract the hazards for human beings and the environment resulting from POPs. The environmental assessment of existing chemicals is performed according to the REACH Regulations (EU Regulation on Registration, Evaluation, Authorization and Restriction of Chemicals).

Plant protection products (PPP), also called pesticides or biocides, are selectively applied to the soil or incorporated at rates of 1–5 kg ha^{-1};

new, specifically acting substances such as sulfonylurea derivatives, are only applied with 0.1–0.2 kg ha^{-1}. In doing so, usually several applications are performed during the year; crops such as vine, hops, fruit and vegetables are often particularly intensively treated. The chemical or biological active substances serve to protect the plants from harmful organisms, to influence their growth or to eliminate undesirable plants and plant parts.

PPPs are classified on an international level according to their biological effect or the target organisms, whereby the different groups have a different meaning (target organisms and proportion of the sales volume of 32,683 t in Germany in 2007 in parentheses): fungicides (fungi, 33.5 %), herbicides (weeds, 52.5 %), insecticides (insects, 3.3 % incl. miticides against mites), molluscicides (snails, 0.9 %), soil decontamination agents and nematicides (nematodes, 0.3 %), rodenticides (rodents, 0.3 %), growth regulators (growth regulators, sprout inhibitors, desiccants, 8.6 %).

PPP preparations are mixtures of active substances and co-formulants. The latter promote wetting, film formation and adhesive properties, efficacy and storage stability of commercial products. Based on their chemical composition, the active substances in PPPs are grouped into substance classes: aromatic nitro compounds, urea derivates, sulfonylurea compounds, triazines, acetic acids (herbicides), azoles, dithiocarbamates and thioram disulfides, morpholins (fungicides), phosphoric acid esters, and chlorinated hydrocarbons (insecticides). Like for other organic substances, the environmental behavior depends on the physicochemical properties, which vary considerably between the individual substance classes (ranges in Table 10.11). The large part of the consumption comprises only a few active substances: growth regulators—chlormequate, herbicides—glyphosate (phosphonomethyl glycine), isoproturone (urea derivate), metamitrone (N-heterocyclene), fungicides—mancozeb (dithiocarbamate), which are comparatively polar compounds with a log K_{ow} of −4.00 to 2.87. The poorly decomposable and strongly accumulating chloro-organic compounds that are prohibited today, such as aldrin, dieldrin, DDT and hexachlorobenzene, in contrast, have log K_{ow} values between 5.20 and 6.91. In terms of their degradability, most of the agents authorized today are classified as being readily to very readily decomposable (more than 75 % <6 weeks or 6–18 weeks). Today, the authorization tests for pesticides in Germany are based on simulation models for assessing the substance behavior in different environmental scenarios. The environmental relevance of pesticides results mainly from possible effects on non-target organisms and translocation in the groundwater and surface waters. Older model estimations determined an input in Germany's most important lakes and rivers of up to 14 t of PPP (sum of 17 active substances).

Aromatic hydrocarbons are compounds that are derived from benzene. In this substance group, benzene, toluene, phenol and their derivatives play an important role. Benzene and phenol have natural sources (animals and plants) and are found in black coal and mineral oil, from which they are extracted. Phenol is a component of medium heavy oil, and benzene, toluene and xylene are contained in light oil. The latter compounds are grouped together with ethylbenzene under the term BTEX aromatics. They serve to increase the octane number in gasoline and are also used as solvents and degreasing agents or as a raw material in the chemical industry. Phenol is used as a solvent and disinfectant.

Due to their high volatility, aromatic hydrocarbons enter soils through atmospheric deposition, Direct inputs result from averages and accidents, especially involving fuel transport. Local accumulations in soils of up to several thousand mg kg^{-1} were observed due to the seepage of fuels. Several hundreds of these compounds have been found to date in environmental samples, and several thousand are known.

Polycyclic aromatic hydrocarbons (PAH) are compound 17304–17526 s with different numbers of condensed benzene rings in their molecules. Their arrangement is linear, angular or in clusters. The hydrogen atoms can be substituted by various polar and nonpolar groups such as $–CH_3$, $–C_2H_5$ $–NO_3$, –OH, $–NH_2$, etc.

Table 10.11 Ranges for selected physicochemical properties, for soil adsorption coefficients (linear: K_d and K_{OC}, nonlinear K_F) as well as the time periods for the decrease in concentration of organic xenobiotic substances in soils by 50 % (DT_{50}) caused mainly by microbial activity

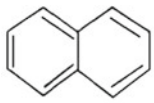
Level	Molar mass (g mol^{-1})	Water solubility (mg L^{-1}) (25 °C)	Vapor pressure (hPa) (25 °C)	Polarity log K_{OW}	Protonation const. pK_a	K_d, K_{OC} (ml g^{-1}) K_F	Degradation DT_{50} (d)
0	<100	<0.1	$<10^{-10}$	<−1.38	<0	<0.5	>1000
1	100–200	0.1–1	10^{-10}–10^{-5}	−1.38–0	0–4.0	0.5–50	1000–356
2	>200–300	>1–10	$>10^{-5}$–1	>0–2.5	>4.0–6.1	>50–150	365–128
3	>300–500	>10–100	>1–50	>2.5–4.0	>6.1–7.9	>150–500	128–42
4	>500–1000	>100–1000	>50–100	>4.0–6.5	>7.9–14.0	>500–5000	42–1
5	>1000	>1000	>100	>6.5	>14.0	>5000	<1

Substance group	Molar mass	Water solubility	Vapor pressure	Polarity log K_{OW}	Protonation const. pK_a	Sorption$_0$			Degradation DT_5
						K_d	K_{OC}	K_S	
[a]Aliphatic HC	0–1	4–5	3–5	2–3		0–2	1–4	1–2	0–4
[b]Aromatic HC	0–2	0–5	2–5	2–4	2–4[l]	0–5	1–5	0–4	0–4
[c]Nitroaromatics	1–2	2–5	1–2	2–4	0–4[l]	0–1	1–4	0–1	3–5
[d]PAH	1–2	0–3	1–2	3–5		0–5	3–5	0–5	0–5
[e]PCB	1–3	0–3	1–2	4–5		1–5	4–5	1–4	0–1
[f]PCDD/PCDF	3	0	0–1	5		4–5	5		0
[g]Phthalates	1–3	1–5	1–2	2–5		0–1	1–5		3–5
[h]Surfactants	1–3	2–5	1–2	0–4	1[l, m]	1–4	1–5	0–3	3–5
[i]PPP	0–4	0–5	0–5	1–4	0–2[l]	0–5	1–5	1–2	0–5
[j]Organotin comp.	1–3	0–5	1–5	0–5		1–5	4–5		2–4
[k]PhAC	1–5	0–5	0–2	0–4	0–4[m]	0–5	1–5	0–3	0–5

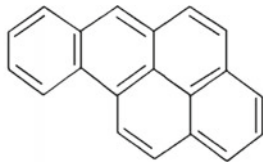
[a]Halogenated hydrocarbons, among others, VCH: (chloro)2-4-methane, -ethane, -ethene, -propane, (bromo)2-methane
[b]BTEX (benzene, toluene, ethylbenzene, xylene), phenol and chlorinated aromatics: $(methyl)_{2–3}$-, ethyl-, butyl-, propyl-, $(chloro)_{1–6}$-benzene, ethyltoluene, phenol, $(chloro)_{1,5}$-phenol
[c]$(nitro)_{1-3}$-benzene, -toluene, -phenol, hexogen (RDX)
[d]Polycyclic aromatic hydrocarbons: 2- to 6-ring PAH
[e]Polychlorinated biphenyls: Biphenyl, $(chloro)_{1-8}$-biphenyl
[f]Polychlorinated dibenzodioxins and –furans: $(chloro)_{4-6,8}$-dibenzodioxin, $(chloro)_{4-6,8}$-dibenzofuran
[g]Dimethyl-, diethyl-, bibuthyl-, di(2-ethyl-hexyl)-, butylbenzylphthalate
[h]Linear alkylbenzenesulfonate (LAS), nitrilotriacetate (NTA), stearyltrimethylammonium chloride (STAC), distearyldimethylammonium chloride (DTDMAC), octylphenol, nonylphenol
[i]Plant protection products: Herbicides, insecticides, fungicides: e.g. phenoxy fatty acids, pyridine salts, s-triazines, phenylureas, sulfuronureas, thiadiazoles, carbamates, pyrethroids, phosphorus esters, benzimidazoles, acid amides
[j]$(methyl)_{1-3}$-tin, ethyltin, $(butyl)_{1-3}$-tin, triphenyltin, triphenyltin acetate, tripentyltin, tripropyltin
[k]Pharmaceutically active chemicals: Antibiotics: Tetracyclines, sulfonamides, macrolides, fluoroquinolones, benzimidazoles, polypeptides, lipoglycosides, quinoxaline derivates. Human pharmaceuticals: Carbamazepine, diclofenac, clofibric acid, propranolol, propyphenazone. Estrogen acting substances: Estrogens, bisphenol A
[l]Only a few compounds in the substance group exhibit an acid dissociation constant
[m]Various compounds in the substance group exhibit several acid dissociation constants

(alkyl PAH, nitro PAH, hydroxy PAH, amino PAH etc.), and in the same way, N, O or S can be incorporated into the ring structure instead of the carbon (so-called hetero PAH). The most well known representatives from a total of several 100 compounds are naphthalene (2 rings),

phenanthrene (3 rings), chrysene, pyrene (4 rings), benzo(b)fluoranthene, benzo(a)pyrene (5 rings), benzo(g,h,i)perylene (6 rings). Compounds with 4 and more rings exhibit carcinogenic and mutagenic effects. In the PAH substance group, mostly benzo(a)pyrene, benzofluoranthene and fluoranthene are used as indicator substances (Leitsubstanzen). Benzo(a) pyrene counts among the particularly toxic and persistent compounds. As recommended by the US Environmental Protection Agency (EPA), environmental samples are routinely analyzed for 16 PAHs and their sum is given as a "total content".



Naphthalene



Benzo[a]pyrene

PAHs are not specifically or intentionally produced, but are rather produced with the incomplete combustion of organic substances (coal, heating oil, fuels, wood) in conventional power plants, with coking, through motor vehicles, but also with forest, moor and other open fires. Simple PAHs can be formed by microorganisms.

In addition to the deposition of tar oils and combustion residues, atmospheric deposition is the primary entry path for PAHs in soils. In industrial areas, ca. 0.1–1 mg ΣPAK ha^{-1} a^{-1} was deposited from the atmosphere. On agricultural land, there may be inputs from sewage sludges and composts.

Background levels in soils from natural sources are estimated at 1–10 μg ΣPAH kg^{-1} m_D. In arable and grassland topsoils in Germany, the contents lie between 100 and 300 μg ΣPAH kg^{-1} m_D. In forest soils, PAHs accumulate in the organic humus layers due to the filtering effect of trees (median values 750 μg ΣPAH kg^{-1} m_D). In urban areas, the PAH contents are much higher at 0.4–3.6 mg ΣPAH kg^{-1} m_D. Extremely high concentrations of up to several g ΣPAH kg^{-1} m_D are found in soils of former gas plants and coking plants.

Chlorinated hydrocarbons (CHC) are defined as aliphatic and aromatic (chlorobenzene, chlorophenol) compounds where one or more hydrogen atoms are substituted by chlorine. They are used in large quantities for a wide variety of industrial and commercial purposes. Furthermore, they are sometimes also used as insecticides and fungicides in agriculture and forestry as well as for horticulture. Because of their high persistence, a global accumulation in soils and sediments has been observed. Hexachlorobenzene and DDT count among the POPs, among others.

Chlorobenzenes (1,2-di-, 1,2,4-tri- and hexachlorobenzene) count among the chlorinated hydrocarbons. They are used for organic synthesis and the production of pesticides, amongst others. Hexachlorobenzene (HCB) was used as a fungicide and as a flame retardant. **Chlorophenols** (di-, tri-, pentachlorophenol) are used as preservatives and pesticides (pentachlorophenol as a wood preservative).

The substance group of the **volatile chlorinated hydrocarbons** (**VCH**) includes chlorinated derivates of methane and ethane. These compounds include, among others, tetrachloroethene, trichloroethene, *cis*-1,2-dichloroethene, 1,1,1-trichloroethane, trichloromethane, 1,2-dichloroethane, vinyl chloride, dichloromethane, tetrachloromethane and 1,1-dichloroethane.

Most of these compounds are used as extraction agents and solvents. **Tetrachloroethene** is also used as a fabric-cleaning agent. ***cis*-1,2-dichloroethene** is formed through anoxic/anaerobic transformation of highly chlorinated ethene in landfills, in digested sludge or in anoxic soils. It is also formed as a residue during PVC production. **1,1,1-trichloroethane** is used for the production of 1,1-dichloroethene, for the synthesis of polychlorinated organic compounds.

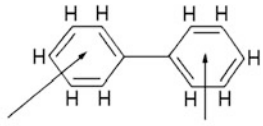
Vinyl chloride is almost only used for the production of PVC and copolymers. Its former use as a propellant gas is forbidden today. **Tetrachloromethane** is mainly used for the production of chlorofluorocarbons. To a lesser extent, tetrachloromethane is also used in organic analytics as an extraction agent.

In terms of inputs into the environment, the **atmospheric path** plays a significant role

because of the comparatively high volatilization potential. Individual compounds from the VCH groups can be detected virtually ubiquitously. **Direct inputs** take place with the production, processing and use of VCHs (e.g. errors when filling and emptying storage and transport containers) as well as in arable soils due to the application of sewage sludge.

With the exception of *cis*-1,2-dichloroethene, which is formed with the decomposition of tetra- and trichloroethene, soil contaminations are predominantly from anthropogenic sources. Contents measured in polluted soils range between 1 and 210 µg kg^{-1} tetrachloroethene and 10–690 µg kg^{-1} vinyl chloride after sewage sludge application.

Polychlorinated biphenyls (PCB) ($C_{12}H_{10-(x+y)}Cl_{(x+y)}$)) represent a substance class consisting of 209 congeners with different chlorine contents. Up to 10 chlorine atoms can be incorporated into the molecular structure. In order to name them, Balschmitter systematically recorded, categorized, and assigned them with individual numbers between 1 and 209. In investigations, generally only the congeners no. 28, 52, 101, 138, 153 and 180 are taken into account. Because of their physical and chemical properties (low thermal conductivity, high dielectric constant, high aging and temperature stability, low flammability), PCBs found broad technical uses as emollients (e.g. in joint sealants and plastics) and flame retardants (e.g. as a coating for ceiling panels). Furthermore, the high dielectric constant enables a broad spectrum of use as a dielectric medium in condensers.

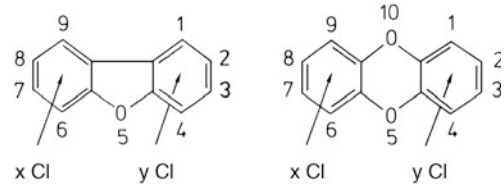


Substitution of x Cl by x H and y Cl by y H

Deposition from the atmosphere is the main entry path for PCBs into soils. The ubiquitous occurrence of PCBs demonstrates that transport can occur over great distances. Direct inputs through the escape of PCB mixtures from closed systems are possible in the case of accidents or landfilling of wastes containing PCBs as well as in the fields of production and processing. In agricultural soils, PCBs can be added through sewage sludge and compost applications.

Background levels in agricultural soils are <1–20 µg Σ PCB_6 kg^{-1} m_D. The contents have significantly increased due to long-term sewage sludge applications. In metropolitan areas, elevated contents up to 140 µg Σ PCB_6 kg^{-1} m_D were also observed. They are attributed to elevated atmospheric inputs and landfilling of wastes. Extreme contaminations occur in the case of accidents and in production plants (up to 53 g ΣPCB kg^{-1} m_D).

Polychlorinated dibenzodioxins (PCDD) and **dibenzofurans (PCDF)** are known as extremely toxic compounds with high stability. They consist of two phenyl rings with various degrees of chlorination, which are connected by one oxygen atom in the furans and by two oxygen atoms in the dioxins. Altogether, there are 135 PCDFs and 75 PCDDs.



Hydrogen atoms are bound in the positions 1–4 and 6–9, which can be substituted against chlorine atoms. For example, the incorporation of 4 chlorine atoms in the dibenzodioxin molecule in the positions 2, 3, 7 and 8 results in the formation of extremely toxic 2,3,7,8-tetrachlorodibenzodioxin (TCDD).

PCDDs and PCDFs are by-products of the large-scale production of a series of chlorinated chemicals, e.g. the herbicides 2,4-D and 2,4,5-T as well as the wood preservative PCP. They are also produced with various combustion processes (through to forest fires) in the temperature range

between 300 and 600 °C from inorganic and organic chlorine compounds (especially PVC).

Dioxins enter the soil mainly through atmospheric inputs. Direct inputs are possible through the spreading of sewage sludges, composts and liquid manure.

Dioxin and furan are always found in mixtures. For the assessment of their toxicity, the concentrations of dioxin and furan mixtures in environmental samples (sludges, soils, plants) are given in toxicity equivalents ng I-TEQ kg^{-1} m_D. In doing so, the concentrations of the individual congeners are multiplied with a factor (from 0.001 to 1) corresponding to their toxicity and added up to a total content. By convention, the most toxic congener 2,4,6,8-tetrachlorodibenzodioxin (TCDD) is weighted with the factor 1. A dioxin/furan with the factor 0.5 is considered to be half as toxic as 2,4,6,8-TCDD.

Background levels (50th percentile) lie in the range between 0.16 and 15 ng I-TEQ kg^{-1} m_D, whereby the highest concentrations were measured in organic humus layers of forests. Extremely high contents were observed in wire pyrolysis plants (reclamation of copper by smoldering the plastic coating) with contents up to 98,000 ng I-TEQ kg^{-1} m_D.

Nitroaromatics are aromatic compounds that carry one or several nitro groups ($-NO_2$) on a benzene ring. Nitroaromatics represent a large class of environmentally relevant contaminants. They include nitrobenzene, 1,3-di- and 1,3,5-trinitrobenzene, nitrotoluene, 2,4-dinitrotoluene, 2,4,6-trinitrotoluene and hexogen (RDX). Many of them were or are produced as intermediate products not only for the manufacturing of explosives, but also for pigments, herbicides, pharmaceuticals, polyurethane foams, and also for widespread fragrances (musk xylene and musk ketone).

Soil contamination occurs mainly on armament industry sites (release during operation and especially through war damage) as well as on military sites.

Surfactants are surface-active substances that are concentrated at the contact surfaces of two media (e.g. water/air). Surfactants reduce the surface tension of water and increase the apparent water solubility of hydrophobic substances. This improves the wetting of surfaces and adhered substances are more easily removed. Surfactants are therefore the most important group of laundry and cleaning agents. Furthermore, surfactants find a wide range of uses as emulsifiers, textile additives, static inhibitors, flotation chemicals etc. in numerous technological fields. According to the electric charge, a distinction is made between anionic (linear alkylbenzene sulfonates LAS, alkane sulfonates SAS), cationic ((9)bis-(hydrated tallow alkyl)-dimethylammonium chloride (DTDMAC)), nonionic (nonylphenol ethoxylate NPEO, nonylphenol), and amphoterous surfactants.

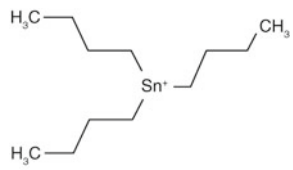
Atmospheric inputs are negligible. Surfactants enter soils mainly directly with wastewaters (domestic sewage, dairy and beverage processing) and sewage sludges. **Background levels** in the soil are considerably below the detection limit. After the application of sewage sludge, 16–25 mg LAS kg^{-1} m_D were detected in soils. A single application of pesticides can lead to 24 μg NPEO kg^{-1} of soil up to a depth of 20 cm.

The **phthalate** substance group includes ca. 50 different esters of o-phthalic acid. Phthalates are detectable in all environmental compartments, and are used in large amounts as emollients in plastics (PVC) as well as in paints and varnishes. Dimethyl phthalate (DMP), diethyl phthalate (DEP), dibuthyl phthalate, (DBP), di (2-ethyl-hexyl) phthalate (DEHP), butylbenzyl phthalate (BBP), and dioctyl phthalate (DOP) are significant in terms of quantity.

Companies that produce and process phthalates are sources of phthalate emissions; they can also be liberated by waste incinerating plants, and in addition to atmospheric deposition, they can also enter soils through sewage sludge applications.

Phthalate contents in uncontaminated soils are of ca. 0.02–0.03 mg kg^{-1} m_D. Arable land is generally less strongly polluted than grassland soils. Contents in arable soils are <0.8 mg kg^{-1} m_D, and in grassland soils <0.9 mg kg^{-1} m_D. Values between 0.4 and 5.3 mg kg^{-1} m_D were measured in residential areas.

Organotin compounds (OTC) are organometallic compounds with one or more Sn-C bonds, which, with few exceptions, are derived from tetravalent tin. Sn(IV) organic compounds have the general formula: $R_{(n+1)}SnX_{(3-n)}$ (R = alkyl and/or aryl groups and X = halogens, H, hydroxy or acyloxy groups). Technically significant subgroups are compounds with monobutyltin (MBT), dibutyltin (DBT), tributyltin (TBT), dioctyltin (DOT) and triphenyltin (TPT). Most of these compounds are used as stabilizers in PVC. Other fields of application include antifouling paints in the marine industry, crop protection agents, wood preservatives and disinfectants.



Structural formula of the tributyltin cation

OTCs enter soils through the air, precipitation, wastewater, sewage sludges and pesticide applications. Background concentrations are of 2.4 mg kg^{-1} m_D. Tributyltin contents in contaminated soils are <0.01–0.1 mg kg^{-1} m_D, and soils treated with pesticides contain 0.1–1.0 mg kg^{-1} m_D.

Pharmaceutical substances are usually rapidly excreted by the treated organism after their administration. Mammals also excrete natural hormones, particularly during pregnancy. These active substances, some of which are highly efficient, enter the environment and particularly agricultural soils through sewage and contaminated farmyard fertilizers. Sewage sludge and animal manure often exhibit individual hormones or mixtures of several hormones and antibiotics with contents of up to several mg kg^{-1}. In soils, mainly residues of **antibiotics** from administration to farm animals have been detected until now. In soils fertilized with liquid manure, concentrations of the tetracyclines chloro- and oxytetracycline as well as tetracycline of up to 7 or 200 μg kg^{-1} were measured; after fertilization with sewage sludge, fluoroquinolones were detected at concentrations of up to 320 (norfloxacin) and 400 μg kg^{-1} (ciprofloxacin). Through the wastewater path, more and more pharmaceuticals such as painkillers, rheumatic medication and radio-opaque substances enter the environment.

10.3.2 Processes at the Soil Surface

The fate of organic active substances and pollutants in soils is determined by processes of fixation, translocation and decomposition (Fig. 10.1). They reach the soil surface through various paths, where they are subject to surface processes before they penetrate deeper into the soil.

Depending on the substance persistence, **photochemical decomposition processes** of varying intensity take place directly at the soil surface up to a depth of ca. one millimeter, or already in the atmosphere, under the influence of short-wave UV radiation from the sunlight. In addition to the absorption of UV light, good water solubility and a low vapor pressure are particularly favorable chemical properties for photodegradation on soil surfaces. Readily soluble compounds, e.g. from pesticide, phthalate or organotin compound groups, reach the soil surface with rising capillary water. There, they can be decomposed directly by sunlight or indirectly by other substances, which become chemically reactive under the influence of UV light. Even hydrophobic chemicals are subject to photodegradation. Compounds such as hexachlorobenzene (HCB), polychlorinated biphenyls (PCB) as well as polychlorinated dioxins and furans (PCDD/F) are decomposed by light at the soil surface, while they are very stable inside the soil.

Chemicals with a high **vapor pressure** (Table 10.11) exhibit a strong tendency towards dispersion and can be subject to considerable **volatilization** if there is sufficient gas transport in the soil. BTEX, low-molecular PAHs (e.g. naphthalene) and fumigation agents such as methylbromide extensively escape from soils in gas form. The contents of PCBs are also reduced

by volatilization. However, this does not represent a true decomposition of the active substances and pollutants, but rather a translocation into other environmental compartments; through the air path, the vaporized chemicals can be absorbed by plants or reenter soils at greater distances. This often results in elevated concentrations of pollutants, e.g. PAHs, in the upper soil horizons and organic humus layers (Fig. 10.15). The volatilization rates vary with the wind velocity and the temperature. Because the losses from moist soil surfaces are usually higher than from dry surfaces, the **Henry constant** (distribution coefficient solution/gas phase) of a chemical is a better measurement than the vapor pressure for assessing volatilization.

All compounds are subject to transport through **surface runoff** and **erosion** of soil material, whereby they can even reach the receiving waters. The installation of filter strips along the banks is an effective method for reducing such soil and substance losses. Using the example of pharmaceutical compounds, it was determined that the surface runoff from grassland areas increased following liquid manure application due to a temporary surface sealing of the soil pores.

10.3.3 Fixation in the Soil

Interactions with the exchange media lead to the sorption of active substances and pollutants in soils. The interactions are based on physical attraction mechanisms such as Waals forces, hydrogen bonds, and charge exchange complexes or the formation of chemical complexes, covalent or ionic bonds as well as ligand exchange. Likewise, diffusion in the micro- and nanopores of soil particles contributes to the sorption and particularly affects the adsorption and desorption kinetics. The linear sorption coefficient K_d (ml g^{-1}) describes the distribution equilibrium established between the adsorbed fractions x/m (e.g. in mmol g^{-1}) and the solution concentration c (e.g. in mmol mL^{-1}) of a compound. Sorption coefficients therefore enable a comparison of the solubility and adsorption behavior of different chemicals in soils with different mineral contents.

$$K_d = x/mc^{-1}$$

On the one hand, the distribution equilibrium is determined by the chemical properties, especially the water solubility, the vapor pressure, and the polarity, the latter being expressed by the octanol/water distribution coefficient (K_{ow}) (Table 10.11). For this reason, sorption coefficients can also be estimated using quantitative structure/activity relationships (QSAR) or quantitative structure/property relationships (QSPR) by means of molecular descriptors, such as the K_{ow}. The latter is particularly true for nonpolar compounds with log K_{ow} >4.0, which are also called hydrophobic organic chemicals (HOC) (e.g. various chlorinated aromatic hydrocarbons, and most PAHs, PCBs, PCDD/Fs). The sorption coefficients generally increase within a substance group with the molecular mass and the degree of chlorination, if applicable.

On the other hand, the soil mineral contents affect the extent and nature of the sorption. In addition to the electrolyte content of the soil solution and the redox conditions, the soil colloid content is also important. This includes clay minerals as well as pedogenic oxides and hydroxides, which are significant sorbents particularly for ionic compounds such as the surfactant LAS and organotin compounds. However, for most organic active substances and pollutants, already low contents of organic matter mask the influence of mineral sorbents. For example, saturated hydrocarbons (n-alkanes), aromatic hydrocarbons (benzene, toluene, naphthalene, phenanthrene, etc.) as well as various hetero-compounds and asphaltenes contained in mineral oil as a heterogeneous substance mixture are mainly adsorbed on the soil organic matter. The often close correlation between the SOC content and the magnitude of the sorption coefficient is shown in Fig. 10.11 using the example of 4-nitrophenol. This outstanding significance of the soil organic matter is taken into account by normalizing the sorption coefficient to the organic carbon content (SOC).

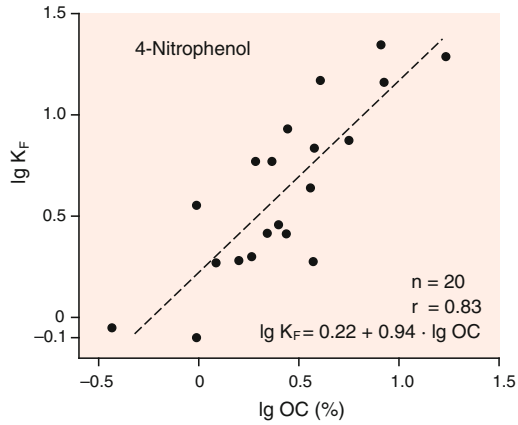


Fig. 10.11 Correlation between the K_S values for 4-nitrophenol adsorption and the SOC content for 20 soil samples with very different mineral contents (regression line for 17 A and 3 B horizons) (after Kukowski and Brümmer 1988)

$$K_{OC} = K_d/SOC(\%) \cdot 100$$

However, the calculation of **K_{OC} values** is only sensible for soil materials with SOC contents <0.1 % and a clay/SOC ratio <40 in combination with nonpolar compounds, especially HOCs such as PCBs, PCDD/Fs and PAHs. Because of their hydrophobic properties, nonpolar compounds are mainly associated with the soil organic matter and therefore accumulate in topsoils. For polar and hydrophilic compounds, the relationship with the SOC content is much weaker. The K_{OC} values for the different chemicals range from <10 (e.g. for chlorobenzene) to >107 (PCDD/F; Table 10.11). While compounds with a high vapor pressure (e.g. lower branched chain alkanes, BTEX aromatics) have low Koc values (some <100), poorly volatile compounds such as phenanthrene, hetero compounds and asphaltenes have high values (103 to >105). The KOC values of the individual compounds vary between different soils much less than the Kd values. The deviations still observed can be attributed to the fact that the K_{OC} not only depends on the quantity of organic exchange media, but also significantly on their spatial conformation and chemical composition. This becomes particularly clear in conjunction with coal-related substances such as coal, kerogen and black carbon (Chap. 3), which sometimes accumulate considerably, especially in contaminated sites, and are capable of sorbing HOCs 10–100 times more strongly than humic substances. Especially at low solution concentrations, e.g. PAHs can be almost exclusively adsorbed on coal-related substances.

Especially with higher active substance and pollutant concentrations, with $c > 50$ % of the water solubility, and also overall for polar and ionizable compounds, the course of the sorption isotherms is often not linear. This means that every combination of solution concentration and adsorbed concentration has a different linear sorption coefficient (K_d). The **Freundlich equation** (Sect. 5.5.6.1) is often used to describe these isotherms. In contrast to linear models, it is not based on the homogeneity of the binding site energies; however, it contains the linear isotherms as a special case ($n = 1$).

$$x/m = K_F \cdot c^n$$

For very strongly sorbing and nonpolar compounds, such as PCDD/Fs, nonlinear sorption has not been determined until now. In addition, K_F values for different compounds are not available (Table 10.11), because the experimental determination of non-linear isotherms is laborious.

Pronounced nonlinearity of the sorption indicates an association with heterogeneous organic and mineral sorbents through specific, mostly chemical sorption mechanisms. Even for HOCs as well as PAHs, it is meanwhile assumed that the significance of such specific binding mechanisms is considerable. With PAHs, the π electrons of the aromatic double bonds form charge exchange complexes or π-π complexes with corresponding structures of the soil organic matter. Especially polar compounds and those forming anionic and/or cationic species depending on the pH value of the medium, such as many pesticides and antibiotics, are sorbed nonlinearly. This property is characterized by the **protonation constant** (**pK_a**) (Table 10.11), whereby some compounds have several pK_a values, e.g.

the imidazoles form five different species. The change in the charge state as well as the K_{OW} distribution coefficient and sometimes the water solubility of ionizable compounds is sudden in the pH range surrounding the acidity constant. If the pK_a lies in the pH range of central European soils of 3–8, it is of great significance for the sorption. Here, in terms of the sorption on organic solid constituents, charged species, especially acid anions (e.g. phenols and phenoxycarbonic acids), are generally much more poorly adsorbed than neutral species because of their higher polarity (or lower hydrophobicity). The cationic species of alkaline organic compounds (e.g. paraquat, sulfonamide antibiotics), in contrast, are often very strongly fixed mainly on mineral exchange media. The K_{OC} values of pentachlorophenol (PCP) increase considerably in soils from neutral to strongly acidic soil pH values (Fig. 10.12); with sinking pH, PCP is increasingly transformed by protonation from the phenolate anion into the phenol molecule (pK_a = 4.7). Adsorption through the formation of hydrogen bonds increases in the process. This effect is also observed with trichlorophenol (2,4,6-TCP: pK_a = 6.0) in the pH range from 8 to 5; in contrast, it is no longer measurable for undissociated nitrophenol (pK_a = 7.2) (Fig. 10.12). Like with PCPs and TCPs, the K_{OC} values and therefore the adsorption capacity (=buffer capacity) of soils increase strongly from neutral to strongly acidic soil pH values for a whole series of organic chemicals that are transformed from anions to neutral molecules by protonation. The course of the buffer capacity of soils as a function of the soil pH for a series of organic chemicals is then the opposite of that for heavy metals (Sect. 10.2.4). Furthermore, the soil pH affects the charge state of the exchange media. The variable charge of the soil decreases with decreasing pH value.

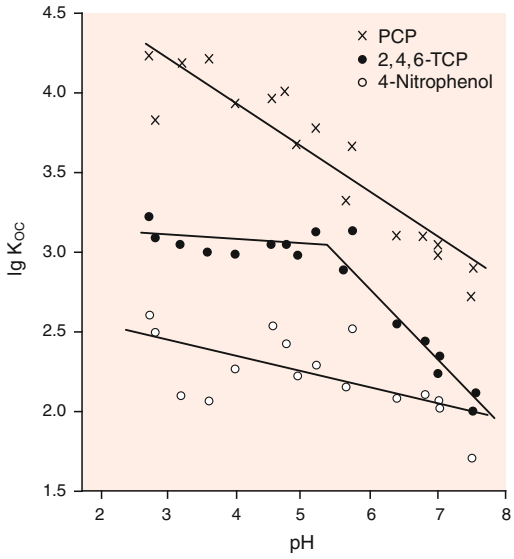


Fig. 10.12 Relationships between the lg K_{OC} values of pentachlorophenol (PCP), 2,4,6-trichlorophenol (2,4,6-TCP) and 4-nitrophenol for 17 soil samples from A horizons and their pH-($CaCl_2$) values (after Kukowski and Brümmer 1988)

The sorption of organic active substances and pollutants on the soil organic matter takes place in two phases. It can be distinguished into a rapid and a slow process. The rapid sorption process results in a relatively stable equilibrium distribution between the soil solution and the solid phase within a few minutes, hours or days. It is the basis for the determination of the sorption coefficients described above. Many authors assume that the binding of hydrophobic active substances and pollutants involves a pure distribution process between two phases or surface adsorption phenomena. In doing so, organic active substances and pollutants can be embedded in hydrophobic regions of organic macromolecules. Furthermore, it is long known that the extractability and bioavailability of pesticides and organic pollutants decrease strongly on the long term, even without being chemically modified. This phenomenon is also called aging. Finally, **non-extractable residues** (=bound residues) can be formed. This slowly progressing process is explained with the incorporation in humic substance molecules via covalent bonds (bound residues) or as a result of a very advanced intramolecular diffusion process in the soil matrix (**sequestration**). The formation of bound pesticide residues is promoted by microorganisms and the addition of readily decomposable organic matter (e.g. cow manure). Small fractions of bound residues can be liberated by

physicochemical and biochemical reactions. This hardly leads to a risk for soil organisms and plants. The bonding of organic active substances and pollutants in the humic substance fraction is already used for the remediation of TNT-contaminated soils. Bound residues can be detected through the use of active substances and pollutants marked with isotopes, e.g. through the determination of the non-extractable radioactivity, or using magnetic resonance spectroscopy of stable isotopes with low natural occurrence.

The adsorbed fraction of organic chemicals is generally found in a state that is largely protected from microbial decomposition as well as from leaching and uptake by higher plants. Persistent organic chemicals therefore accumulate in soils with strong adsorption (e.g. organotin compounds, PCBs, PCDD/Fs), however, in soils with low adsorption, they can be translocated into the groundwater and surface waters (e.g. various pesticides such as atrazine, bentazon, imazaquin). Active substances and pollutants are only ecologically active after desorption and transition into the soil solution, so that the reversibility of the adsorption processes in soils is highly significant. Elevated microbial activity as well as changes in the soil pH (Fig. 10.12) and the electrolyte concentration can cause mobilization. In doing so, both the microorganisms and the active substances and pollutants preferentially accumulate on exchange medium surfaces of the clay and fine silt fraction, so that there is often direct spatial proximity.

Soil-borne **dissolved organic substances** or those added e.g. through animal manure (dissolved organic matter—**DOM** or dissolved organic carbon—**DOC**) can bind organic active substances and pollutants and therefore significantly increase their mobility and translocability. For this reason, in addition to binding on the organic solid phase, binding on the DOM, which is in turn subject to adsorption and desorption processes on the solid phase, must also be considered for the evaluation of the environmental behavior of these substances. Among other methods, fluorescence quenching, solid phase extraction as well as dialysis and ultrafiltration are used for determining the distribution coefficients between the dissolved hydrophobic organic chemicals and the DOM (K_{DOC}). While preferential adsorption of TNT on DOM compared to particulate organic matter was observed, the K_{DOC} values for phenanthrene, benzo(a)pyrene and PCB 52 were found to be in the same order of magnitude as their K_{OC} values. This leads to the conclusion that the distribution of hydrophobic organic chemicals in the soil takes place in a three-phase system (Fig. 10.13), which has a considerable influence on the bioavailability and the mobility of these substances. In such a system, in addition to the distribution coefficients for the solid phase (K_d^X or K_{OC}^X) and the DOM (K_{DOC}), the interactions between the DOM and the solid phase must be taken into account (K_d^{DOC}). Furthermore, particularly in contaminated sites, it must be considered that the sorption is also significantly affected by water-miscible organic solvents as **cosolvents**, **non-aqueous phase liquids** (NAPL) as well as **competitive adsorption** of other active substances and pollutants competing for the sorption sites.

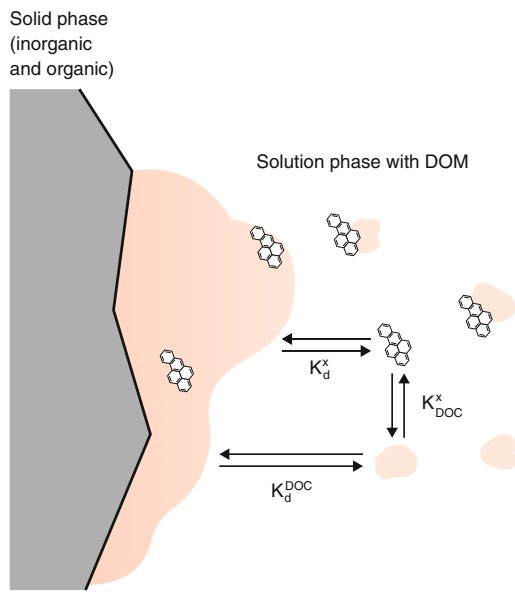


Fig. 10.13 Partitioning of hydrophobic organic compounds (x) in the three-phase system between solid phase, solution and DOM (after Marschner 1999)

10.3.4 Decomposition and Translocation

The input of active substances and pollutants in soils triggers decomposition and transformation processes. Chemical decomposition takes place in the aqueous phase of the soil through hydrolysis (e.g. parathion, triazine), through oxidation or reduction depending on the redox conditions, and through catalysis on soil components (Fe, Mn oxides, clay minerals, etc.). For example, in the presence of reduced iron compounds, nitroaromatics are effectively reduced to the corresponding amino compounds. However, decomposition and transformation processes in soils are primarily based on transformation processes by bacteria and fungi. Microbial biodegradation essentially determines the residence time and the effect of chemicals in the environment (Table 10.11). The type and extent of biodegradation are significantly influenced by the living conditions for the organisms and therefore by the environmental conditions such as temperature, moisture, pH, substrate supply, etc. Readily decomposable chemicals are generally considered to be unproblematic substances. For example, carcinogenic nitrosamines are particularly instable in soils and are therefore hardly relevant in ecotoxicological terms. Even with the addition of large amounts, strongly carcinogenic aflatoxins produced by fungi are completely decomposed by soil microorganisms within 2–3 months. In contrast, HCBs are not decomposed by microorganisms, or only to a very limited extent. There are only little data or estimations on the microbial decomposition of PCDD/Fs in the soil. Mean half-lives of 2–3 years up to >100 years are given for 2,3,7,8-TCDD under environmental conditions (Table 10.11). Field and laboratory experiments suggest that PCDD/Fs as well as PCBs are mainly removed from the soil through volatilization and/or photolysis.

Biological decomposition generally takes place much faster and more completely under **aerobic condition**s than under anaerobic conditions. For example, estrogens, phthalates and surfactants such as LAS and nonylphenol ethoxylate are rapidly decomposed under aerobic conditions. For PAHs with two and three benzene rings (naphthalene and anthracene) under favorable decomposition conditions, half-lives of <6 months were measured for the microbial decomposition. Bacteria from the *Pseudomonas* and *Flavobakterium* genera completely decomposed naphthalene and phenanthrene. The decomposition was metabolic, where the organisms used the pollutant as an energy source. More highly condensed PAHs, which have a greater binding strength and lower solubility than 2- and 3-ring PAHs, are mainly decomposed cometabolically, which means that the microorganisms only decompose the compound in the presence of a nutritive medium, without using it as an energy and carbon source.

In contrast, dechlorination reactions and nitrate reduction increase with decreasing oxygen content in the soil. For example, the decomposition of hexachlorocyclohexane (HCH) in the soil under aerobic conditions takes place so slowly that it takes several decades to decontaminate polluted soils. Under **anaerobic conditions**, in contrast, much faster decomposition is possible. The same is true for PCBs. The very slow microbial decomposition of various PCBs under aerobic conditions depends, among other things, on the number and position of the chlorine atoms in the molecule. Coupling of aerobic and anoxic environmental conditions can lead to an effective decomposition of PCB contaminations in soils. This is also true for nitroaromatics. For example, 2,4,6-trinitrotoluene (TNT) is reduced to the corresponding amino compounds under anoxic conditions, which are then further decomposed under aerobic conditions or incorporated into the soil organic matter.

The decomposition of harmful and active substances in soils often follows first order **kinetics**.

$$c_t = c_0 \cdot \exp(-k \cdot t).$$

Here, the concentration c_t after a period of time t depends on the initial concentration c_0, the rate coefficient k and the length of time. An initially rapid decomposition decreases exponentially

over the course of time; an asymptotic end concentration is reached. Especially through the aging process and therefore decreasing bioavailability of the active substances and pollutants, there are often residual contents in the soil that are practically not decomposable. This is shown in Fig. 10.14 for PAHs in contaminated sites, where the total concentration was only incompletely eliminated through more than 3 years of repeated measures within the scope of a biological remediation procedure. If the pollutants and active substances are present on heterogeneous sorbents and are retarded at different rates, two- or even multi-phased time responses are observed with different decomposition rates. In the four soils shown in Fig. 10.14, after an initial phase of rapid decomposition of ca. 3–17 weeks, there was a second phase with low to non-detectable reductions. Both phases can be described through separate first order kinetics.

In the ideal case, the active substances and pollutants are mineralized to CO_2 and water. In any case, at least interim **metabolites** are formed. These decomposition products are usually more strongly water soluble and more mobile than the initial compounds, but often also more reactive; they have a stronger tendency towards pH-dependent sorption.

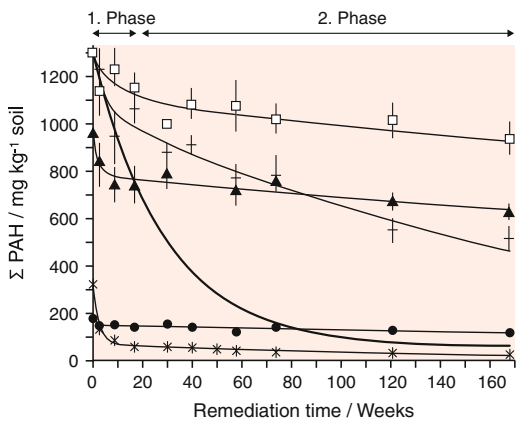


Fig. 10.14 Decrease in the PAH contents (sum of 15 PAH according to US-EPA) on five contaminated soils within the scope of open field pot trials on biological soil remediation (bold line is the theoretical course of the PAH reduction with first order kinetics); (after Thiele and Brümmer 1998, supplemented)

In contrast to decomposition, **microbial biosynthesis** of antibiotics in soils has also been observed and was also proven for methyltin and PAHs. The latter are mainly formed in reduced subsoil horizons (Fig. 10.15a). The resulting soil concentrations can reach several μg kg^{-1}. The significance of biosynthesis of phthalates by microorganisms and higher organisms requires further research.

If the active substances and pollutants are not rapidly eliminated in the soil, the **solubility behavior** in soils determines their **translocability** and possible accumulation in the groundwater as well as their availability for plants and possible accumulation in the food chain. In doing so, the solubility of chemicals in soils is affected both by their water solubility and by their adsorbability on the soil solids. Retarded chemicals are desorbed through repeated flow of seepage water through the soil, which can be detected in drainage pipes and in surface-near groundwaters of treated areas. Seepage water prediction aims to determine whether and to what extent the groundwater is contaminated by active substances and pollutants. It depends on the substrate properties of the subsoil, the depth to water table, the depth of the water seepage (and its influencing parameters), and the diffusion. In doing so, the diffusion provides the replenishment of the substances in the water-conducting pores. In addition to low-humus sandy soils, strongly swelling and shrinking soils as well as soils perforated by soil fauna are particularly susceptible to rapid translocation of substances into the subsoil due to **preferential** flow. They can be transported both in dissolved and particle-bound forms.

More strongly water-soluble active substances and pollutants are found more in the dissolved phase (e.g. pharmaceutical painkillers, BTEX, aliphatic hydrocarbons), and the less water-soluble are bound to particles (e.g. pharmaceutical antibiotics, PAHs; cf. Table 10.11). Translocation of strongly sorbing compounds such as chlorinated hydrocarbons, HCH and HCB with the seepage water only takes place to a very limited extent. Even though PAHs are strongly bound in the humus layers and A horizons, they

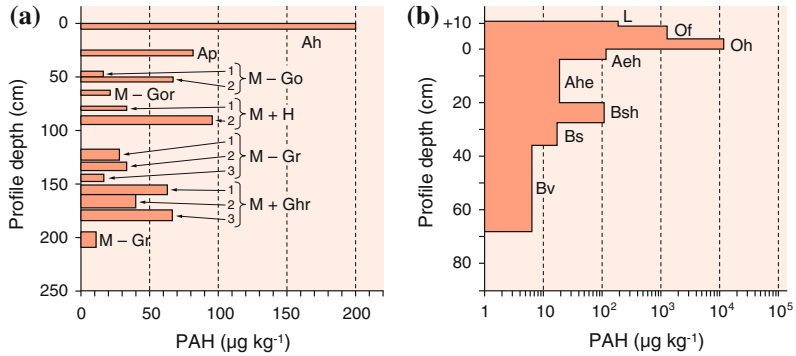


Fig. 10.15 Depth profiles of PAHs in soils contaminated by atmospheric immissions. **a** Sum of 15 PAHs according to the US-EPA (without acenaphthylene) in a gleyic Colluvisol with biosynthesis of the PAHs in reduced subsoil horizons (after Atanassova and Brümmer 2004). **b** Changes of PAH concentrations (sum of 20 PAHs according to the US-EPA plus triphenylene, benzo[j] fluoranthene, benzo[e]pyrene, perylene) with profile depth in a Podzol with a mor humus layer and DOM mediated transport (after Guggenberger et al. 1996); note that scale is logarithmic

have already been detected in subsoils. This indicates that they are translocated either in particle-bound form, through bioturbation or bound on DOM. In Podzols, PAHs accumulated in Bsh horizons (Fig. 10.15b). In low-humus sandy soils, in contrast, there can be considerable translocation of strongly sorbing compounds like PCBs into the subsoil. Here, the solubility of lower chlorinated biphenyls is greater than higher chlorinated biphenyls.

10.3.5 Uptake by and Effects on Organisms

Pollutants are defined as substances that, after their liberation, are capable of long-term contamination of environmental compartments such as soils, or cause damage to soils or organisms. In doing so, many pollutants have unintentional toxic effects on ecosystems and organisms. In contrast, active substances are specifically used to effectively control certain organisms. For example, pesticides are used to control animal and plant pests to protect crops, stored products and materials. Other active substances such as wetting agents, stalk reduction agents and defoliants are used for similar reasons. Pharmaceutical antibiotics are used to inhibit or eliminate specific microorganisms. However, active substances often also have toxic effects on non-target organisms and beneficials. The ecotoxic effects of different chemicals depends on their substance-specific toxicity, the emitted quantity of chemicals, and the resulting concentration in the soil as well as the persistence of the chemicals, which essentially determines the duration of the possible harmful effects. The substance-specific toxicity can vary considerably within a substance group and even between isomeric compounds. The persistence of a compound in the soil is determined by decomposition and fixation processes (Sect. 10.3.2). This leads to a reduction in the bioavailability, i.e. the fraction of a compound that can be absorbed by and affect organisms in its existing state. Methods for determining the bioavailable fraction of active substances and pollutants in soils instead of the total contents use e.g. extraction methods with gentle solvents or materials for solid phase extraction as an infinite sink.

Various compounds tend to accumulate in organisms. Particularly the bioaccumulation of lipophilic pollutants such as HOC is mainly attributed to the fact that considerable fractions of biomembranes consist of lipids. For example, microorganisms have a hydrophobic exterior; the fatty tissues of higher organisms are accumulation sites. For example, hexachlorobenzene (HCB) and PCBs accumulate in the fatty tissues

and serum of **organisms**, or also in breast milk, due to their highly lipophilic properties and the poor biological degradability. Earthworms are often used as bioindicators for monitoring the bioaccumulation of compounds in the soil fauna. The extent of absorption varies with the substance properties as well as between different species and organs. If there is an accumulation of persistent compounds in organisms, it can then lead to an accumulation in the higher trophic levels of the food chain. Chlorinated hydrocarbons such as DDT and PCB were detected in elevated concentrations in predatory animals and birds.

On the other hand, uptake by organisms, especially microorganisms, is in most cases the basis for metabolic decomposition of active substances and pollutants. In contrast, xenobiotic substances are often not or only partly metabolized by higher organisms, e.g. by conjugation increasing the water solubility, but are rather preferentially excreted. Following uptake by plants, many pesticides are metabolized e.g. through ring closure, hydrolysis, aliphatic hydroxylation or glucosidation. Several compounds are very strongly absorbed by plants and sometimes hyperaccumulated, so that phytoremediation is possible. For example, nitrotoluenes are effectively absorbed by plants, especially by the roots of alfalfa and bush beans. In addition, the rhizosphere is a soil zone with intense microbial colonization and activity, so that rapid biological decomposition can be expected here. This was already proven for trichloroethylene (TCE), various pesticides and surfactants as well as PAHs.

The desired decomposition is compared to concentration-dependent effects on the organisms, e.g. damage to parts of the organism and the metabolic functions, increased lethality, reduction of reproduction and of activity parameters or changes to the functional or structural diversity of populations. The toxicity can be described using the dose or actually measured concentration at which effects occur to a specific extent. Parameters are, among others, the lethal dose, e.g. LD_{10}, the application of which results in death of 10 % of the existing individuals, or the effective concentration, e.g. EC_{50}, at which the biotic activity is inhibited by 50 %.

Toxic effects on **microorganisms** in soils have been proven for numerous substances. Especially readily water-soluble and poorly sorbing substances with corresponding substance-specific toxicity, such as aliphatic and aromatic hydrocarbons (Table 10.11), affect microorganisms, whereby the effects vary depending on the substance and species. Effects of the aliphatic chlorinated hydrocarbons tri- and tetrachloroethene as well as dichloromethane were observed starting at 1–10 mg kg^{-1} of soil, and for HCH already at 0.18 mg kg^{-1}. Nonylphenol ethoxylate, LAS, and other surfactants inhibit microbial processes such as the dehydrogenase activity (ED_{50} <0.4 % active substance in the soil), Fe(III) reduction, and ammonium oxidation. Organotin compounds have numerous physiological effects and are used accordingly in various biocides. The effects increase in the following sequence: tetra- < tri- < di- < monoalkyltin, methyl- < butyl- < pentyl- < phenyltin. Long-term negative effects on microbial activities such as soil respiration, cellulose decomposition or nitrification were observed with different pesticides. In contrast, for many other, particularly newer pesticides, only short-term or no effects were observed on non-target organisms. The proof of safety is part of the testing procedure for the authorization of these products. The often biostatic effect of antibiotics on microbial activities can only be detected in long-term tests (>24 h), if the growth phase of the microorganisms is also recorded. This is particularly true for changes in the structural and functional diversity as well as the development of resistance. Resistance, as an acquired insensitivity towards an active substance, can also be triggered by pesticides.

The toxic effects of HOC are limited by their low solubility and strong fixation in soils. With increasing degree of chlorination, the efficacy of PCBs decreases because of their reduced mobility and availability. The comparatively readily water-soluble (5000 mg L^{-1}) congener PCB 1 inhibits the microbial reduction of Fe(III) in soils after the addition of 0.5–8 mg kg^{-1}. In contrast,

the more highly chlorinated congeners 28, 52, 153 as well as technical mixtures demonstrate weaker effects. In the same way, the toxic effects of other HOCs such as HCB, PCDD/F, and PAH are limited by their low solubility. On the contrary, PAH concentrations <100 mg kg^{-1} as well as low concentrations of TCDD lead to a stimulation (hormesis) of microbial activity. However, such stimulations as a deviation from the normal state are also to be assessed critically.

Representatives of the soil fauna are also affected by active substances and pollutants. The reproduction of collembolans (*Folsomia candida*) was significantly reduced by the addition of 0.32 mg kg^{-1} HCH. Earthworms, arachnids and collembolans are inhibited depending on the PAH content in the soil. For example, the addition of 1 mg benzo(a)pyrene kg^{-1} affected the cocoon deposition of earthworms. The LC_{50} of TNT for earthworms is of 143 mg kg^{-1}.

Especially active substances and pollutants that are mobile in soils are absorbed by plants. Aromatic hydrocarbons such as BTEXs and phenols as well as VCHs are significantly absorbed by plants (up to >40 % of the soil contents) and can sometimes lead to phytotoxic effects. The toxic effects of mineral oil contaminations with 0.1–1 % oil in the soil are mainly caused by the displacement of soil air and soil water by the oil components. On soils that are strongly contaminated with HCH, the cultivated plants absorb considerable amounts of HCH, in pot trials with ryegrass or oats up to 22 or 34 (in the oat straw) mg HCH kg^{-1} m_D. There are significant correlations between the HCH contents in soils and in plants; however, there are differences depending on the plant species. In the various plant parts, the HCH contents increase in the sequence grain < fruit < root < shoot.

Due to their low solubility and strong fixation in soils, the uptake of HOC in plants is usually low (<1 % of the total contents). These substances are generally only bound in or on the root surface and can, e.g. in root vegetables, be removed with the skin. Thus, plants only absorb very small amounts of HCB, PCB and PCDD/F from the soil (usually <1 μg kg^{-1}). However, the uptake varies among different plant species. Zucchini exhibited a significantly higher uptake of PCDD/F compared to other crop species. The availability of PAHs for plants is largely dependent on the molecule size. PAHs with 2 and 3 benzene rings can apparently sometimes be absorbed by roots and transported up into the shoots. In contrast, more highly condensed PAHs, due to their exceptionally low solubility and greater molecule size, can hardly be absorbed, but are rather absorbed only to a small extent in roots and on root surfaces. The PAH contents of aerial plant parts do not exhibit a relationship with the PAH contents of soils; they are predominantly immission-related. PAHs can penetrate into the shoots through the gas phase or be deposited bound to particles. This is suggested by the increasing PAH contents with increasing leaf surface area of the plants, and the similarity of the PAH profile in the dust and in plants. The same is true for other HOCs such as HCB and PCDD/F as well as phthalates.

In higher organisms as well as in human beings, chlorinated compounds such as HCB, PCB and PCDD/F etc. lead to damage of the skin, the nervous system and the liver. Many compounds such as PAHs and PCDD/Fs are carcinogenic, mutagenic and teratogenic. Organic pollutants are increasingly also attributed with hormonal effects. For example, nonylphenol, as a base material for nonylphenol ethoxylate surfactants, flame retardants (polybrominated diphenyl ether, tetrabromobisphenol A), phthalates, PAHs, and PCBs, have estrogenic effects (feminization) in higher organisms. In addition, natural (17 β-estradiol) and synthetic hormones (17 α-ethinyl estradiol) enter the environment e.g. through sewage sludge and wastewater.

10.4 Farmyard and Secondary Raw Material Fertilizers, Dredged Material

Farmyard fertilizers are animal excrements such as liquid manure, dung and poultry manure as well as harvest residues (e.g. straw). They are used in crop production as a fertilizer and for increasing the humus content. With respect to soil protection, special attention must be paid to fertilizers incurring from animal production. On the one hand, they can contain heavy metals and organic pollutants (veterinary drug residues, see also Sect. 10.3), and on the other, improper application can lead to groundwater contamination (see below).

Secondary raw material fertilizers include **sewage sludges** (**biosolids**) and **biowaste**. Sewage sludge is produced in communal sewage treatment **plants** as liquid sludge with a mean solids content of 5 %. Sewage sludges are used in agriculture, agricultural recovery/recycling or for composting. The portion of sewage sludges that is not used is thermally treated.

Biowastes are wastes of plant and animal origins that are recycled through decomposition by microorganisms, soil fauna or enzymes. Depending on the type of treatment, a distinction is made between: **composts** (aerobically treated) , fermentation residues (anaerobically treated), and **other sanitized biowaste**. Biowaste must be collected and treated separately from the remaining household wastes. **Municipal composts**, produced from the organic fraction of the total household waste, are no longer authorized in Germany for use on agricultural or horticultural fields since the implementation of the Biowaste Ordinance. The quantity of **biowaste** has been constantly increasing. The majority is used in agriculture (36 %), landscaping (21 %) and in private gardens (14 %).

Dredged material incurs in the context of watercourse maintenance and water engineering measures. It can consist of sediments or subhydric soils from the waterbed, soils or their parent material in the immediate surroundings of the waterbed, and topsoil material in the bank and flooding zone of the watercourse. The contamination of the dredged material varies greatly. It increases in flowing water when approaching the input sources. The pollutants mainly accumulate in the fine-grained sediments that are deposited in areas with slow currents. Recycling on land is generally only possible after previous treatment (remediation).

The main components of **farmyard and secondary raw material fertilizers** are organic matter as well as nitrogen, potassium, calcium, magnesium and phosphorus (Table 10.12). Thereby they promote microbial activity, soil fertility, mobilization of nutrients and decomposition of organic pollutants. They are therefore true soil conditioners . Furthermore, they can partly replace mineral fertilizers.

The nutrient effect of liquid farmyard fertilizers, especially **liquid manure**, is mainly due to its nitrogen content. 50–70 % of the total nitrogen is present as unstable ammonium N, which can escape to 100 % in gaseous form as NH_3 under hot and humid weather conditions. Spreading when it rains and/or drilling are effective options to prevent ammonia losses.

Table 10.12 Nutrient and organic matter contents in farmyard and secondary raw material fertilizers in (g kg^{-1} m_D)

Fertilizer	Organic matter	N	P	K	Mg	Ca
Liquid cattle manure	750	50	10	66	6	3
Liquid swine manure	700	105	25	69	10	7
Poultry manure	700	55	16	30	6	26
Cattle dung	680	25	8.3	32	4	17
Swine dung	680	35	22	37	5	–
Sewage sludge	530	50	25	4	5	50
Compost	330	12	3.5	12	8	40

After 1–3 days, the majority of the ammonium is transformed into nitrate. After 2–6 weeks, large amounts of the organically bound nitrogen are also mineralized. Because nitrate is not bound in the soil, liquid manuring can lead to translocation into the groundwater. For this reason, liquid farmyard fertilizers must be applied shortly before or at the peak demand times in early spring. Legal regulations on this subject can be found in the Fertilizer Ordinance. Ammonia/ammonium inputs from agriculture contribute significantly to the acid and nitrogen contamination of forest ecosystems (Sect. 10.2.1), but can also considerably increase tree growth.

The fertilizer effects of phosphorus, potassium and magnesium contained in liquid manure largely correspond to those of barn manure. 60 % of the total content is available in the spreading year, and 40 % in the subsequent year. Because of the high fraction of readily convertible organic compounds with a narrow C/N ratio, the humus effect of liquid manure is limited.

Average nutrient contents of **dung** and **poultry manure** are listed in Table 10.12. The nutrient effect is determined by the binding/chemical form of the nutrients, the spreading date, weather conditions and soil texture. Under favorable conditions (immediate incorporation, less than 30 days between the spreading and seeding of the subsequent crop etc.), the plants can use up to 40 % of the **nitrogen**. For the **phosphorus** effect, it is assumed that 60 % is used in the year of application, and 40 % in the following year. The fertilizer effect of **potassium** and **magnesium** strongly depends on the soil texture. The mean efficacy ranges between 60 and 80 % on sandy soils, 80 % on loamy sandy soils, and 100 % on all other soils. In contrast to liquid manure, barn manure has a positive effect on the humus balance . In crop rotations with low proportions of root crops, 8–10 t ha^{-1} a^{-1} are sufficient to prevent humus losses.

Average **heavy metal contents** of farmyard fertilizers are generally in the range of precautionary and background levels (Table 10.3). Exceptions to this are liquid and solid swine manure, which often have significantly elevated copper and zinc concentrations (Table 10.13). Both elements are added to feed as a nutrient and to achieve pharmacological special effects (farrow growth). From a biological point of view, the practice of excessive dosage is considered as a misuse of copper and zinc. Both metals are not resorbed in the animals' bodies and are excreted.

In addition to heavy metals, farmyard fertilizers can also lead to inputs of pharmaceuticals from livestock in soils. This mainly involves antibiotics (tetracycline, sulfonamide) that are administered to the animals preventatively and to treat disease. Tetracycline and chlortetracycline were detected especially soils treated with liquid swine manure. The concentrations generally lie below 10–20 μg kg^{-1}, in some cases, contents of more than 300 μg kg^{-1} were observed. Current research is investigating the extent to which these concentrations have harmful effects on soil functions, especially on microorganisms and their transformation processes.

Sewage sludge, sewage sludge composts and composts can also represent valuable soil conditioners. Because of their high content of

Table 10.13 Heavy metal contents in farmyard and secondary raw material soil fertilizers in (mg kg^{-1} m_D) (after Bannick et al. 2001)

Fertilizer	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Cattle liquid manure	0.28	7.3	44.5	0.06	5.9	7.7	270
Swine liquid manure	0.40	9.4	309	0.02	10.3	6.2	858
Poultry manure	0.25	4.4	52.6	0.02	8.1	7.2	336
Cattle dung	0.29	12.9	39.0	0.03	5.2	5.8	190
Swine dung	0.33	10.3	450	0.04	9.5	5.1	1068
Sewage sludge	1.4	46	274	1	23	63	809
Compost	0.51	25.6	49.6	0.16	15.9	52.7	195

organic matter and other structure-improving constituents, they are also used in vine growing to reduce erosion on sloped land. An impairment of the fruit and must quality due higher heavy metal contents could not be detected. Furthermore, sewage sludges and other biowastes are sometimes used with success when establishing green areas.

The **fertilizer effect** of sewage sludges in terms of nitrogen varies greatly depending on the type of sludge. With liquid sludges, about 90 % of the existing NH_4 nitrogen and 25 % of the organically bound nitrogen is considered to be available. In contrast, sludges that have been landfilled for longer periods of time or drained sludges only have a low N effect. On average, with the legally authorized maximum amount of 5 t of sewage sludge m_D ha^{-1}, ca. 250 kg N ha^{-1} can be applied in 3 years, which mainly increase the soils' content of organically bound nitrogen.

Especially in sewage sludges from sewage treatment plants with chemical treatment/cleaning stages, the **phosphorus** content can be very high due to the precipitation of phosphates (up to 7 % P). The use of Al or Fe salts or $Ca(OH)_2$ as a precipitating agent simultaneously leads to a considerable content of Fe and Al oxides or carbonate/lime (up to >60 %) in the sludges. The addition of burnt lime to transform the sludge into a drainable form that is suitable for storage causes high carbonate/lime contents. The composition of sewage sludges can therefore vary greatly, so that precise analysis of the primary as well as the secondary constituents must be performed before application.

The **availability of the phosphates** is sometimes considered to be close to that of mineral P fertilizers, sometimes also considered to be somewhat less favorable. On oxide-rich tropical soils (Ferralsols), the effect of sewage sludge phosphates can also exceed that of mineral P fertilizer.

Only very small fractions of available **potassium** are contained in sewage sludges and municipal composts, so that the spreading of sewage sludges must be followed by K compensation fertilization. The content of available **magnesium** is also sometimes too low. The spreading of lime-treated sewage sludges leads to a high addition of calcium to the soil and can result in a considerable rise in pH.

The soil contents of available **micronutrient elements** (Zn, Cu, B, Mo etc.) are increased through sewage sludge and compost applications, while in contrast, the Mn uptake by plants can sometimes be reduced due to a rise in pH.

The application of sewage sludges and municipal composts is limited by their contents of inorganic and organic pollutants. Sewage sludges with ca. 2.5–7.5 % solids that are used as liquid sludge can contain **pathogenic bacteria**, **viruses** and worm eggs. For this reason, the application of liquid sludges must be performed using a flawless disease control method. The soil flora and fauna generally neutralize pathogens when the sludge is incorporated into the soil (**sanitizing effect** of soils), however, this can sometimes take a long time for resistant pathogens. The application of liquid sludge on vegetable, fruit, grassland and fodder fields is therefore forbidden, as well as in forests. Hygienic problems can be prevented if the sewage sludge is composted or pasteurized before delivery (heating to 65 °C or irradiation with γ rays/radiation). Biowaste may only be spread following prior treatment, which ensures that all pathogens have been eliminated.

To prevent elevated heavy metal contents in plants and ecologically harmful accumulations in soils due to the spreading of sewage sludge, the German Sewage Sludge Ordinance and the EU Council Directive on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture (86/278/EEG) have defined threshold values for the heavy metal contents of the sludges to be spread and also for the authorized contamination of soils. The heavy metal contents listed in Table 10.13 are well below the threshold values for sludges.

Furthermore, sewage sludges can also contain organic pollutants . In 1996, sewage sludges used in agriculture contained on average 17 ng TE kg^{-1} m_D of dioxins and furans, 0.156 mg of PCB kg^{-1} m_D (sum of the congeners 28, 52, 101, 138, 153, 180) and 196 mg kg^{-1} m_D of organic halogen compounds (measured as AOX).

The Sewage Sludge Ordinance requires that sewage sludges be analyzed before they are spread. At the same time, this Ordinance limits the spread quantity of sewage sludge to 5 t m_D ha^{-1} in 3 years or 1.67 t ha^{-1} a^{-1}. Furthermore, the spreading of sewage sludges is only permitted on soils where the **heavy metal contents** are below the soil threshold values defined in the Sewage Sludge Ordinance. For the particularly mobile metals zinc and cadmium, lower threshold values were defined for soils with a sandy texture and pH values between 5 and 6. The sewage sludge can only be spread on soils with pH values >5, because some heavy metals, especially Cd, Zn and Ni, have high mobility and availability in strongly acidic soils (Sect. 10.2.4). For this reason, forest soils, which usually have pH($CaCl_2$) values between 2.8 and 4.5 in Central Europe, also cannot be considered for the application of sewage sludges.

Composts often contain less organic matter, N, P, and heavy metals (Table. 10.12 and 10.13) than sewage sludges. In recent years, separate waste collection has resulted in a significant decrease in the pollutant content of composts. In Germany, their use in agriculture and forestry as well as on horticultural soils is regulated by the Biowaste Ordinance . The soil threshold values in the Biowaste Ordinance are identical to the precautionary values of the German Federal Soil Protection and Contaminated Sites Ordinance (Table 10.3). The soil threshold values in the Sewage Sludge Ordinance only concur numerically with the precautionary values for the clay soil texture. A comparison of the Sewage Sludge Ordinance with the Federal Soil Protection and Contaminated Sites Ordinance is required to achieve precautionary soil conservation.

Even when complying with the currently authorized load rates for sewage sludges and biowaste, the application of farmyard and secondary raw material fertilizers can result in undesirable substance accumulations.

This involves mainly the metals copper and zinc. Under the assumption of average load rates, their precautionary values are filled in sandy soils within 42–120 years of regular sewage sludge applications. The same is true also for organic pollutants. Contents of up to 15 mg kg^{-1} m_D were measured in sewage sludges. Based on this value, this results in an annual increase in the soil contents of 6.4 μg kg^{-1}. In this case, the precautionary values would be reached in about 47 years. There are two possible courses of action for counteractive measures:

1. The heavy metal contents in the respective fertilizer correspond to the contents in the soil at the application site (same to same).
2. The added load of heavy metals per unit of area and time is equal to the tolerable losses (uptake by plants, leaching to the groundwater). The first course of action is only allowed if the quality of the added material corresponds to the local requirements, i.e., only materials that are considered to be similar to soil (e.g. composts). For all other materials, which only contain low mineral fractions in their dry mass (liquid manure, sewage sludges), the first course of action would lead to very high pollutant contents in terms of the fraction remaining in the soil on the long term. In this case, only the 2nd option input = losses can be used.

10.5 Toxicological/ Ecotoxicological Evaluation of Chemical Soil Pollution

Laboratory experiments with plants, soil organisms and microbial processes are generally used to assess whether a substance has toxic effects. To do so, increasing doses of the substance to be tested are added to a control soil, and its effect on the organism itself or on its transforming capacity (in microorganisms) is measured. With acute tests, the endpoint of the investigation is mortality (occasionally the behavior), and with chronic test methods, the reproduction or the biomass production. The test results are then used to derive the dose-effect relationships (Fig. 10.16). They enable the attribution of

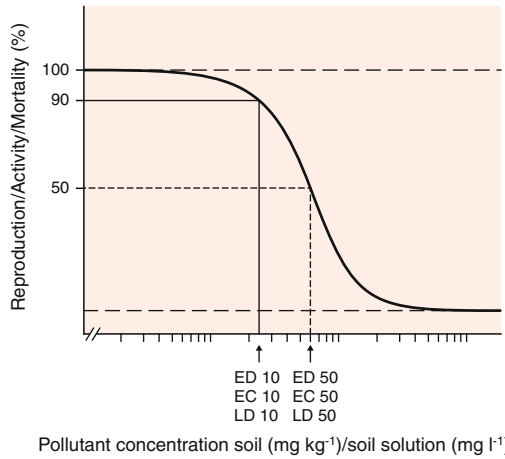


Fig. 10.16 Dose–response curve to record the effect of chemicals on plants, soil organisms and microbial activity

pollutant concentrations to defined effects within the investigated concentration range (e.g. 10, 50 %). The corresponding pollutant additions are called 'effective doses' (ED_{10}, ED_{50}), 'effective concentrations' (EC_{10}, EC_{50}) or with acute toxicity, 'lethal doses' (LD_{10}, LD_{50}) or 'lethal concentrations' (LC_{10}, LC_{50}). The terms 'concentration' and 'dose' are often used synonymously by ecotoxicologists. It would be more precise to use the term 'effective concentration' only when the pollutant effect is based on the substance concentration in the soil solution or in the soil mass. The dose is defined as the quantity of a substance that must be added to achieve a specific effect.

Altogether, pollutant loads in soils can affect soil organisms, plants, animals and human beings through various paths (Fig. 10.17).

Depending on the properties of the soil and pollutant as well as of the respective site, a substance transfer can occur from the soil (1) into the food chain (incl. soil organisms and plants), (2) through the groundwater and surface waters into drinking water, and (3) into the atmosphere. Furthermore, (4) animals (mainly grazing cattle) and human beings can also consume soil material directly. This path can be the most important for the assessment of soil contamination particularly in the case of playing children (who often orally consume 0.5 g of soil material per day at the age of 1–3 years) in industrial and urban regions. Moreover, (5) pollution of uncontaminated soils through relocated or transported polluted soil material can also be significant, which can in turn trigger transfer processes according to (1)–(4) at the new deposition site (Fig. 10.17).

To protect the **soil functions**, the implementation of the German Federal Soil Protection Act (**BBodSchG**, Sect. 11.7.4) in 1998 and the **German Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV)** in 1999 defined standard evaluation criteria for soil contamination for the first time in Germany (Sect. 10.7.4). A distinction is made between three risk areas, which are delimited by **precautionary, trigger** and **action values** (Fig. 10.18). **Precautionary values** mark the boundary between the area of residual risks and the beginning of undesirable risks. They were defined for inorganic and organic substance groups, regardless of the land use, as the extractable contents with aqua regia (heavy metals) or as total contents (organic pollutants), to characterize the long-term effects of a substance under the influence of potential mobilizable fractions.

Their derivation is based on data on the accumulation and effects of pollutants in soils.

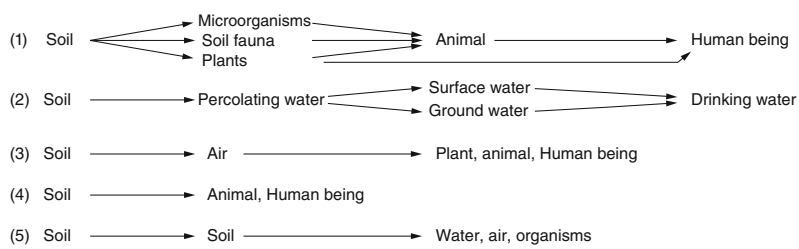


Fig. 10.17 Paths of pollutants in soils to soil organisms, plants, animals and human beings

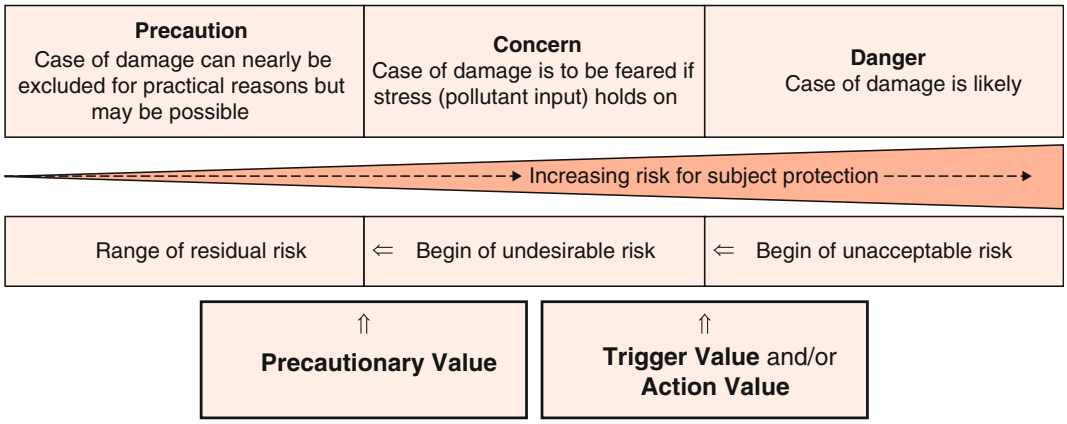


Fig. 10.18 Classification of soil-specific risk areas and soil values (modified after Bachmann and Thoenes 2000)

First of all, the ecotoxicological effects are observed. It is assumed that the precautionary protection of the soil is ensured when the ecotoxicological effect thresholds have not been exceeded. Where possible, additional potential effects of soil contaminants on plants and the groundwater are evaluated. Regarding human health, the precautionary values should have a sufficient difference from the trigger and action values (Fig. 10.18) for the soil–human path.

Differentiations for heavy metals are made according to the soil texture, and for organic pollutants according to the soil humus content. This takes account both of the existing dependencies of these parameters on the background levels and their availability. The **background** content of a soil consists of the **geogenic basic** content (=mineral contents from the parent rock and the natural environment (e.g. saltwater in mudflat soils)) and the ubiquitous inputs. Soils with natural and large-scale human settlement-related elevated background levels are considered to be harmless, as long as the liberation of the contaminants or additional inputs do not lead to adverse effects on the soil functions.

If the precautionary values are exceeded, damage can be expected with the continuation of further effects/actions. To restrict the heavy metal inputs when the precautionary values have been exceeded, additional annual load rates were defined for all the input paths. The permissible inputs therefore result from the sum of the inputs from the atmosphere and watercourses as well as the direct inputs from fertilizers, sewage sludges and the utilization/recycling of wastes. **Trigger and action** values mark the boundary between the precautionary range and the range of hazard prevention (Fig. 10.18). When these values are exceeded, the occurrence of damage is probable. **Trigger values** are values which, when exceeded taking account of the land use, require a case-by-case examination and an assessment to determine if there has been soil degradation or contamination (BBodSchG §8 Para. 1 No. 1). **Action values** are values for effects or contaminations for which, when they are exceeded, soil degradation or contamination can be expected and action is required (BBodSchG §8 Para. 1 No. 2).Trigger and action values were defined in the Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV) for the pathways **soil–human being**, **soil–food plants** and **soil–groundwater** paths. Trigger values for the pathway soil–soil organisms have not been issued. The soil organisms are protected by the precautionary values.

10.5.1 Values for the Soil—Human Path

The derivation of soil values (trigger values) requires basic toxicological data as well as data and knowledge on the direct exposure of human

beings to soil contaminants (e.g. absorption rates). They are based on toxicological substance data, which are used to determined hazard-related doses for each substance, as well as assumptions and insights on the quantitation of the exposure. The scientific basis for a hazard relationship is a hazard-related body dose, which lies between the $NOAEL_e$ (=no observed adverse effect level for particularly sensitive people) and the $LOAEL_E$ (=lowest observed adverse level for healthy adult population). Absorption rates are calculated for the most unfavorable case with differentiation of the land use and the oral and inhalation absorption path.

Tolerable resorbed doses (TRD) are used for the derivation of hazard-related doses. They are defined as "tolerable daily resorbed body dose of a harmful substance which, in the light of the present state of our knowledge and as a result of examining the individual substances, is either not expected to have a harmful effect on a person's health or contains only a slight risk of making the person ill". Combined effects are not taken into account. TRD values are given in milligrams per kilogram of body weight and day (mg kg^{-1} day^{-1}). Ideally, TRD values are based on knowledge of the effects on the most sensitive members of the population. If human data is not available or insufficient, extrapolations are made using data from animal experiments or insufficient human data and referring to safety factors. For inhalative contamination, media-related values are given, e.g. as atmospheric concentration in mg m^{-3}. These values are called reference concentrations (RC).

There are no TDR values for **carcinogenic substances**, because as a matter of principle, one cannot speak of a tolerable substance dose. Here, a resorbable body dose is assumed, corresponding to an additional calculated risk of developing cancer based on a single substance of 1×10^{-5} due to lifelong exposure to the harmful substance.

The hazard-related dose is calculated from TDR values for long-term oral and inhalative contamination, taking account of the assumed resorption and using safety factors.

The background level (especially through food) must be considered for the calculation of the no longer acceptable contamination through the soil path. In doing so, it is generally assumed that 80 % of the body dose is available through the background level, and 20 % through the soil path. Trigger and action values are calculated based on the use for the following scenarios:

- Playgrounds = Recreation areas for children, are accessible to the public
- Residential areas = Designated living areas including the yards and gardens
- Parks and recreation centers = Areas for social, health and sport purposes, especially green areas and unpaved areas that are regularly accessible
- Industrial and commercial areas = Unpaved areas of work and production facilities that are only used during working hours

The following exposure paths are considered:

- Oral soil uptake (playgrounds, residential areas, parks and recreation centers)
- Inhalative soil uptake (all uses)
- Dermal soil uptake (playgrounds, residential areas, parks and recreation centers)
- Inhalation of contaminated ambient air (penetration of volatile harmful substances from the soil into buildings; residential areas, industrial and commercial areas).

Calculation formulas for trigger values were compiled for oral uptake, dermal soil contact and transdermal uptake as well as use-specific for inhalative uptake under the assumption of specific exposure factors. The calculation formula for oral soil uptake for non-carcinogenic effects of substances on playgrounds is shown as an example:

Exposure factors: body weight 10 kg, daily soil uptake 0.5 g day^{-1}, exposure time 240 days.

In addition to the non-carcinogenic effect, the values for carcinogenic effects (if relevant) are calculated. Finally, the calculated values are subject to a plausibility check. Trigger values for the soil–human path are based on the fractions extractable with aqua regia (metals) and the total contents (organic substances). Action values

$$\text{Trigger value}(\text{mg/kg}) = \frac{\text{Risk} - \text{related body dose}}{\text{Soil uptake rate}} = \frac{\text{Ingested dose}\left(\text{risk factor } \text{F}_{(\text{risk})} - \text{standard background value}\right)}{\text{Soil uptake rate}} = \frac{\text{Ingested dose } (\text{ng/kg} * \text{d}) * (F_{\text{risk}} - 0.8)}{33\,\frac{\text{mg}}{\text{kg}_* \text{d}}}$$

should be based on the pollutant fractions in the soil that are available for human resorption. Standardized methods for the resorption availability have only been drafted until now. For this reason, only trigger values have been defined. Dioxins and furans represent an exception. For these substance groups, action values were issued based on the total contents due to the great complexity involved with testing.

10.5.2 Values for the Soil—Crop Plant Path

Soil values for the soil-crop plant path aim to recognize harmful soil changes in terms of the quality of plant food and feed, plant health and the health of grazing cattle (grassland). The derivation of trigger and action values for arable land, fruit and vegetable gardens and grassland in terms of plant quality can be based on food and feed guideline values. The maximum permissible plant contents are compared to the soil contents. In Germany, such data pairs were collected for heavy metals in the TRANSFER database. About 300,000 data pairs are available for the heavy metal contents of soils (aqua regia or ammonium nitrate extraction) and plants. Data from field, grassland and horticultural soils with different properties and heavy metal concentrations were evaluated. The dependencies of the heavy metal concentrations in the plants on the heavy metal concentrations in the soil were proven using statistical investigations. For a given maximum permissible plant concentration, the soil concentrations in aqua regia or NH_4NO_3 extract at which 20, 50 or 80 % of the plants exceed the permissible concentration were derived (Fig. 10.19). For grassland use, because of the inevitable contamination of the feed with soil particles during harvest and the direct soil uptake by grazing cattle, a feed contamination of 3 % with soil particles containing pollutants was taken into account for the calculations. The data analysis demonstrated that the soil/grassland plant contaminant transfer could be better described with aqua regia extraction than with ammonium nitrate extraction. The total heavy metal content in the soil, determined using the aqua regia extractable fraction, is decisive for the soil/plant heavy metal transfer through the pollution path.

Values for arable land with respect to the growth restrictions for crops can be derived from investigations performed using a sufficient number of cases with growth restrictions under field conditions. This is especially true for primary phytotoxic substances, which cause growth and yield restrictions in crops long before concentrations are detected in the plants that would exclude them from being put on the market. This includes, amongst others, arsenic, copper, nickel and zinc. The prerequisite for negative effects of soil pollutants on the health and yields of crops is their systemic absorption by plants. Only then are effects on the plant metabolism possible. For this reason, heavy metal values should be based on the plant-available fraction in the soil. The

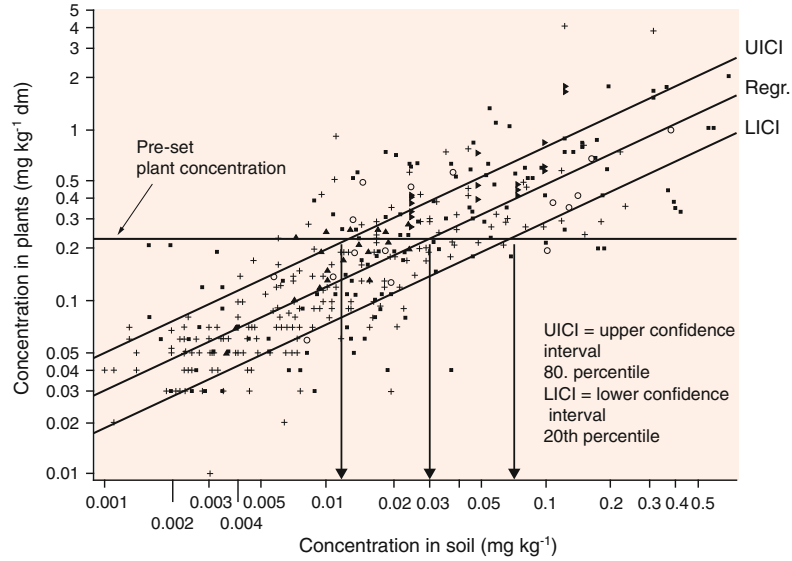


Fig. 10.19 Schematic representation of the evaluation through regression analysis of the heavy metal transfer soil–plant (log. data) and derivation of a soil concentration from a given plant concentration (after LABO-AD-HOC-AG 1998)

ammonium nitrate extraction method is suitable for this purpose.

10.5.3 Soil Values for the Soil—Groundwater Path

Contaminated groundwater is a disruption of public safety, because the groundwater can enter surface waters through springs or can be directly used as drinking water through wells. Hazard control measures are therefore required to prevent the occurrence of groundwater contamination. Groundwater is considered to be contaminated when it exhibits pollutant concentrations that are considerably above the natural concentrations. The thresholds used here are the minimis thresholds derived from the water law criteria. In doing so, it does not matter whether the groundwater is intended for a specific use. It also does not matter if the concentrations in the groundwater are reduced along its path through decomposition or dilution. If it can be assumed that seepage water with concentrations above the minimis threshold will form a new groundwater surface, there is a risk for the groundwater.

There are two basic options for deriving the concentration values for the minimis threshold: orientation on regional background levels or effect-related derivation. In view of the diversity of groundwater landscapes, the use of background levels is unsuitable. For this reason, mainly human- and ecotoxicological criteria are used in Germany. The threshold values from the Drinking Water Ordinance or the quality standards of the EC Directive on the quality of water for human consumption are also often used as a minimis threshold.

Based on soil protection legislation, the soil–soil (seepage) water–groundwater path of action is evaluated through pollutant concentrations in the seepage water in terms of the risk assessment for groundwater. The risk assessment is performed at the transition from the unsaturated to the saturated soil zone (groundwater surface). The seepage water concentration at the assessment site (seepage water prediction) is currently still estimated using conclusions drawn from investigations on the groundwater runoff, direct seepage water analyses or in the laboratory using soil saturation extract analyses and elution methods (inorganic substances) as well as column experiments (organic pollutants), and using substance transport models where required. The laboratory methods still have to be improved and validated. Retrograde calculations and conclusions on the soil seepage water based on

measurements in surface-near groundwater are currently not methodically substantiated and also require further development.

10.5.4 Biological Evaluation of Soil and Soil Material

Contaminated soils are generally polluted with a mixture of harmful substances. Combined effects of harmful substances have not been investigated much until now, and are not taken into account in the definition of trigger and action values. Considering the multitude of harmful substances, it is impossible to derive values for all conceivable combinations. It is therefore recommended, in addition to the chemical analysis, to perform biotests to evaluate the ecotoxicological potential of soils and soil materials (excavated soil material, treated soils), because these tests evaluate the total toxicity potential of the respective mixture inclusively. The test methods are suitable for the following applications:

- Evaluation of the mobilizability and bioavailability of harmful substances and mixtures thereof.
- Supplementary risk assessment for the evaluation of contaminated soils (need for remediation).
- Process controls during remediation measures.
- Decision guidance for the reclamation or recycling of soil and soil material.
- Monitoring of the natural decomposition of harmful substances in soils (natural attenuation).

The methods described in the following are not suitable or only to a limited extent in the case of highly volatile substances, for the testing of uncontaminated soils, and for the recording of contaminant accumulation in biological systems.

Biological testing methods supplement the chemical methods in evaluating the retention and habitat function of soils or after the incorporation of soil material. The **retention function** refers to the capacity of soils to bind contaminants so strongly that they are not translocated into the groundwater with seepage water or enter the food chain through uptake by soil organisms and plants. The habitat function refers to the capacity to serve as a habitat for soil organisms and plants. Investigations on the habitat function are only required for the assessment of topsoils or soil materials that are used as topsoils.

The first step for the assessment of the **retention function** involves taking a soil water extract. The soil/water ratio should be as close to 1: 2 as possible, because this is closest to a soil saturation extract. Alternatively, with strongly binding and humus-rich soils, a soil/solution ratio of 1: 10 can be used. Solids >0.45 μm in the soil extracts have to be separated through ultrafiltration and centrifugation before further use. Ecotoxicological and genotoxicological analyses are performed on the extracts to test the retention function. The following methods have proven their worth in numerous investigations with contaminated soils:

Ecotoxicological methods:

- **Luminescence inhibition test** with ***Vibrio fischeri*** (ISO 11348) or
- **Cell proliferation inhibition test** with ***Pseudokirchneriella subcapitata*** (ISO 8692).

Genotoxicological methods:

- **Umu test** with ***Salmonella choleraesius* ssp. *chol***. (ISO 13829)
  With these testing methods, the soil extracts are diluted repeatedly until no more effects can be detected (e.g. 20 % inhibition of luminescence or induction rate >1.5 in the umu test). The results are given as G or LID values. The G/LID value is the smallest reciprocal dilution of the soil extract at which no effects were observed under the experimental conditions. A G/LID value > 8 means that the soil extract is ineffective at a dilution of 1:8.

Genotoxicological analyses are performed on soil extracts and 15-fold concentrated soil extracts.

Based on numerous investigations, the following hazard thresholds were defined for the discharge/output of ecotoxic and genotoxic pollutants through the water path:

Vibrio fischeri	Inhibition of light emission	LID > 8
Pseudokirchneriella subcpitata	Growth inhibition	$G_A > 4$
Salmonella choleraesius ssp. *chol.*	Induction rate of umuC genes	$G_{EU} \geq 3$
	Induction rate of umuC genes in concentrated water extract	$G_{EU} \geq 3$

The **habitat function** of soils and soil materials is analyzed with microbiological testing methods and plant, collembola and earthworm tests (Table 10.14). The selection of these species was based on pragmatic aspects. The focus here was put on different combinations of trophic levels, colonized pores/habitats and the exposure path. **Soil microorganisms** colonize the water film of medium-sized and coarse pores. They are exposed to harmful substances through the water path. Suggested test methods are soil respiration curves and the potential ammonium oxidation. These include the majority of aerobic and facultative anaerobic microflora (microbial respiration). Furthermore, they provide information on specialists through the potential ammonium oxidation as part of nitrification.

Collembola belong to the mesofauna and live in air-filled pores in the soil, and their skin and gastrointestinal tract are being discussed as a primary exposure path for harmful substances. The significance of collembolas for the ecosystem is mainly attributed to their microphytophagous function. By grazing on bacterial lawns and fungal hyphae, they cause bacteria and fungus populations to remain in a phase of maximum reproductive activity and ensure a high decomposition capacity in these groups (e.g. with the decomposition of organic matter).

Earthworms belong to the macrofauna and colonize the soil body. With these organisms, the discussed primary exposure paths are uptake through the skin (pollutant uptake from the water phase) as well as food (uptake of particle-bound pollutants). Investigations on the reproductive capacity are recommended for the assessment of pollutant effects on soil animals (Table 10.14).

After microorganisms, **plant roots** represent the greatest biological surface in soils. Their contact area to the soil particles is increased through the formation of root hairs as well as through colonization with mycorrhiza (VA mycorrhiza in crop plants, also ectomycorrhiza in ligneous plants). To represent the species found in nature, plant tests usually use crop plants due to their good availability and easy handling, particularly with field mustard (*Brassica rapa*) representing the dicotyledonous and oats (*Avena sativa*) the monocotyledonous plants. The use of two species can be considered to be the minimum.

With the exception of soil respiration curves, the assessment of **habitat functions** requires the use of control soils (e.g. LUFA standard soil 2.2, artificial soil according to DIN ISO 11268-1.2).

Table 10.14 provides information on the toxicity criteria for the individual testing methods. The toxicity thresholds were derived based on numerous investigations involving contaminated and uncontaminated soils and soil materials. For the assessment of the **retention function** of soils and soil materials, the risk of damage is considered to be high if a testing method shows effects. For the assessment of the **habitat function**, damage is highly probably if two testing methods show effects. If only one test shows an effect, a critical compilation must be made with all the results taking account of the chemical/physical properties of the soil/soil material.

10.6 Remediation of Chemical Contaminations

Persistent contaminants cause long-term damage to the soil functions. Protection and decontamination methods can be used for hazard prevention. Security/Safeguard measures prevent the

Table 10.14 Procedures for the assessment of the habitat function and toxicity criteria (after Dechema 2001)

Organism	Trophic level	Habitat/exposure	Test method/ parameter	Toxicity criterion
Microorganisms	Decomposer	Water film/soil water	Soil respiration curves	Respiratory activation quotient
			ISO 17155	Q_R (R_B/R_S) ≫ 0.3
			basal respiration (R_B), substrate-induced respiration (R_S)	Time to peak maximum >50 h
			Potential ammonium oxidation	Soils and soil materials, the activity of which in the mixture with a control soil deviates by more than 10 % from the mean value of the activities of both soils, are to be classified as toxic
			ISO 15685	$Mg + SD_{Mg} < 0.9 * M_s$
				Mg = measured activity of the mixed sample
				SD_{Mg} = standard deviation of the mixed sample
				M_s = calculated mean value from both samples
				$M_s = (activity_{soil} + activity_{control\ soil}) * 2^{-1}$
				0.9 = tolerance of 10 %
Collembola *Folsomia candida*	Primary decomposers	Air-filled soil pores/food, skin	Reproduction inhibition	Reproduction rate reduced by more than 50 % compared to the control soil
			ISO 11267	
Earthworms *Eisenia fetida*	Primary decomposers	Air-filled soil pores/food, skin	Reproduction inhibition	Reproduction rate reduced by more than 50 % compared to the control soil
			ISO 11268-2	
Plants *Avena sativa* *Brassica rapa*	Producers	Medium-sized and coarse pores/soil water	Biomass formation	Soils and soil materials, the yield of which in the mixture with a control soil deviates by more than 10 % from the mean value of the yields of both soils, are to be classified as toxic
			ISO 11269-2	$Mg + SD_{Mg} < 0.9 * M_s$
				Mg = measured biomass yield of the mixed sample
				SD_{Mg} = standard deviation of the mixed sample
				M_s = calculated mean value from both samples
				$M_s = (yield_{soil} + yield_{control\ soil}) * 2^{-1}$
				0.9 = tolerance of 10 %

transfer of contaminants to subjects of protection (human beings, plants, soil organisms, groundwater), and decontamination measures remove the contaminants from the soil.

Protection measures can be divided into contaminant immobilization, hydraulic measures and encapsulation. Immobilization aims to influence the contaminated soil such that pollutant emissions are prevented. This can be achieved e.g. by liming or adding phosphates in heavy metal-contaminated soils. Phytostabilization represents a special case. The contaminated soil is planted with pollutant-resistant plants to protect the soil from erosion. Hydraulic measures prevent the elution of pollutants in the saturated soil zone from leaching into the groundwater. Encapsulation (e.g. with steel pilings) of contaminated areas serves the same purpose. This measure is often used in former waste disposal sites (landfills). Finally, excavation and deposition of contaminated soil in landfills represent a security/safeguard measure.

Decontamination measures include in situ and ex situ methods. With the former, the soil remains in its natural packing. The contaminants are removed from the soil or transformed into harmless substances.

Ex situ methods result in the destruction of the soil as a natural body. They serve to decontaminate the excavated soil, and are therefore forms of substrate cleaning, and according to waste regulations, they produce wastes that require particular monitoring. Decontamination takes place in technical installations, which are used on-site as mobile facilities for the duration of the site remediation or off-site as stationary facilities. Compared to the mobile facilities, the stationary facilities are generally conceived for greater throughput capacities, and they should be capable of treating changing soil charges in terms of the soil characteristics and contamination to ensure a good constant workload.

Regarding the processes involved in removing contaminants, a distinction can be made between chemical-physical, thermal and biological methods.

The **chemical-physical methods** include pneumatic, hydraulic, and electrochemical measures (in situ) and soil washing (ex situ). **Pneumatic methods** are used to remove highly volatile pollutants (e.g. BTEX aromatics) in the saturated and unsaturated soil zone. **Hydraulic measures** are used to remediate contaminated groundwater. This includes removal and cleaning (e.g. with active carbon filters) of the water, and chemical treatment of organic and inorganic pollutants in permeable reactive barriers . This involves wall-shaped permeable underground components that conduct groundwater and are filled with reactive media, usually installed transverse to the direction of flow. The filling of the walls is selected corresponding to the contaminants in the groundwater (e.g. elemental iron for VCHs). **Electrochemical methods** serve to remediate soils with a high binding capacity that are contaminated with heavy metals and organic pollutants. **Soil washing** is used to remediate sandy soils.

Biological methods (in situ and ex situ) can be divided into microbiological remediation and soil remediation with plants (phytoremediation, in situ).

Thermal methods are generally only used ex situ. A distinction can be made between combustion methods with temperatures <500 and >1000 °C and smoldering methods.

The selection of the remediation measure to be used in each case of damage depends on the contaminants, the local pedogenic and geological conditions as well as the concerned subjects of protection. Treatability tests are carried out for the performance of ex situ remediations. These are divided into **material, method and product tests**. They serve to address the following questions:

- Is the soil material treatable as a matter of principle?
- Is the soil material technically treatable?
- Is the treatment reasonable/worthwhile in technical and financial terms?

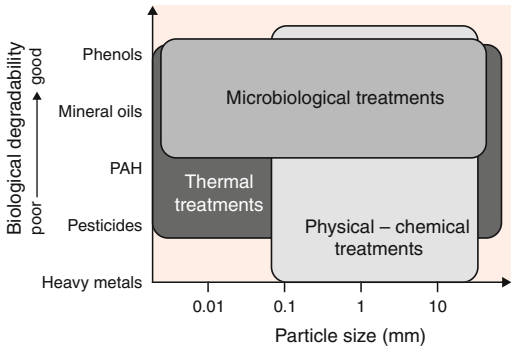


Fig. 10.20 Schema for decisions regarding the treatability of contaminated soils (after Bunge and Gälli 1996)

The most important properties for the treatment of soil material are the type and concentration of the pollutants involved as well as the soil texture and humus content. Figure 10.20 shows a diagram on the basic treatability of contaminated soil.

10.7 Threats to Soil Functions Through Non-chemical Contaminations

10.7.1 Soil Erosion

Soil erosion is defined as the detachment and transport of soil particles (primary particles or aggregates) along the soil surface. Depending on the transport medium, a distinction is made between **water erosion** and **wind erosion**. There are also special forms such as snow scouring, forms of "mass transfer", and the rearrangement of soil material by human activities involving soil tillage. This process is also called tillage erosion. All removal forms are based on natural processes that begin when the mechanical stability has been exceeded. The arrangement of the particles and the interparticle forces acting between the soil particles are affected by water infiltration, swelling and shrinkage, redistribution of air and water-filled pore fractions in the soil, and by the associated changes in pore air pressure through to complete blasting. Knowledge on soil erosion and on the processes involved is required, because it usually leads to irreversible, cumulative long-term damage and therefore reduces the depth to bedrock as well as the water and nutrient storage capacity of the soil. This is also reflected by the fact that the rate of soil formation is lower than the rate of soil erosion by at least one order of magnitude. In soils developed from unconsolidated rock, the rate of new formation is 10^{-1}–10^{0} t ha^{-1} a^{-1}, and in soils developed from hard rock, 10^{-2}–10^{-1} t ha^{-1} a^{-1}. For this reason, the evaluation of the estimated eroded quantities does not use the rate of new formation in view of the preservation of soil fertility, but rather a time period of 500 years per convention as the critical magnitude for the tolerable erosion.

Especially water and wind erosion are strongly promoted by the practice of keeping soils bare in agriculture. Likewise, losses due to the clinging of soil on root crops (sugar beet, potato, carrot, chicory) are also only caused by human activities. Especially with sugar beet, these soil losses can be substantial (>5 t ha^{-1} a^{-1}). The losses through clinging soil increase with increasing stickiness (clay fraction, moisture during harvest), the surface of the harvested product, and the low cleaning efficiency of the harvesting equipment.

10.7.1.1 Significant Causes for Soil Erosion

Under the respective management and climatic conditions, as described in Sects. 6.3.1 and 7.2.7, all soils are not only subject to interparticle and/or inter- and intra-aggregate forces, but also the interaction between the soil strength and the hydraulic situation at the site.

As a result, in conjunction with soil erosion by wind and water, the persisting forces resulting from the position of the particle/aggregate in the profile or also in the landscape must be compared to the current shear resistances, which strive towards movement depending on the stress (Sect. 6.3.2). Here, primarily the processes relevant to soil erosion will be explained. A detailed individual representation of the erosion processes is omitted here, because there is extensive specialized literature on the subject where these

topics are explained in detail and regional differences are also described.

In physical terms, the process of soil erosion can be described as an interaction between hydraulic or hydrological (water binding and flow) as well as pneumatic (wind energy and the formation of gradients) parameters and the respective mechanical strength. Regardless of the form of erosion, chemical (sorption, concentration, valence and precipitation processes) and biological (formation of organo-mineral compounds) interactions between the particles, the individual aggregates or the overall structure of the soil must also be considered under the respective slope and cover situation.

Any flow over a soil surface always creates flow gradients. In doing so, a great difference in the length of the flow lines means that there are greater hydraulic or also pneumatic gradients between them. The latter therefore also determine the detachment of particles or smaller aggregates, whereby the uplift forces must be compared to the weight forces and sedimentation.

As long as the uplift forces dominate, there is further transport of the soil particles until the weight of the grains and gravity cause resedimentation. Here, the greater the viscosity of the transporting medium, the longer the particles remain in the flow medium. On the other hand, because air has a much lower viscosity than water, this also means that maintaining particle erosion in the air requires a much higher flow velocity than in water. Regardless of this, the fundamental processes involved in erosion by water and wind are largely identical.

Hillside slumping or mass transfer also leads to soil erosion. This is mainly observed in mountainous regions and is promoted by deforestation and especially also by the establishment of ski trails (see Sect. 7.2.7).

10.7.1.2 Water Erosion

Figure 10.21 shows the sub-processes that are relevant for soil erosion by water. Here, the destruction of the aggregates and the resulting weakening processes especially in the topmost soil layer are considered. The drop size and intensity can strongly reduce water infiltration through the process of aggregate destruction. The erosion process through water erosion is therefore essentially characterized by the following two sub-processes:

1. Detachment of soil particles and breakdown through the impact of raindrops and then through the flow force of surface runoff,
2. Sediment transport with flowing water and the associated change in the suspension viscosity (Stoke's Law, Sect. 6.1).

Furthermore, particles that are detached by the kinetic energy of raindrops transmit their energy to the other aggregates. They contribute to a further breakdown of the soil structural forms, to a reduction of the shear resistance, and to the sealing of the soil surface. Aggregates can also be destroyed by pressurized air in the pores (=air blasting), because moistening of the aggregate volumes from the outside due to water infiltration leads to a reduction in the shear resistances compared to the air '(over) pressure' inside the aggregates. In the process, aggregates that are weakened by air blasting and swelling are further broken down by the forces of the raindrops. With increasing rain intensity (=rain quantity per unit of time), the diameter and therefore the mass of the drops increase. However, because the drops also fall faster with increasing diameter, the kinetic energy of the drops increases disproportionately with increasing rain intensity ($E_{kin} = m/2 \cdot v^2$). Therefore, with the same total volume, the energy also increases with the drop diameter (Table 10.15).

The impact of raindrops on the soil surface results in temporary (50 μs) very high pressures, which can reach up to 10^6 Pa on rigid surfaces. However, because the water drops cannot infiltrate the soil with the fall velocity at which they hit the ground, they must deflect to the side along the soil surface. The drops can then cause local compaction, especially on moist surfaces. The lateral deflection of the water causes shear stress,

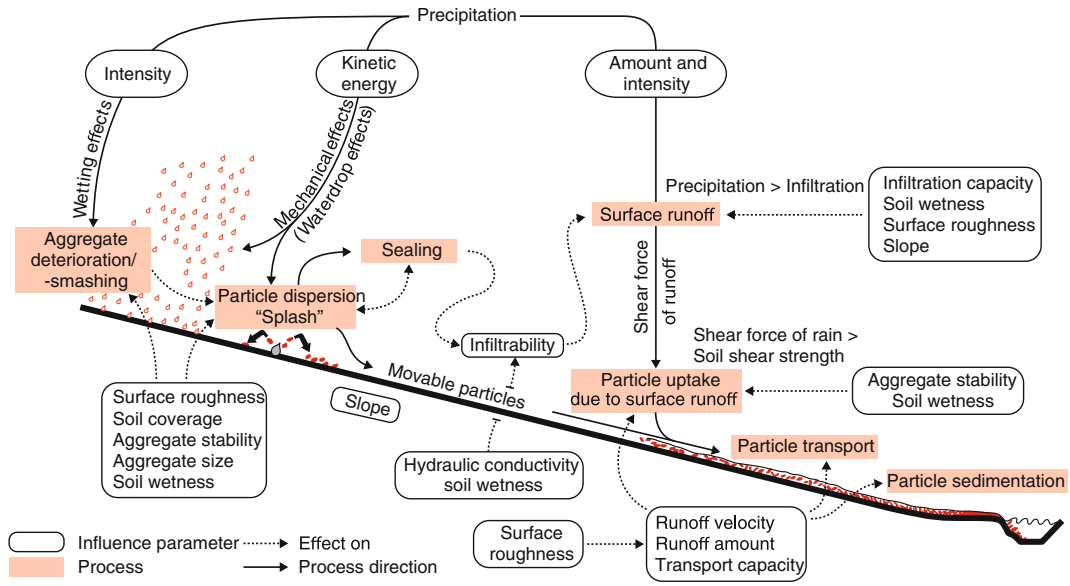


Fig. 10.21 The soil erosion process—influencing parameters and sub-processes (from Duttmann 2001)

Table 10.15 Effect of the drop size and drop height on the sedimentation velocity and momentum of water drops

Diameter (mm)	Fall velocity (m/s)		Number	Mass (g)	Energy (mJ)	
	Drop height (m)				Drop height (m)	
	2	∞			2	∞
2	4.92	6.58	1	0.0042	0.051	0.091
			200[a]	0.8377	10.140	18.136
5	5.79	9.25	1	0.0655	1.097	2.800
			13†	0.8508	14.261	36.400

[a]The total volume of 13 large drops corresponds about to that of 200 small drops (after Becher 2005)

which becomes greater with increasing difference in velocity between the water and the surface and with decreasing distance to the surface (Sect. 6.4.2). This can result in shear stress of a magnitude of several hPa, which, especially in low-cohesive soils or individual aggregates, can locally detach small particles from the soil surface. The detached fine particles can then clog the pores if they are washed into the soil by infiltrating rainwater. Soil surface sealing (sometimes >1 mm) can result from the closure particularly of rapidly draining coarse pores and coarse medium-sized pores, which further reduces the infiltration and promotes the occurrence of surface runoff (Fig. 10.21).

The more completely the soil volumes are saturated depending on the infiltration rate, the more readily this saturation leads to an aggradation of the unstable soil material due to the onset of upwelling (e.g. all the way to the compacted plow pan). As a result, all of the softened soil material is transported down the slope. Progressing downstream, the initially shallow rills turn into deeper furrows and finally also into gullies, which can stretch over increasing areas and greater flow lengths.

The process of structure destruction at a given kinetic raindrop energy is affected both by the valence and concentration effects of the sorbed cations and by freeze/thaw effects. In the case of dominating saturation of the sorbent surfaces with monovalent cations, the soil structure is more easily dispersed (see also Sect. 6.1—particle size analysis) and subsequently causes pronounced surface sealing of the topsoil. This process is described by the term slaking, and especially in soils of arid climates, it can lead to the formation of a throttle layer, a dense and impervious soil horizon that is saturated with Na.

Freeze/thaw effects break down the aggregates due to the volume expansion associated with the freezing process, whereby the translocation of these new smaller aggregate units can take place over greater distances at low flow velocity (see also Sect. 6.6.5).

(a) **Transport forms**

Transport by splash drops

Both the drops and the runoff are involved in the transport of the loosened particles. The splash drops, which can fly up to 1.5 m high and to the side with the impact of raindrops, produce a net downwards transport, because they fly further down the slope than up the slope. The detachment and transport by impacting drops are affected by the presence of a water film on the soil surface. The highest detachment and transport rates were observed with thin films (1/10 to 3/10 of the droplet diameter). The drop impact can be neglected for both rates if the film is thicker than 2–3 drops diameters, because the drop energy is completely compensated by the water film.

Transport by surface runoff

The transport capacity of the runoff increases with increasing flow velocity and therefore with increasing layer thickness and sole slope and with decreasing sole roughness. If the runoff is concentrated in channels, this is where the main transport takes place due to the high transport forces and high flow velocities (10^{-1}–10^{0} m s^{-1}), these forces can then even be strong enough to transport stones, while the drop impact can only move particles up to a maximum size of sand grains.

Drop-induced runoff transport

At the transition between drop and runoff transport, the water film is already too thick for pure drop transport, but is not yet thick enough for runoff transport over the whole surface. Nevertheless, particularly this thin layer runoff is capable of transporting abundant solid material, because it is kept in suspension by the turbulence of the drop impacts. This form of transport dominates where there is not much water flow, i.e. on short slopes or in the area between the channels. In many cases, it is the dominating erosion process.

(b) **Forms of water erosion**

Rapid wetting of the soil surface, dispersion of the aggregates, and raindrop impact have a uniform effect on unprotected surfaces. Extensive detachment and transport take place where these processes dominate (**surface** or **sheet erosion**). In contrast, the detaching forces of surface runoff have a small-scale effect. This results in **linear erosion**. When this occurs simultaneously at several points, only shallow (ca. 10 cm) rills are formed, in which the runoff is distributed (**rill erosion**). With surface erosion, the transport path from the inter-rill area to the rill is generally short. The formation of rills depends on the previously shaped rills (e.g. wheel marks, seed rows) and the tendency of the soils to form rills, and usually increases with decreasing cohesiveness. As a result, surface erosion still contributes significantly to the total erosion. For this reason, surface and rill erosion are determined by similar influences and there are often transitions. Both forms are therefore usually treated together in modeling, mapping or for protection measures.

With increasing concentration of the runoff, the distance between the linear forms becomes greater, and the detachment by runoff becomes more significant. The rills become wider and deeper. In contrast, the detachment in the inter-rill area loses significance because of the increasing transport path to the next linear form. If the erosion furrows can still be

filled by normal soil tillage, it is referred to as **rill wash erosion** (<30 cm depth). The interaction of rill out-washing and refilling leads to the formation of shallow depressions on slopes ("Talweg"). If the rills get deeper, so that they can no longer be removed by soil tillage, it is called **gully erosion**. With this form of erosion, the detachment by drops is no longer relevant. The drop impact then only causes soil surface sealing and therefore promotes the formation of runoff, which flows together in the ditch and washes it out. The required large runoff volumes can also come from the exfiltration of groundwater, interflow or from the discharge of surface water from sealed areas (e.g. roads).

The fourth type of erosion is **tunnel erosion**. It is observed when a stable topsoil covers an instable subsoil. The stability of the topsoil can be attributed e.g. to intense rooting or to cementation by carbonates or Fe oxides. The instability of the subsoil with a high tendency towards dispersion is usually attributed to low aggregation, low organic matter or a high proportion of monovalent cations in the exchange medium occupancy. Infiltrating rainwater can then flow laterally under the stable zone and wash out the instable subsoil. Tunnels with a diameter of up to 2 m can be formed in this way, until the ceiling finally collapses when the load-bearing capacity of the topsoil is exceeded.

10.7.1.3 Wind Erosion

When wind blows over a surface, its velocity increases considerably with increasing distance. Depending on the roughness of the soil surface, the height at which no air movement can be measured is shifted a few millimeters above the soil surface. This height is called the 'aerodynamic datum or reference level'. The latter can reach several decimeters on surfaces with vegetation cover. The faster the velocity above this reference level, and therefore the steeper the velocity gradient, the greater the shear forces acting at the reference level. This can lead to the movement of particles along the soil surface. The particles also protrude into the air current and therefore restrict it. Through the Bernoulli effect, a vacuum is formed on the upper surface of the particles, so that in addition to the tangential shear forces, there are also vertical forces acting on the particles at the soil surface.

With increasing wind velocity, the particles are captured by the wind current, lifted steep up into the air ($\sim 80°$), accelerated, and after a transport distance corresponding to 10–15 times the lifting height, fall back down to the surface at a flat angle (~ 6–$12°$). A portion of the kinetic energy is transformed into detachment at the moment of impact by dislodging particles out of the soil and aggregate structure. Another portion is transferred to the kinetic energy of particles that are still on the ground, and together with the wind energy, these particles can now be transported. The process is called '**saltation**' and is capable of moving 50–75 % of the eroding masses. The number of saltating grains increases with a snowballing effect in the wind direction, because the increasing impacts create more transportable particles that are lifted into the airflow, until finally the wind's transport capacity is exhausted.

Through the energy transfer by saltating particles, additional particles can be set into movement that are too heavy for the airflow, but that can roll along the soil surface. In doing so, they can break down aggregates and rub off fine particles adhering to sand grains. These fine particles are also captured by the air current, and because of their low weight, they are carried up by eddies and sometimes transported over thousands of kilometers. Although rolling and saltating particles account for the greatest portion of the moving masses by far, they do not cause any important net losses, because the transport distances are short, often only within a field, and in the case of opposite wind directions, they can sometimes even be transported back. In contrast, the 'blowing out' of fine particles leads to a coarsening of the texture. Especially on sandy soils prone to wind erosion, however, these fine particles are important for nutrient sorption and the storage of plant-available water. For this reason, this selective loss leads to a much stronger deterioration of soil fertility than would be expected solely due to the soil losses. The

loamier the eroding soil, the lower the qualitative differences between the initial soil, the suspension loss and the residuum.

(a) **Transport processes**

Saltating particles are predominantly 0.1–0.5 mm in size, rolling particles are larger, and suspended are smaller. The grain diameter that can still be transported at a specific velocity increases with decreasing water content or/and more negative matrix potential and lower bulk density in the topsoil. However, despite the low aggregate bulk density compared to the ρs value of sandy soils containing quartz (2.65 g cm^{-3}), aggregated topsoils are less subject to wind erosion than smaller but heavier sand grains, because their mass is greater.

Because of their particularly low density (0.1–0.4 g cm^{-3}), dried-out peat soils can be blown away already at low wind velocities. In contrast, moist soil surfaces are less susceptible to deflation. As a general rule, the higher the unsaturated hydraulic conductivity and the greater the matrix potential-dependent degree of water saturation of the soil (χ factor of the effective stress equation, Sect. 6.32.3), the more strongly the water menisci pull the individual soil particles together and hold them tight, making the soil heavier due to the additional weight of water.

Wind erosion begins in mineral soils when the wind velocity 30 cm above the soil is of 4–6 m s^{-1}. Above this velocity, the transport increases with the third power of the wind velocity. The critical shear velocity is lowest for particles with a diameter of 0.05–0.2 mm and increases strongly for smaller and larger diameters. For larger particles, the increasing weight is responsible for this rise, and for smaller particles, the increase in the cohesive forces and the wind protection by surrounding larger particles. The resistance towards wind erosion increases strongly in mineral soils above a diameter of 1 mm. When 60 % of the soil surface is covered by stable particles >1 mm, it is sufficient to almost completely stabilize the soil surface. Strong aggregation is therefore effective at reducing wind erosion.

In temperate climates, the required high wind velocities occur mainly near the coasts or on vast plains with few trees particularly during spring and autumn storms, especially since the fields often have insufficient vegetation cover at these times. Large fields without higher boundary structures (hedges, balks, windbreaks) promote high wind velocities close to the soil.

Soil cover with mulch reduces soil losses to a similar extent as with water erosion. In contrast to water erosion, a standing cover is even more effective, because the wind is more strongly decelerated and the aerodynamic reference level is lifted.

10.7.1.4 Tillage Erosion

Any loosening soil tillage lifts the soil a little bit. On sloped surfaces, this occurs perpendicular to the soil surface. The soil then falls back down, but now perpendicular to the horizontal plane in the direction of gravity. The different direction of the two vectors results in a net transport down the slope, regardless of the direction of tillage. This leads to a net loss at the upper field boundary and a net gain at the bottom. This explains why many fields are particularly strongly eroded at the upper boundary, even though usually not much water can flow there and therefore the erosion by water is still low. Between the upper and the lower field boundaries on evenly sloped fields, the input from the top compensates for the losses at the bottom, so that there is no net loss. However, this means that the topsoil no longer belongs to the subsoil in situ, but rather to a subsoil further up the slope, which makes the genetic interpretation of arable soils very difficult.

Translocation always occurs regardless of the direction of soil tillage. In addition, soil is translocated when the tillage is aligned. This is especially the case where the tractive forces do not allow soil tillage going up the slope, e.g. on steep slopes or with low-technology farming involving animals or manual hoeing.

Soil transport increases with the number of tillage passes, the working depth, the implement-

and speed-dependent lifting, and with increasing slope inclination. In contrast to the other parameters, the slope inclination generally changes within a field. On convex parts of the slope, where the slope becomes steeper towards the bottom, because of the smaller slope inclination at the upper boundary, the input from the top is less than the losses downwards/at the bottom. For this reason, the balance of inputs and losses on convex sites can no longer be compensated and there is a net loss of soil. This process is responsible for the often strongly capped soil profiles on summits and slope shoulders, while the erosion by water on such sites is less than on an elongated slope.

On concave slope areas, in contrast, because of the decreasing slope inclination towards the bottom, there are less losses than inputs, so that a net accumulation is observed. Many colluviums owe their existence to this process, because tillage erosion primarily translocates soil within a field, while with water and wind erosion, there is little deposition near the erosion site (rarely more than 10 %) and a large portion is transported over great distances, sometimes all the way to the ocean.

10.7.1.5 Extent of Soil Erosion by Water and Wind

Water and wind erosion are natural processes that are not very active under natural conditions. Natural ('geological') erosion has its maximum in semiarid to arid regions due to the sparse vegetation cover. Rare, but sometimes violent rain or strong winds can then trigger considerable matter transport. Also in mountainous areas, because of the steep slopes, occasional strong winds near the peak, and frequently unfavorable vegetation conditions, strong local erosion is natural and impedes the normal soil development at these sites.

However, erosion is mainly a problem in agriculture, because the soils are periodically bare and are moved by tillage. Erosion is therefore considered to be the most important form of soil damage on a global scale. In Central Europe, wind erosion occurs most frequently in coastal regions, where high wind velocities and sandy soils are common. Also the great plains, e.g. in Ukraine, Hungary or the Great Plains in the USA, are predestinated for wind erosion. However, except for a few regions, wind erosion is less significant than water erosion. For the United States, it is assumed that the soil volume lost through wind is less than 1/10 of the volume lost by water.

Tillage causes similar quantities of soil transport as soil erosion by water. Because of the different mechanisms, however, the spatial patterns of both processes vary both within a slope and between landscapes.

The proportions of the different forms of water erosion in the total erosion vary across a wide range. In general, the surface erosion fraction is particularly large in small erosion events; these, however, represent the majority. With increasing event magnitude, the proportion of linear erosion forms increases. For a particularly strong event with a return period of 250 years at the concerned site in Southern Germany, the surface erosion accounted for 40 %, rill erosion 31 %, rill wash erosion 17 %, and gully erosion 12 % of the total erosion of 174 t ha^{-1}.

The **erosion rates** vary across a wide range. Under arable land use, the average erosion by water measured over many years in temperate climates is often of a magnitude of 10^1 t ha^{-1} a^{-1}, but erosion rates of up to 10^2 t ha^{-1} a^{-1} were observed at individual sites over longer periods of time. The highest amounts of erosion with a magnitude of 10^3 t ha^{-1} a^{-1} are observed in SW Asia due to the concurrence of readily erodible volcanic soils, high precipitation and steep slopes. Also in other tropical regions (Brazil, West and East Africa, India) with high amounts of precipitation that are often concentrated in a short period of time, there are reports of high soil erosion rates (10^1–10^2 t ha^{-1} a^{-1}). In all cases, the variability is large (one power of ten) between the individual years, and very large (several powers of ten) between the individual events.

Erosion losses through flowing waters are less than losses from surfaces, because a considerable fraction of the eroded material remains as colluvium on the lower slopes and especially as fluvial sediment in the floodplains. The fraction that is carried out decreases with the size of the catchment area. In a catchment area of 10 km^2, ca.

20 % of the eroded material is transported out, and only 10 % in an area of 100 km^2.

10.7.1.6 Soil Deterioration

Wind erosion mainly causes damage to plants by saltating sand grains through exposure of the roots, covering or injury to the leaf surface. Furthermore, there are significant nutrient and humus losses in the deflation area and often uneven sedimentation in the lee area. With water erosion, precipitation runs off unproductively and farming is impeded by the uneven crop development and by rills and gullies. With both forms, there is a lack of nutrients, and pesticides are overdosed on the eroded sites and the accumulation sites.

In addition to the damage on the eroding surfaces ('on-site damage'), there is 'off-site damage' on the areas where the sediment and discharge accumulate. Examples for this are the pollution of roads and houses, the siltation of watercourses, and the input of nutrients, pesticides and heavy metals in waters and in other neighboring ecosystems. On the other hand, there is considerable nutrient accumulation in the colluvium, while the aeration is improved due to the greater distance of the new surface from the possibly originally high groundwater table. However, gas exchange with the atmosphere and vertical water flow are significantly delayed, because the new pores are mainly formed on a horizontal plane due to the sedimentation.

10.7.1.7 Erosion Protection

The best protection from erosion is a constantly covered soil surface. A mulch cover of 30–50 % is usually sufficient, since erosion is reduced disproportionately. The ground cover protects from drop impact, reduces wind and runoff velocity, increases the soil moisture at the surface, and promotes the formation of vertical pores by earthworms. The soil does not have to be constantly covered, but rather at times with erosive rain or winds. In conventional agriculture, the soil has the least cover immediately after seeding. Minimum or conservation tillage can help to achieve sufficient cover even when seeding. Tillage erosion is also prevented by reduced tillage frequency and depth.

In addition, runoff and wind can be decelerated by a rough surface, which is achieved by tilling across the slope or perpendicular to the prevailing winds. A small-scale, diverse land use, where areas with different levels of erosion protection are beside each other, prevents the collection of large amounts of runoff or eroding saltation material and the development of high wind speeds. This mutual protection of different crops is purposely utilized in strip farming, by establishing the individual crops in long strips with a width of 10–50 m across the slope or perpendicular to the prevailing winds. With wind erosion, the protection results from the retention of rolling and saltating particles in the strips with vegetation cover, and for water erosion, in contrast, from the retention of surface runoff in the strips with less cover. The runoff can be further decelerated by the construction of terraces, and wind by hedgerows. Hedgerows decelerate the wind optimally when they have a porosity of ca. 50 % over the entire height and are at least 20 times wider than they are high. Protection can then be expected over a distance of up to 20 times the height of the hedge.

10.7.2 Mechanical Soil Deformation

In contrast to the stresses discussed in the previous chapters, mechanical soil deformation represents a stress in the true sense of the word. Section 6.3 explained the basic principles and processes that are important in understanding the mechanical strength, which now serve as a basis for explaining soil deformation and therefore also soil compaction. In terms of the process, it is irrelevant whether the causes are pedogenic, geogenic or anthropogenic, because every increase in the inherent strength through soil deformation also affects physical, physicochemical and biological soil functions (Fig. 10.22). The concept of 'soil compaction' defined in the German Federal Soil Protection Act as the cause for

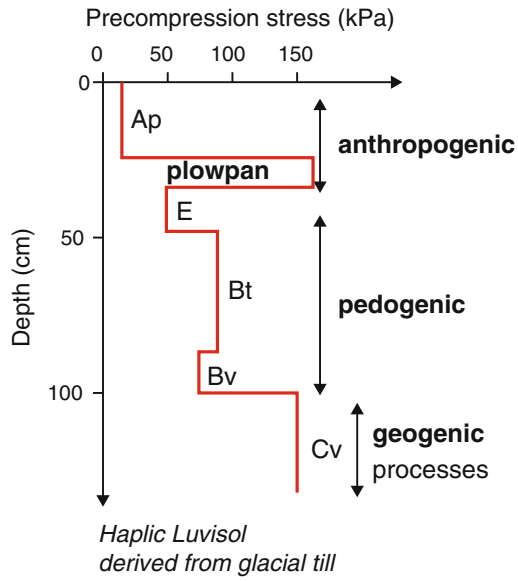


Fig. 10.22 Depth distribution of the precompression stress due to pedogenic, geogenic and anthropogenic processes using the example of a Luvisol developed from calcareous glacial till

lasting soil degradation will be further discussed in the following.

10.7.2.1 Definition of Soil Deformation

Soil deformation comprises the process of soil compaction and the change in the structure of the soil's three-phase system caused by shearing.

Soil compaction leads to a reduction in the pore fraction filled with water and gases in the soil with a simultaneous increase in the volume of the solid phase; and therefore both the total pore volume and the pore continuity decrease. **Shearing** results in a change in the pore functions of varying intensity depending on the stress at the identical pore volume or void ratio while the pore continuity changes and the horizontal anisotropy of the water and air conductivity increases. Accordingly, there are differences in e.g. the consequences of the two processes regarding the mechanical soil strength, matter fluxes, storage of water, gas, heat, nutrients, plant growth, and living conditions for the fauna.

Soil deformation therefore involves several sub-processes in soils, which have to be separated in terms of their modes of action and their implications for the overall soil strength.

- The existing structural units are increasingly densely packed by a reduction in the coarse interaggregate pore system, and the bulk density increases as long as a more stable packing can be achieved with the given void system and inherent stability of the aggregates. This increase in soil strength and bulk density is characterized by the process of soil compaction.
- In the case of very high inherent strength, shearing with the preservation of the aggregate shapes results in loosening and therefore leads to a decrease in bulk density.
- The higher the effective deforming shear forces and the less stable the aggregates, the more strongly the soil aggregates are aligned and the pores are arranged perpendicularly. Further shearing breaks down the individual aggregates and the entire soil is eventually homogenized. This can also produce a loose packing suitable for a seedbed. These latter processes are defined as shear deformation. In agriculture and forestry, the process of shearing is omnipresent and is caused by the slipping effects of the driving tires or chains, by kneading strains from animals (hoof treading, scratching) or through puddling (=kneading) in rice cultivation, leading to extensive alignment, and especially in moist soils, to destruction of the structure, homogenizing and reestablishment of the proportional shrinkage state.

10.7.2.2 Stability in the Recompaction and Virgin Compaction Range

The question as to whether a mechanical—static or dynamic—stress leads to additional soil deformation and therefore possibly also to degradation can be answered using the mechanical strength of the individual horizons in conjunction with the respective load-dependent pressure

propagation. Every soil or soil horizon has its own inherent strength corresponding to its previous history, the **preload** (Sect. 6.3.2). In general, soils or soil horizons are more stable

- the coarser and the rougher the texture with the same bulk density,
- the stronger the aggregation with comparable texture (e.g. single-grain < coherent < prismatic < polyhedral < subangular blocky),
- the more intense the precompression (e.g. plow pan horizons (App) with platy structure),
- the higher the organic matter content or the higher the fraction of unsaturated fatty acids and lipids with a comparable content of organic matter,
- the more wetting-inhibited the grain contact points at the same matrix potential,
- the drier, i.e. the more negative the matrix potential or the pore water pressure,
- the higher the remaining hydraulic conductivity and therefore the faster the expelled soil water can be drained away,
- the higher the valence of the exchangeable ions (monovalent < divalent < trivalent),
- the higher the salt concentration in the soil solution,
- the lower the swelling capacity of the clay minerals.

While stress in the recompression stress range does not lead to a further change in the soil functions, it always causes plastic deformations in the virgin compaction range and therefore also higher bulk densities, because there are time-dependent changes in the strains in all three soil phases (solid, liquid, gaseous). Three phases are distinguished in the time-strain settlement process:

The first settlement fraction is defined as immediate settlement and comprises at most the soil volume that is filled with air; because the gas conductivity in soils is high, the strains transmitted through the gaseous phase can dissipate immediately and result in a corresponding volume decrease.

In contrast, the strains that are transmitted through the liquid phase, depending on the hydraulic conductivity and the building-up of hydraulic gradients, can be expressed as pore water pressures and can therefore be measured over a longer period of time. As a result of this, the soil-stabilizing water meniscus forces are now transformed into destabilizing convex meniscus forms (Fig. 6.2.5). In this phase, the soil matrix loses its inherent strength, and the effective strain is largely relieved. Strains can also reduce the diameter of the pores through 'stress induced strain of air-filled pores, and therefore contribute to a redistribution of water in the pores. A further decrease in the negative pore water pressure (= matrix potential) can be measured during this process. The finer pores are filled again due to settlement only when the load-dependent inherent strength has been reached, and water saturation or even positive pore water pressure is finally reached. With their degradation, reequilibration is the **primary settling** largely concluded, and the strain fraction that is transmitted through the solid phase increases due to an increase in the grain contact points.

Under sustained stress, e.g. in conjunction with soil mechanical foundation measures, especially in clayey soils, the secondary settlement must also be considered, which is caused by particle alignment and can lead to long-term creeping movement and therefore to fissuring.

In addition, the 'strain prehistory' is reflected by corresponding different values for the concentration factors. The concentration factors are much smaller in more strongly aggregated and/or drier and therefore more stable horizons, and likewise in mechanically pre-compacted soils. They indicate more horizontally aligned lines of equal pressure or more densely concentrated equipotentials under the load surface. In contrast, in less aggregated, moister or more loosely packed soils, the soil pressures reach deeper into the profile, but are also propagated more narrowly, concentrated around the load surface, which results in greater values for the concentration factors. Depending on the soil development and land use, the stress propagation therefore varies extensively, so that horizon-, matrix potential-, structure-, load surface- and load-dependent values for the concentration factors must be used. However, if the acting

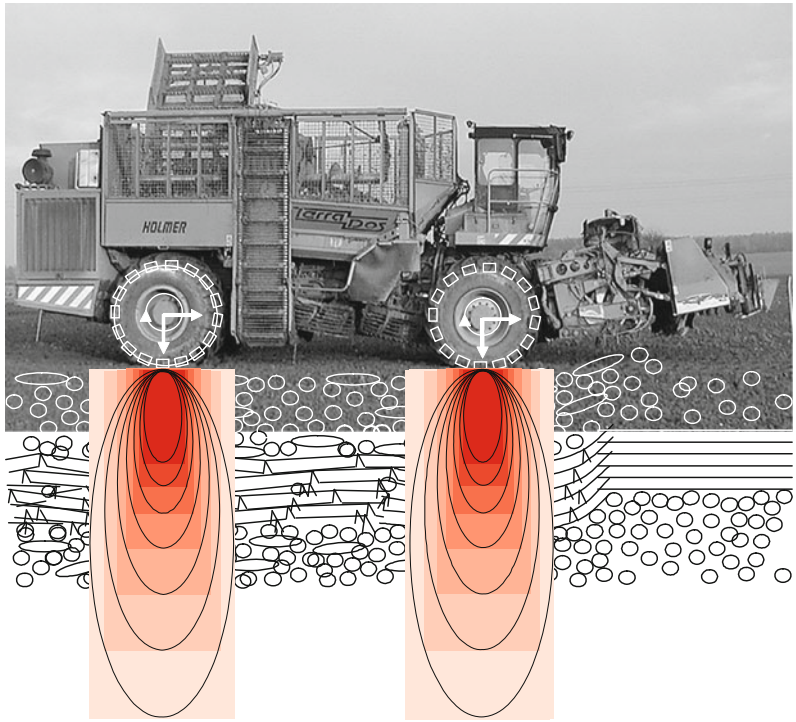


Fig. 10.23 Intense pressure propagation due to the exceedance of the soil stability through cleavage and new formation of the plow pan at greater depths (after Peth et al. 2006, supplemented)

pressure exceeds the inherent strength e.g. of the existing plow pan, and due to the mechanical or hydraulic prehistory, there is a less stable horizon underneath that cannot compensate the remaining pressures, the plow pan ruptures and the total soil volume is further compacted to greater depths (up to ca. 6–8 dm) (Fig. 10.23).

In doing so, the higher the shearing component, the more pronounced and also the more sustained the soil deformation.

In addition, there is a lateral bulging of the soil surface in the area surrounding the load surface (wheelmark, footsteps), whereby the shape and extent can be described using the Rankine-Prandtl failure theory. The pattern of the flow lines, which are always perpendicular to the equipotential lines, therefore depends on the soil development and land use. In the boundary state, there is a complete soil failure which results in a landsliding. This process is particularly enduring on slopes in the form of mass transfer, because here the persisting, i.e. stabilizing forces are even smaller due to the lacking outer support at the sides (further detailed information can be found in the extensive specialized literature on soil mechanics).

10.7.2.3 Consequences of Soil Deformation for Soil Parameters

Every mechanical stress that exceeds the inherent strength of the soil or the individual soil horizons not only changes the volume fractions of the solid, liquid and gaseous phases in the soil, but also the soil functions (e.g. as a habitat for plants and animals, as a reservoir for water and gas, as a filter and buffer for the quality and quantity of groundwater). The decrease in the pore cross-section and the reduction in pore continuity decrease the water flow, among other things, and also the gas flow and its composition in conjunction with the load-dependent degree of saturation. Because of the partial reduction in the coarse pore cross-section, which was originally filled with air, the filling of water in the pores leads to an increase in the flow resistance for gases. The rate of diffusion decreases up to

10,000-fold particularly due to the sustained water saturation in the pores. With a further reduction of the conducting flow cross-section, the hydraulic conductivity and therefore the total water transport decrease under saturated conditions. Compaction and also shearing lead to anisotropic pore systems, where already a slight slope causes preferential lateral flow, e.g. to the receiving waters, and the seepage water does not reach the groundwater. Soil deformation decreases the air capacity, while especially in sandy and silty soils, the plant-available water initially increases, and then decreases again with further increasing loads in the initial (=virgin) load range. The lower the hydraulic conductivity, the lower the groundwater recharge and the stronger the risk of soil losses through water erosion (on-site and off-site damage) on sloped terrain (resulting in gully erosion or mass transfer, see Sect. 10.7.1). Furthermore, due to the particle alignment and the stress relief perpendicular to the input direction, the horizontally aligned pores are larger than the vertical pores (i.e. the pore system exhibits horizontal anisotropy, see Sect. 6.3). This also accelerates soil losses through water erosion down the slope because the vertical flows are reduced, leading to buoyancy (Archimedes' principle). Already with low amounts of precipitation, erosion channels can develop reaching down to the plow pan.

Moister soils are warmed up later in the vegetation period, but also release the stored heat longer into autumn, provided that the pore functions and the contact points between the soil particles or aggregates are still intact. Otherwise, there can be an interruption in the thermal lines, therefore inducing stronger surface cooling despite higher water contents.

Finally, shearing deformation in moister soils causes more aggregate destruction, and increases the accessibility of the soil particle surfaces as well as water deposition and swelling. Under these conditions, even with a high bulk density, i.e. a denser packing, the soil loses its inherent strength and is transformed into the state of the subsequent normal (proportional) shrinkage. This phenomenon is particularly observed in moister wheelruts on the field, on the headlands when harvesting under moist conditions, in forestry when harvesting timber with heavy skidders, in the area of footprints, and in the areas surrounding livestock watering tanks.

Depending on the intensity of soil deformation and the physical and chemical boundary conditions, the effects of soil deformation on the soil fauna range from reduced abundance through to changes in the composition (Fig. 10.24 summarizes the general processes).

10.7.2.4 Counteractive Measures and Their Limits

Soils compacted by agriculture and forestry can only be loosened again, if at all, through climatic parameters, e.g. freezing/thawing, swelling/shrinking, as well as through suitable plant cultivation and associated management (load restriction and reduced soil tillage) over very long periods of time.

The only directly effective measure for re-loosening compacted soils in a shorter period of time is subsoiling in very dry soils (almost pF 3 in the entire depth to be loosened). However, the associated creation of coarse pores is not equivalent to a corresponding improved pore connectivity. Furthermore, long-term maintained loosening success requires a significant reduction in the mechanical stress that is transmitted to the soil up to now. In the following applied stresses must be adjusted to the smaller precompression stress values over a longer time period (years/decades). This is the only way to ensure the restructuration of soils that were loosened up to the virgin compaction range and are now instable. If the soil's inherent strength is preserved, targeted heterogenization of the dense subsoil through vertical 'punched' pores in a narrow grid pattern can improve rooting depth and the flow of water, gas and heat. The process of slotting has already made use of this concept for a long time.

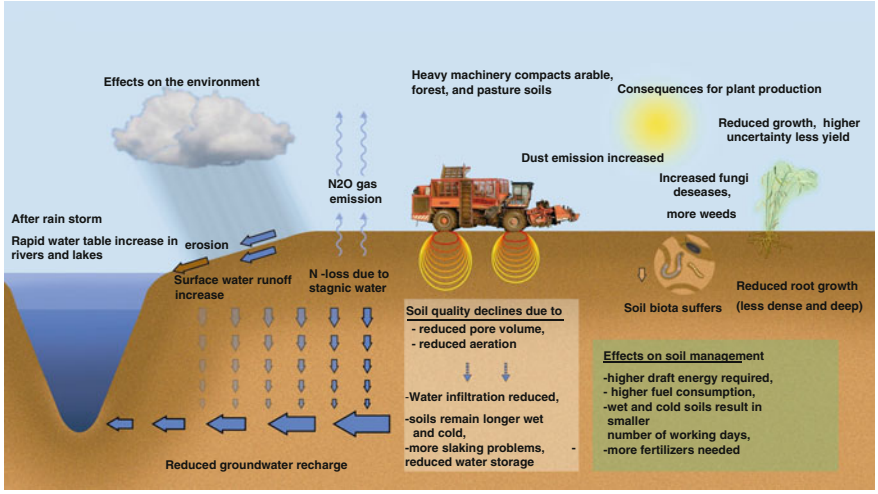


Fig. 10.24 Consequences of soil deformation for soil functions (from van der Ploeg et al. 2006, slightly modified)

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11 Land Evaluation and Soil Protection

All soils on our planet are useful. They serve the ecological balance, plant and animal production or various uses of civilization (cf. Sect. 1.2). The larger the population of our Earth, the more different uses are competing for one and the same soil. This is why the following fundamental question is being raised more and more frequently: Is this soil suitable for a specific use? This question is as old as human interactions with soils. Already in the Stone Age, people had to ask themselves whether it would be profitable to clear the forest and convert it for agricultural purposes. The beginnings of soil classification are also rooted in the suitability of soils (cf. Chap. 7). The most important assessment is still the question of soil fertility or yield potential of soils for different crops. This is best portrayed in Roman and Greek literature, with the coincidence of the classification of soils and their suitability for use.

The **German Soil Protection Act** (1998) protects important **soil functions**, in principle, the 'natural functions' of the soil as a vital basis and habitat for human beings, animals, plants and soil organisms; as a component of the ecological balance, as a filter, buffer and transformer; in particular for the protection of the groundwater and also as an archive of the landscape history. It also protects the 'utilization functions' of the soil as a source of raw materials, surface for settlement and recreation, and sites for agricultural and forestry use, transportation, supply and disposal (cf. Sect. 11.7).

The **Soil Protection Ordinance** (1999), provided under statute, defines assessment threshold values at which **harmful soil changes (deterioration)** can be observed when they are exceeded (cf. Chap. 10 and Sect. 11.7). In order e.g. to be able to conclude that soils are damaged, a soil evaluation must be performed, i.e. modern soil evaluation, including all areas of **land use**. This is aggravated by the fact that soils inherently have different, simultaneous functions, e.g. the archive function, by which soils preserve characteristics from periods long past, and at the same time, they are sites for crop production as well as regulators and filtering bodies in the landscape's water balance. In the future, therefore, soil evaluations will have to also integrate several competing uses into one matrix. Undesirable developments in soil evaluation always arise in areas where soils are considered in isolation. A soil-related evaluation can always only be applicable within a regional framework. Supraregional soil evaluations must consider the entire ecosystem. Already in times of Aristoteles (384–322 B.C.) and his student Theophrast, it is mentioned that good soils can be affected by poor climates and vice versa. They use soil, climate and relief for site descriptions.

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11.1 Principles of Soil Evaluation/Assessment

In the end, all attempts to evaluate different types of soils are not oriented to the soil itself, but rather to its productivity. That is why it can be assumed that all evaluation methods are effective.

Which results can be obtained from soil evaluations?

- In principle, the **suitability** for use can be good, poor, or non-existing. Although such a classification is always qualitative, it provides important tips for alternatives. If a decision has been made for a specific use, then
- the **productivity** of the soil or the ecosystem is to be evaluated quantitatively. Many uses of soils place a physical demand on the bearing capacity or a physicochemical demand on the buffering capacity of soils. Therefore, here
- the **soil strength** must be evaluated. The methods of use taking place at a site usually change the soil strength. For this reason, the use can represent a threat or stress for the site. Therefore, the evaluation methods applied here must
- enable **risk assessment**.

The methodological approach for evaluating soils can be portrayed on three directions (iteratively, effectively and causally) of increasing abstraction and scientific progress.

1. The simple procedural form is the iterative approach (trial and error). Here, a use is basically attempted at a site without any previous experience, and the results obtained increase the **knowledge of the site**. By changing the use, knowledge can be increased at the same site until satisfactory results or sufficient knowledge has been obtained. In principle, if such a trial is only performed at one site, these results are not transferable to other sites. In this way, a field trial associated with a yield determination enables determination of the actual productivity of a soil for a specific crop. However, to be able to also include the influence of varying weather conditions, the trial must be repeated over several years, making the procedure very elaborate. Should the trial be valid for a region, several trials must be distributed over characteristic sites throughout the region. Furthermore, the yield integrates the influence of all **site factors** and **plant cultivation methods**. That is why it is hardly possible to determine causal correlations for yield development or growth-restricting external factors with a simple field experiment. But this is necessary if the crop is to be systematically adapted to the site, or the site to the crop.
2. On the one hand, effective soil evaluation methods measure the achieved result of a use, yet on the other hand, they also describe the soil and the site. When such observation pairs of **effect** and **soil property** are obtained from many sites, a relationship between yield and soil properties can be determined through correlation. This approach is based on the assumption that similar soils in a region have similar site properties. Once such a correlation has been made, interpolations can be performed within the observed spectrum and other sites can be evaluated in terms of their suitability or capacity within an evaluation framework. This group of methods includes **phytosociological site surveys** and the conventional **soil analysis**. **Plant sociology** deals with the mutual relationships between the plant community (abstract vegetation units, e.g. association, subassociation, variation) and the site. Phytosociological systematics is based on the typical combination of species in the plant communities as a comprehensive expression of site conditions, i.e., on sociological and synecological criteria. It is therefore possible to use plant communities or groups of species in these communities as **indicators** for the site conditions. This has been used extensively for the ecological characterization of forest stands (Sect. 11.3) and was also used by Ellenberg (1979) on sites under arable and grassland use. However, they can only be used when restricting a climatically uniform growing area (so-called ecoregions). The suitability is to be considered within the framework of the entire species spectrum, in which the species are in

competition with one another. When eliminating this competition, the amplitude of the site distribution of a species is considerably greater, and as a result, usually less specific. The plant communities and ecological groups of species, as significantly more refined indicators, are used today instead of the **indicator plants** used in older literature. For vascular plants of Central Europe, Ellenberg offers a compilation of ecological groups, which e.g. characterize the water (and air) balance of soils with the wetness number (1 very dry, 5 fresh, 9 wet and low oxygen), the nitrogen supply with the N value (1 very low, 9 very high) and the remaining nutrient conditions with the reaction value (1 very acidic, 9 alkaline, calcareous). The moisture classification for alternate dry and moist to alternate wet and dry sites was refined by the AG Boden (Soils Working Group), (2005). In principle, agricultural or forestry **soil investigations** enable the analysis of all soil-dependent site characteristics and therefore also the explanation of growth-restricting influences. In both the plant sociology site survey as well as the soil analysis, quantitative statements about the productivity or the general capacity of a site are only possible if a calibration has been performed (cf. Sect. 9.5).

3. The third stage of the evaluation method is the **causal** procedures. Here (Fig. 11.1), the soil requirements for use or for the use system are defined, and on the other hand, the soil properties corresponding to the demands are recorded in the same units of measurement. Subsequently, the degree of fulfillment of the **site requirements** is determined through a static, or even better, a dynamic comparison between the site requirements and the **site properties** (Fig. 11.2). If the site requirements are not completely met and the use is still implemented, there is **strain/stress** on the site that can be determined using the same method. For causal evaluations, dynamic **water**, **matter** and **energy balance models** are increasingly used to predict the behavior of a site using scenarios and projections, even without trying the use. In this procedure, the field experiment and the soil analysis each have their place by quantifying the definition of requirements and soil properties. If soil evaluation at a site is already problematic due to the numerous parameters to be considered, it is all the more true for a **regionalization**. If the requirements for certain uses or certain crops are precisely known, it should, in principle, then be possible to regionalize the results of a soil analysis using maps or geographical information systems. Here, it is important that the decisive parameters for use are also recorded during mapping and in the legend of the soil map, and are used in the separation of mapping units. In most cases, this is only possible if the map shows **soil forms** that were recorded in terms of the **soil typology** and the **substrate typology**. For the ecological assessment, it is generally necessary to reach the lowest categories of the soil classification systems. In Germany, this would be the **subvariety**, and in the USA the

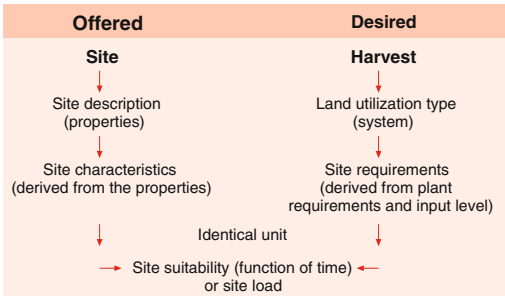

Fig. 11.1 Evaluation of the suitability and contamination of soils according to the causal principle

Plant requirement	Site characteristic
Rooting zone	Rooting depth and rootability
Water supply	Water regime
Air supply	Air regime
Energy supply (heat, light)	Energy regime
Nutrient supply	Nutrient regime
Stability	Site dynamics
Other requirements	Other characteristics
Ø Degree of fulfillment	

Fig. 11.2 Ecological site requirements and site characteristics for the example of plants

soil family. This is the only way to ensure that differentiating properties are also included. There is a general limitation to all evaluation methods: Each evaluation requires knowledge of the utilization system and the resulting requirements for land use as well as the most comprehensive knowledge possible of the soil or of the site and its limitations. It is based on the comparison between **requirements** and **supply**. As a matter of principle, it is not transferable, especially not when one of the two components, soil or land utilization system, is exchanged.

The results of soil evaluations can be presented in different ways depending on the method and current state of knowledge. In the iterative method, the results can easily be formulated in view of the intended use (e.g. the yield was 6 t ha^{-1} wheat or the soil bears a load of 2 MPa). In effective evaluation methods, it is often sufficient if a **threshold** or **boundary value** is identified, at which a specific use is possible or can be ruled out respectively when exceeded (e.g. if the rooting zone <25 cm, agricultural use is ruled out). A **qualitative** means of assessment and **categorical** classification have prevailed for effective or causal evaluation methods. Such a categorical classification is a discontinuous function, which separates up to 7 suitability or yield categories, e.g. *Agroecological Zones Project* (Sect. 11.5) or the suitability of sites for fruit cultivation (Sect. 11.2.3). If an individual parameter is regionally decisive for the land use and a positive or negative correlation can be determined between the success of the use and this parameter, then an arbitrary, **scalar** distribution can be made (e.g. dependence of wheat yield on the available nitrogen). Such scales can be shown in part of a non-linear dependence, if the differences are of interest for economic use.

Today most soil evaluations are carried out **parametrically**. In doing so, different parameters that are decisive for a specific use are linked for an evaluation. Such multivariate dependencies for a use can be portrayed with **vector addition**, with **linked estimation tables** or with nomographs. The scale used for the evaluation is then generally dimensionless and continuous. For simplification purposes, it can be reverted back to a categorical scale using threshold values. If possible, the parameters should be linked according to the effect of these parameters. **Additive**, **multiplicative** and complex **functional** methods are most commonly used. **Simulation models** represent a further development of the parametric method, which can map processes and therefore provide a complex, realistic decision-making aid.

When considering such systems, it is important that **optimal success** is achieved, by which a **minimum of input** as well as a minimum of losses occur. The system should enable testing for **sustainability** through repeating the use at different periods. All soil evaluation methods must be secondary to the goal of preserving soils, in particular in their biological capacity as well as in shaping the ecological balance of the landscape in terms of an optimal land use and the highest possible degree of stability.

11.2 Evaluation for Taxing and Agricultural Use

In Germany, the law for the assessment of arable and grassland soils (**Bodenschätzungsgesetz**) **(German soil taxation law)** (from 16.10.1934/ last revision from 20.12.2007) made it possible to numerically record the productivity of soils under agricultural and horticultural use.

The soil evaluation provided an excellent overview of German soils in cultivation. The relationships between yield and soil value number are not very close since cultivation measures, the weather conditions and economic factors strongly influence the yield. Since then, the entire agriculturally used area in Germany has been recorded by the soil taxation and follow-up assessments are being performed.

The soil values only characterize the productivity of soils as a whole. They do not provide the reasons leading to a poor evaluation. This is why soil values are particularly unsuitable for land use planning or agricultural consultation when site ameliorations are planned through appropriate amelioration measures.

In this respect, the overall estimation results, including the soil profile description provides a higher information value (see below). However, comprehensive conclusions would only be possible if all site properties were analyzed.

11.2.1 Soil Evaluation—German Soil Taxation Framework

In the German Soil Taxation Framework, the soil properties of a field site are evaluated by the soil rating, whereas additional consideration of climate and relief gives the field rating (Fig. 11.3).

The **soil rating** is an approximate measure for the productivity of a soil. It is based on the soil description from analytical soil pits as well as of additional boreholes. The description includes:

1. The soil texture,
2. The geological age (or parent rock) and
3. The soil development stage.

1. **The soil texture** (=textural class) of the profile up to a maximum depth of 1 m. A distinction is made between eight mineral soil textures and one peatland group. If the profile consists of different soil textures, then the overall character of the soil is expressed by the **average soil texture**. During soil evaluations, soil classification according to the soil texture is only performed according to the content of suspended particles in the soil (fraction <0.01 mm) (Table 11.1).
2. **The geological age** of the parent rock. According to this, the soils are divided into four groups: **Diluvial soils** (D), developing on deposits from the glacial periods (except for loess soils), including soils from tertiary deposits; **loess soils** (Lö); **alluvial** or **floodplain soils (Al)** on the most recent fluviatile deposits in lowlands, floodplains and at the coast; **weathered soils** (V), developed from Paleozoic or Mesozoic parent material without relocation. Stone-rich weathering soils from crystalline rock are sometimes called Leptosols (Vg).
3. The term **soil development stage** reflects the developmental stage reached by a soil during its formation from an immature soil through a stage of maximum productivity to severe depletion and acidification. The depth of the root zone and the plow layer play an important role for the classification in the soil development stages. A distinction is made between seven soil development stages, whereby stage 1 describes the most favorable state, and stage 7 the most unfavorable state, i.e. the least development or the most severe depletion (Fig. 11.4). The evaluation of peat soils is primarily based on the properties of the organic matter and the groundwater level.

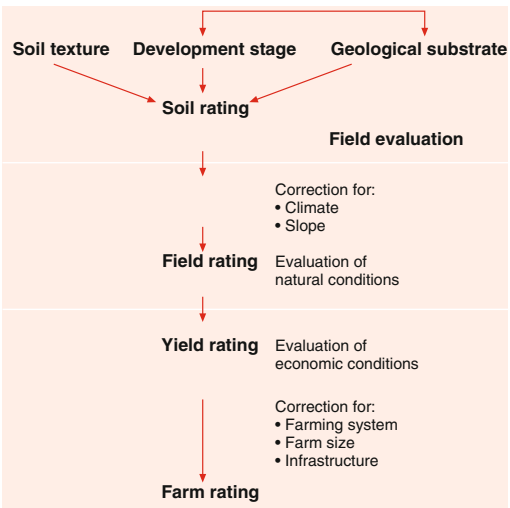

Fig. 11.3 Flowchart for the German soil taxation

Table 11.1 Subdivision of texture according to the German soil taxation

Fraction <0.01 mm (%)	Soil texture	Abbreviation
<10	Sand	S
10–13	Slight loamy sand	SI
14–18	Loamy sand	IS
19–23	Strong sandy loam	SL
24–29	Sandy loam	sL
30–44	Loam	L
45–60	Clayey loam	LT
>60	Clay	T

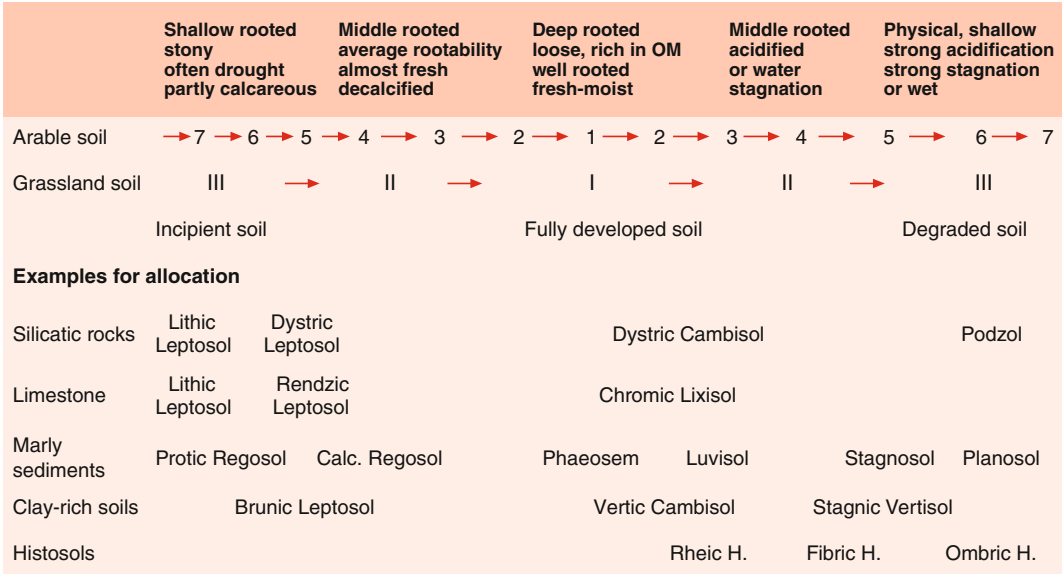

Fig. 11.4 Diagram of soil development stages (German soil taxation) for field and grassland sites with examples of the assignment of soil types (units)

Soil development stages for cultivated mineral soils can be assigned characteristic features:

Level 1: Crumbly structure of the plow layer, oxygen-rich subsoil, gradual transition from the topsoil to subsoils containing mostly $CaCO_3$; no mottles, no signs of acidification or compaction.

Level 3: Humus content of the topsoil lower than in Level 1, rougher transition to the subsoil, which often exhibits pale mottles and grey coloration; greater depth of decalcification, onset of acidification and first signs of translocations.

Level 5: Clearly delimited topsoil, occurrence of a depletion zone, first signs of compaction of the subsoil and the onset of podzolization or reductomorphism, usually severe acidification.

Level 7: Clearly delimited topsoil; strong acid bleaching over a consolidated hardpan or water bleached over strong mottling or compacted bog iron.

Depending on the soil type, geological age of the parent rock and soil development stage, soils in the **German Soil Taxation Framework** (Table 11.2) were assigned specific ratings (soil values) with greater or smaller ranges. These soil values are ratios; they express the differences in net yield, which are solely due to the soil properties. The best soil receives a soil value of 100 (Chernozems of the Magdeburg Börde).

For the establishment of the taxation framework, climate conditions and land forms as well as economic conditions are defined as reference values: 8 °C mean annual temperature, 600 mm precipitation, level to slightly inclined location, close to optimal groundwater level and economic conditions of medium-sized farm operations in Central Germany.

According to B. Heinemann, the soil values—with the soil texture and soil development stage in brackets—for the Chernozems consisting of loess vary between 85 and 100 (L1–L2), for Rendzic Leptosols with an Ah horizon <10 cm between 35 and 50 (LT5) and >25 cm between 50 and 70 (LT3), for Luvisols consisting of loess between 70 and 80 (L3), for Stagnic Luvisols consisting of loess between 65 and 70 (L4), for Pelosols (Vertic Cambisols) between 36 and 60 (T5–LT4), for Stagnosols consisting of loess between 35 and 65 (L7–L5) and consisting of calcareous glacial till between 30 and 50 (lS5–sL5), for Cambisols

Table 11.2 Section from the German soil taxation framework for agricultural soils (soil texture: sandy loam)

Soil texture	Parent material	Soil development stage						
		1	2	3	4	5	6	7
sL Sandy loam	D	84–76	75–68	67–60	59–53	52–46	45–39	38–30
	Loess	92–83	82–74	73–65	64–56	55–48	47–41	40–32
	Al	90–81	80–72	71–64	63–56	55–48	47–41	40–32
	V	85–77	76–68	67–59	58–51	50–44	43–36	35–27
	Vg			64–55	54–45	44–36	35–27	26–18

between 35 and 65 (Sl3–sL3), for Podzols between 10 and 20 (S6–S5, hardpan-fragipan), for Rankers (Dystric Leptosols) = 10 (S7) and Plaggensoils (Plaggic Anthrosols) between 30 and 40 (S3–S2).

The **field rating**: Should climate conditions and land forms deviate from the reference values, the soil values are accordingly subject to additions or reductions; the field rating is provided as a measure for productivity resulting from the yield potential and natural factors. The following examples provide a reference point for the amount of additions and reductions.

In low mountain ranges of the Bavarian Forest with unfavorable climate conditions, there are reductions of up to 30 %, in contrast, additions of 12 % in the climatically favorable Cologne Lowland, even between 16 and 18 % on the Bergstrasse (Upper Rhinegraben). The high precipitation climate at the coast of the German Bay has a very favorable effect for sandy soils (additions of 12 %), however, not for heavy marsh soils (reductions of 8 %). At a slope of 5°, there are deductions of 2–5 %, and for a 20° slope, 18–26 %.

Thus the overall evaluation result is e.g. **L 4 Al 65/70**. This represents the loamy soil texture, Level 4 soil development, alluvial rock type, a soil value of 65 and a field rating of 70.

11.2.2 Soil Evaluation—Grassland Taxation Framework

With the **assessment of grassland**, the evaluation is less differentiated according to the soil texture and soil development stage, since here mainly water, air and temperature conditions are decisive for the productivity. Only four soil textures and the peatland group are differentiated as well as three soil development stages (Fig. 11.4). Classification according to the parent rock is no longer required. In contrast, the **water and air conditions** are divided into five levels, whereby Level 1 (fresh) characterizes the best, and Level 5 (wet to boggy or very dry) the worst conditions. **Climate classification** records the average annual temperature in three groups (a ≥ 8.0 °C and more, b = 7.9–7.0 °C, c = 6.9–5.7 °C). The values resulting from soil texture, development stage, water conditions and climate are the **grassland base values**, which lead to the **grassland values** through supplements and reductions taking account of local characteristics such as vegetation period, crop, atmospheric moisture, and land form. The **grassland assessment** corresponds to the German Soil Taxation (Table 11.3).

11.2.3 Assessment for Special Crops

For **fruit cultivation sites**, an assessment scheme was developed based on soil identification (depth to bedrock, soil texture, carbonate content and phytosociological surveys (Ellenberg values), taking into account the exposure and inclination (Sect. 7.1.5) as well as heat and the risk of late frost.

Vineyard soils, mainly Regosols or Anthrosols (German Rigosols) (see Sect. 7.6.5), were classified in wine-growing areas into one of eight site levels according to the parent rock, soil texture, stone and carbonate content, plant-available water, ecologically effective wetness

Table 11.3 Section from the grasslands taxation framework (soil texture: loam)

Soil texture	Soil development stage	Climate level	1	2	3	4	5
L Loam	I	a	88–77	76–66	65–55	54–44	43–33
	(75–70)	b	80–70	69–59	58–49	48–40	39–30
		c	70–61	60–52	51–43	42–35	34–26
	II	a	75–65	64–55	54–46	45–38	37–28
	(60–55)	b	68–59	58–50	49–41	40–33	32–24
		c	60–52	51–44	43–36	35–29	28–20
	III	a	64–55	54–46	45–38	37–30	29–22
	(45–40)	b	58–50	49–42	41–34	33–27	26–18
		c	51–44	43–37	36–30	29–23	22–14

index and heat conditions. From this, crop recommendations (variety selection) are derived.

11.3 Assessment for Forest Use

Central European and worldwide forestry is much more strongly directly linked to the natural properties of their forest stands than agriculture. The length of time from germinating or planting until harvest of trees ready for felling is anywhere from 50 to 300/120 years. From a profit and an investment point of view, these long periods of time generally exclude the use of soil tillage, the application of fertilizers or other soil additives to increase yields. For this reason, the relatively few land improvement measures that have been implemented in the past mostly served to eliminate very serious site weaknesses, such as **extreme acidification**, **air deficiency**, **formation of hard pans** and degradations after heavy **litter raking**, and were implemented for economic supply and employment reasons. In addition, the use of light soil tillage (harrows, cultivators) and occasional starter fertilizer is widespread in order to facilitate the stand establishment.

The recognized general principle of 'nature-oriented forestry' only allows for soil tillage measures for site maintenance and restoration aspects. This includes **soil protection liming** to increase the buffering capacity towards anthropogenic acidic substance depositions in forest soils. Where it cannot be avoided, traffic is focused on log trails.

One fundamental land use limitation results from the weak site suitability of the sites historically remaining under forest. Despite the absolute or relative unsuitability of many forest sites for primary agricultural use, the forest, depending on the distance from the villages, was used as agricultural auxiliary areas throughout the entire Middle Ages, and still today in the residual areas. Forest use was only one among many uses, which only became increasingly important in the 17th century due to the capital needs of the landlords. Wood pastures, the use of litter and sod, and burning wood ashes are some of the formerly vital but devastating forest uses, which led to the export of the low nutrient capital on the often already primarily base-poor sites. In Europe, the forest pattern of the Middle Ages corresponded in many cases to a forest pasture as commonly seen e.g. in Spain today. Dense forests, which shape our current forest pattern, were only established in the 18th century.

Loss of bases through the input of anthropogenic acid producers on the one hand, base accumulation through ash and lime dust on the other hand, and especially recent changes in the nutrient balance due to the increasing nitrogen load in the depositions has led to more recent site changes in forest soils. The forested area in Central Europe has grown substantially during the 19th and 20th century through the abandonment of agricultural use.

Accordingly, forest soils are soils that, on the one hand, have only been minimally altered through direct tillage, but due to their weak buffering capacities, have been significantly

altered in their soil chemistry through indirect disruptions.

Today, the principle of **sustainability**, comprehensively in terms of the preservation and enhancement of the utilization, protection and recreation functions of the forest, characterizes not only in Central Europe forestry. Proper eco-management with the general principle of 'nature-oriented' forest requires knowledge of the forest site as the most important basis of the forest ecosystem. The protection of the forest soils itself is also a component of sustainability concept. Forestry site mapping provides the basis for this purpose.

The pioneers for site mapping methods widely used in Germany were G.A. Krauss in Southern Germany and W. Wittich in Northern Germany. **Forestry site surveys** provide a framework for the definitions of terms and the basic surveys of federal forestry administrations.

The objective of forestry site mapping is to record the **forest site** as a whole with the environmental conditions that are important for the **growth** of forest trees. The site properties are assessed using the site characteristics.

The smallest ecological forest mapping unit is the **site type** (i.e. **site unit**). This is a summary of sites, which do not deviate substantially from one another in terms of their silvicultural possibilities and their endangerment and have the same productivity. In order to describe a site type for forestry purposes, statements on the following site characteristics are required:

- Climate conditions (heat supply)
- Depth to bedrock and rootability
- The influences of stagnant water and groundwater, soil water balance (water and oxygen supply)
- Soil chemistry (nutrient supply and turnover).

The growth of the main trees species (pine > spruce > beech > oak) responds very strongly to the water balance, which therefore plays a significant role in mapping methods. In the Federal States with high geological diversity, the parent materials are strongly emphasized.

'Combined methods' have prevailed over pure phytosociological or pedological mapping methods. Classification and mapping using these methods require the geographical, petrographical, pedological, climatological, vegetational, pollen-analytical and historical facts and testing methods according to pragmatic considerations. The significance of individual indicators is attuned to the respective site spectrum.

In terms of the fundamental principle of the procedure, two different approaches are used (Figs. 11.5 and 11.6). The most common is the **two-stage** or **regional approach**. Here, the first step involves a regional classification of the landscape into ecoregions and ecodistricts, frequently after a rough preliminary survey of the site.

At the ecoregion level, the focus is mainly on geological-geomorphological criteria, in contrast, at the ecodistrict level, a uniform climate and landscape history play an important role. In landscapes with strong relief such as the low mountain ranges, elevation zoning is also carried out. Within these units, the local mapping units are defined and delimited. The strongest drives for the development of this method come from the **Southwest German site survey method** of Baden-Württemberg.

The regional method has the advantage that it can be used within the regional units with only a few mapping units. Sites with low (area) significance within an ecodistrict are added to comparable mapping units. This method requires a high degree of local previous knowledge on behalf of the cartographer and user. The properties (productivity, chemical properties) of the respective mapping units are determined statistically. One disadvantage is the limited possibility of a supraregional analysis.

At the regional level, ecoseries are first segregated as main groups within an ecodistrict (Fig. 11.6). **Ecoseries** are substrate series that are linked within an ecological framework, which is determined by the altitude level and ecodistrict. The substrate series themselves are local groupings of parent rocks with a characteristic spectrum of soil textures. It is essential that they form a comparable rooting zone in terms of the soil physical and chemical properties.

Since it is of utmost importance for the stability of forest stands, an important criterion is

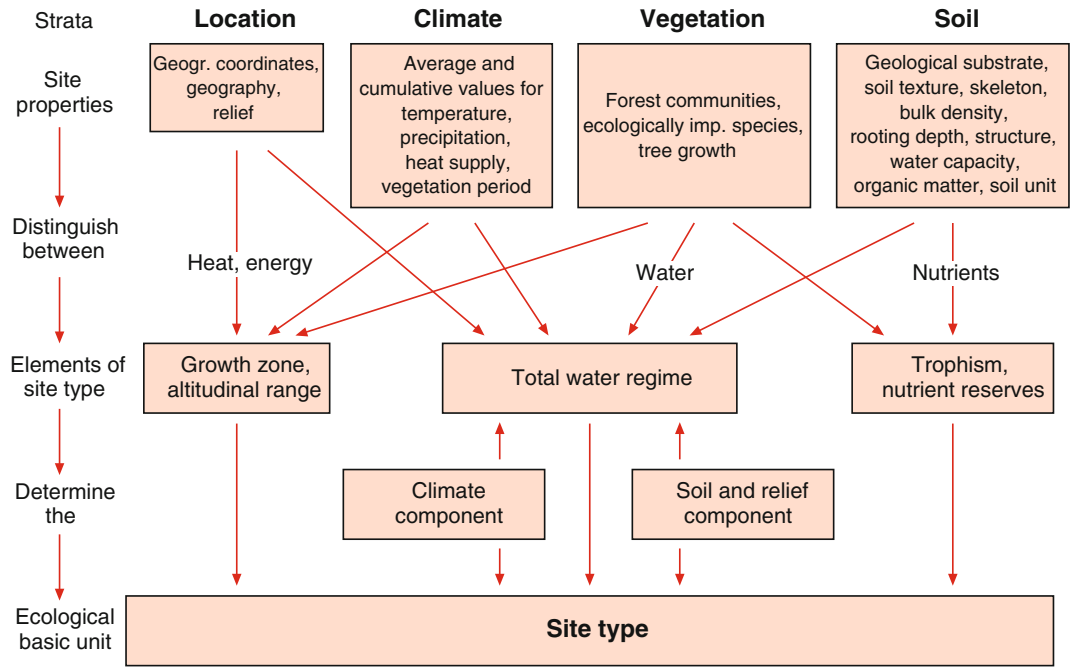

Fig. 11.5 The derivation of the type of site in a one-stage or supraregional forestry site mapping method

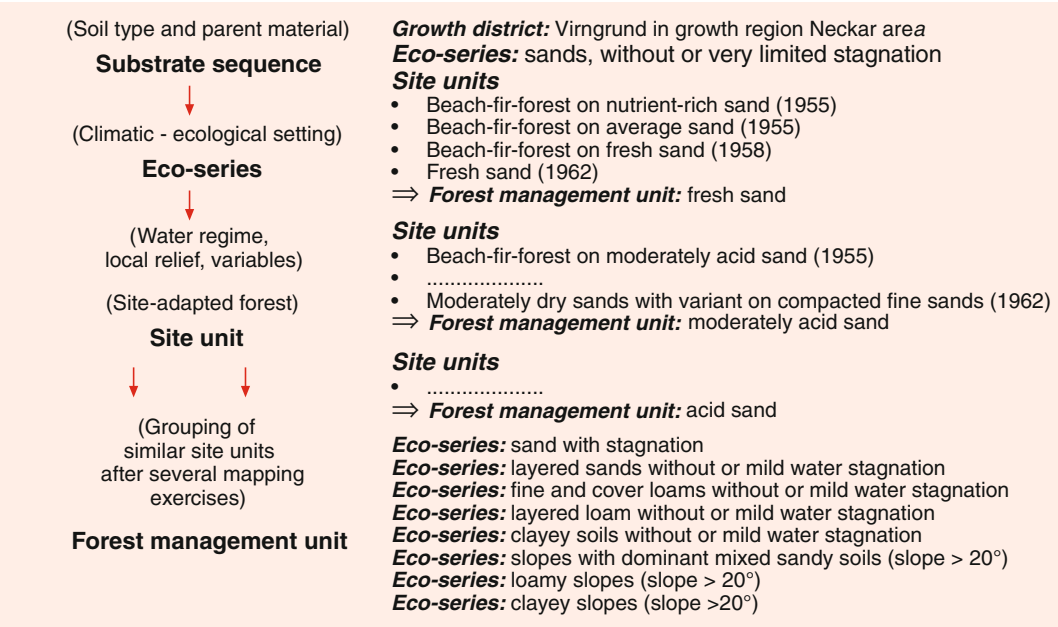

Fig. 11.6 Example of a site classification for the Virngrund ecodistrict (24,000 ha) in a two-stage or regional method (Baden-Württemberg)

the differentiation of terrestrial substrate series or ecoseries from those influenced by groundwater and stagnant water. Relief elements are also considered in the setup of the eco-series (level sites and gentle slopes, hillsides, if necessary subdivided into summer and winter hillsides).

The eco-series become **site types** through a further classification according to water regime levels and acidification states as well as according to anthropogenic topsoil disturbances (e.g. litter raking), whereby ground vegetation in the form of ecological groups of species is frequently included. In order to characterize the silvicultural potential of a site type, it is assigned with a potential forest community.

In the **one–step or supraregional method**, the elements for characterizing the site type are developed directly from the location, climate, vegetation and soil factors (Fig. 11.7) on a Federal State definition level, regardless of regional subdivisions. To do so, the factors for stand growth, which are **water—nutrients–heat**, are scaled. The site type then results from the free combination of the individual site components (Fig. 11.7). This method enables supraregional comparison of the sites. This possibility is achieved with an oversimplification of aspects in the area of soil and substrate classification as well as vegetation assignment.

A very differentiated site mapping method was developed in the East German Federal States. There, a distinction is made between the conservative regular site properties (soil texture, substrate, climate) and the variable state site properties (humus form and immission form). Unlike the West German methods, the soil forms (substrate and soil texture) play a significant role. Local variations of the reference soil types are mapped. These local soil forms are centrally managed in the form of an open catalogue. For application purposes, standard and state forms are summarized into site groups. Parallel to this, a method was developed to summarize forestry data from the local level (topical dimension) for a comprehensive exploration of the natural environment on the level of natural ecodistricts (mesochores) or natural ecoregions (macrochores). Accordingly, the East German ecoregions were inductively derived.

Examples for the classification of individual components in forestry site mapping methods

As a matter of principle, the same site characteristics are compiled in one- and two-stage method site classification. However, the one-stage methods require the development of supraregional scales. With two-stage methods, the focus is on the differences between the sites within the respective ecodistrict.

The **climate classification** includes **temperature** and **precipitation conditions**, and sometimes also the **degree of continentality**. The thermal conditions, predominantly determined by the macroclimate, are differentiated as heat or altitude levels through a combination of climate and vegetation data.

The **water balance or regime** is one of the central parameters for forestry site mapping (Table 11.4). For its classification in stagnant

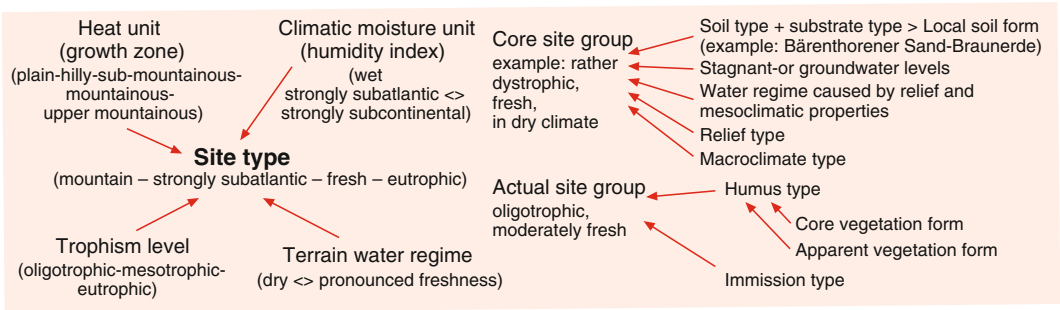

Fig. 11.7 Examples for the site classification in a one-stage or a supraregional site mapping method (*left* Hesse, *right* New Federal States)

Table 11.4 General definitions of water balance levels in forestry site mapping

Very dry	During the vegetation period (VP), significant water deficits can occur rapidly only a short time after precipitation due to the extremely low available water retention capacity of the soils (shallow or strongly permeable, skeleton-rich)
Dry	Regular, longer lasting significant water deficit during the VP
Moderately dry	Temporary significant water deficit during the VP
Moderately fresh	Water deficits can still occur temporarily during the VP
Fresh	Good year-round water supply as a result of a high available water retention capacity; water deficit is only conceivable in pronounced dry periods; high proportion of coarse pores in the soil, therefore also no lack of air with water saturation during the VP
Very fresh	Also during longer dry periods, there is always sufficient water available for tree vegetation; in areas with high levels of precipitation, a lack of air could occur temporarily in deeper soil layers; frequent stagnic mottles in the subsoil (deeper than 60 cm below the soil surface), particularly in loamy/clayey soils

water- and groundwater-free soils, the water balance or moisture levels 'very fresh'–'very dry' are generally used. The general definitions of these water balance levels are initially only of a descriptive nature and are only suitable for a qualitative assessment. With two-stage methods, they enable a relative classification within an ecodistrict, whereby the entire scale range is generally used. Therefore, the sites assessed in this way cannot be compared at a supraregional level.

With one-stage methods, water balance levels must be more precisely quantified. One approach to this is the differentiation into so-called **landscape water regimes**. These result from the water storage capacity of the respective site with additions or reductions for the influence of exposure and relief. The assessment of the overall water balance must then include the atmospheric moisture.

The classification with overall water balance levels goes one step further. This not only includes the passive elements, but also the evaporation. Such a prediction model was developed in Rhineland-Palatinate. Instead of the climatic water balance, precipitation groups are used, which also respectively include a specific thermal climate at a state level. The basic principles and scaling were developed based on investigations performed on spruce and beech trees in a narrow age group.

Stagnant water (partial water saturation with rain water) is characterized as being waterlogged, alternate wetting and drying, moderate alternate wetting and drying, weak alternate wetting and drying, or ground alternate wetting and drying (freshly stagnant), moderately alternated drying and moistening and alternate drying and moistening. The classification results from the assessment of the depth of impeded drainage at the beginning of the vegetation period and the persistence of the stagnant water. **Groundwater** is classified into the following water regime levels: wet, moist, (slope water supplied), ground moist or ground fresh ('ground' meaning water supplied in subsoil).

For the **nutrient regime**, the vegetation trophic conditions (dystrophic, oligotrophic, mesotrophic and eutrophic) are used. This should comprehensively characterize the nutrient supply according to type and diversity (intensity, variability, diversity), which is expressed in the biological activity of the soil, the intensity of the substance/chemical transformation, the occurrence of demanding plants and the biodiversity. Because these states and processes depend on the site heat conditions, the water regime and the rooting zone, they must be taken into consideration. In East Germany, the concept of nutritive levels (poor–fairly poor–moderately nutrient content–strong–rich) is used. The classification is performed empirically from the classification of the humus form, ecological species groups as well as from knowledge on the chemistry of the parent substrate and soil texture.

The classification is very reliable on sites with a rich nutrient supply; however, it exhibits weaknesses in the moderate and low nutrient range. In this site spectrum, the soil assessment in the forest demonstrates extensive acidification and base depletion in the soils, independent of the substrate. The empirical trophic classification of the site mapping results in a greater differentiation. One problem is the lack of reliable weathering rates of silicates for the respective parent substrates. On weak sites, the influence of historical forestry methods, established tree species and anthropogenic topsoil disturbances/disruptions on the site potential is particularly strong.

The **results** of the site mapping are portrayed in maps (1:5000 or 1:10,000) and documented in a report; they can be viewed at forestry offices or intermediate forestry authorities. The mapped forest sites are evaluated according to the following aspects:

- Tree species suitability (competitive strength, manageability, reliability, growth rate, quality, yields, ecological significance)
- Forestry methods (rejuvenation, maintenance and harvest strategies)
- Landscape conservation significance of sites
- Risk reduction (windthrow, soil acidification, pest deposition)
- Damage prevention (soil compaction due to traffic, etc.).

11.4 Evaluation for Societal Requirements Without Use of the Primary Production

While soils were originally evaluated for economic reasons, e.g. for high-yielding forestry or field management, today the focus is increasingly put on ecological soil evaluations, which focus on the protection of the soil, and technical evaluations, which serve civilization.

In addition to their function as a site for crops, soils have numerous other potentials (cf. Sects. 10.1 and 11.7). These can be subdivided into ecological potentials, e.g. retention body in the water cycle' (Fig. 11.8), filter and buffer for toxic substances as well as direct utilization functions for humans, such as development, traffic, recreation areas (Fig. 11.9) and raw material deposits (cf. Sect. 1.2).

Each use involves different requirements for the soil properties, which in turn are implemented differently on the various soils. Soil evaluations aim to illustrate the capacity of different soils. Particularly in residential areas, the focus is on transforming pedological findings into reliable conclusions for planning purposes and soil conservation concepts.

Various proposed methods currently exist to determine these functions, which differ depending on the objectives. As a matter of principle, the following basic evaluation patterns can be distinguished:

Suitability evaluation: This involves recording the capacity of sites for various uses. In doing so, the natural suitability is described depending on ecological factors.

The basis of the evaluation is a comparison of the use requirements with the site properties. Evaluation criteria are established for the considered uses, which are derived from the requirements for the respective use at the site. In doing so, the investigation or limitation of use-specific characteristics is essential. Different uses have different requirements and thus result in different limitations. The requirements must be represented such that they can be compared with data measured or derived from the site. Evaluation levels are defined for each criterion and describe the extent to which the requirement has

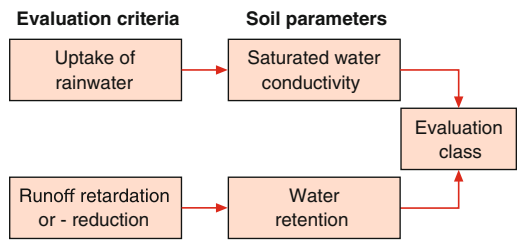

Fig. 11.8 Assessment of the function as "compensation body in the water cycle"

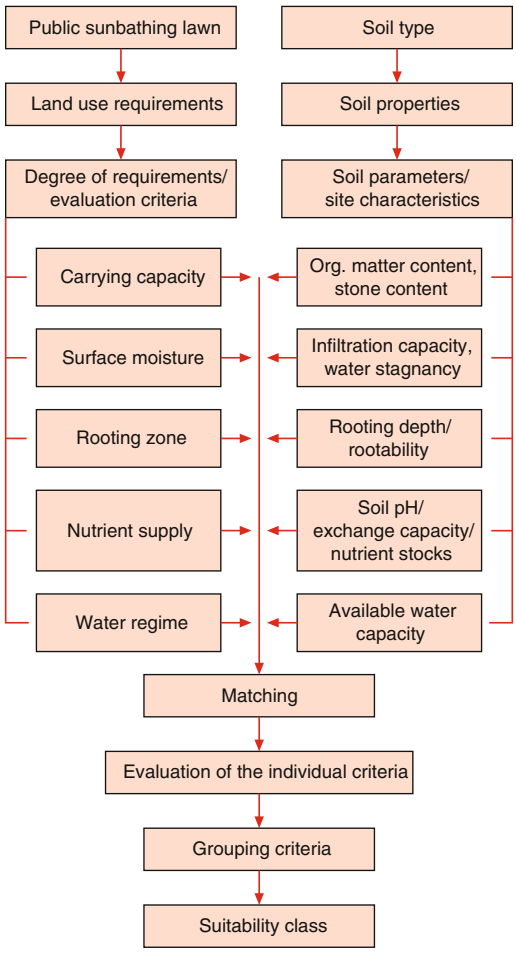

Fig. 11.9 Approach for determining the suitability for use of a site as a sunbathing meadow

been fulfilled. The definition of these levels represents the actual evaluation step.

It is assumed that the suitability primarily depends on the degree of fulfillment of the requirements by the site. Figure 11.9 shows the procedure for determining the suitability for use as a sunbathing or picnic meadow. The criteria for the site properties determining the growth of lawns include rooting depth, nutrient and water supply as well as the basic conditions for the use and load-bearing capacity (carrying capacity) of the surface.

Ecological function evaluation: The ecological function evaluation essentially refers to the evaluation of the soil's natural functions, as mentioned in the German Federal Soil Protection Act (BBodSchG). The example illustrates the evaluation of the function retention body in the water cycle' in accordance with 'Booklet 31' (Umweltministerium B.-W, ministry of the environment Baden-Württemberg 1995).

The determination takes place in three partial steps (Fig. 11.8):

1. Determination of the total hydraulic conductivity for the control area
2. Determination of the water storage capacity
3. Evaluation of the soils in their function as retention body in the water cycle'.

Causal relationships between soil parameters and capacity are represented and qualitatively assessed. This means that the higher the ks value and the storage capacity, the higher the capacity of a soil as a retention body in the water cycle and it is classified into an even higher evaluation class.

Contamination load evaluation: A distinction is made between an evaluation of the actual degree of contamination with regard to a threat to other environmental media and to human beings (**remedial soil protection**) and a contamination evaluation for planned use interventions/impacts (**preventative soil protection**, sustainability).

For the current degree of contamination, e.g. with certain contaminants, test and precautionary values have been defined (Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV), 1999) depending on the form of use, which can lead to use restrictions or remediation recommendations.

When predicting the impacts resulting from a future use, the degree of the deterioration/degradation of the soil properties or functions that are strained and damaged from the particular use is evaluated. The degree of contamination becomes higher the more intensive the use impacts and the higher the ecological value of the soil.

Evaluation principles: The acceptance of each evaluation method depends on the extent to which its statements can reflect real conditions. Even if the evaluation method can only partly record and represent the complexity of ecological correlations, the use of evaluation methods is

sensible and indispensible for all planning and environmental protection measures. Each decision requires an evaluation. Through the implementation of standard evaluation methods, decisions are being made more objectively and more transparently. The accuracy of the expected statements is sufficient for decision-making purposes in most cases. Where required, the accuracy or applicability can be improved through additional investigations. Decisive for this is the transparency and traceability of the evaluation.

11.5 Common International Soil Evaluation Methods

There are a number of methods worldwide for evaluating soils or sites in terms of their suitability for agricultural use. None of these methods have gained the same public acceptance and implementation as the German Soil Taxation Law (Sect. 11.2) (FAO 1976, 1978).

11.5.1 Storie Index Rating (SIR)

The Storie index was developed in California for the taxation of forestry and agricultural areas, and ranks among the most well-known multiplicative, parametric evaluation systems.

The first version appeared in 1933 and has been revised several times throughout subsequent years. The Index that is still in use today is depicted in the box (below). Groups are formed for each factor according to Soil type, Texture, Slope inclination and Miscellaneous and the degree of productivity is evaluated as a percent value. All factors (x : 100) are multiplied; and the final value is expressed in percent (%). The advantage of this system lies in its versatile and easy application. The individual factors can also be easily adapted or exchanged according to the local conditions. The multiplicative structure of the SIR is unfavorable in areas where the factors with the worst evaluations dominate in the end result, while in additive systems, the actual limiting factors do not carry sufficient weight. These disadvantages can be minimized by weighting the individual factors appropriately.

11.5.2 Fertility Capability Classification (FCC)

In contrast to the morphological or genetic systems, the **Fertility Capability Classification** represents a technical classification system. The objective is to group the soils according to their type of soil fertility problems using texture and a number of soil fertility indicators, and to use these to derive soil ameliorating measures (Table 11.5).

The texture in the Ap horizon (and also in the subsoil where there are great differences in texture) determines the classification in the topmost systematic unit, the soil type. The soil type is then described more precisely at the next stage of the system using the soil fertility indicators. In doing so, each indicator is assigned a threshold value. Depending on the indicator, a value that falls below or exceeds this threshold value indicates a soil fertility problem. In this case, a corresponding suffix is added to the soil type as a small letter [e.g. L_{ehk} means loamy soil with good water holding capacity, average infiltration rate, low nutrient retention (e), low to average degree of acidification (h), and low potassium supply capacity (k)]. At the same time, amelioration measures can be deduced from the suffixes, which would contribute to an improvement of the site [e.g. with (h) liming for Al-sensitive

Storie Index Rating (SIR)

SIR =	**A** Soil type	x	**B** Texture	x	**C** Slope inclination	x	**D** Miscellaneous Nutrients Erosion Drainage, etc.

Table 11.5 Soil fertility indicators for subdivision of soils according to the *Fertility Capability Classification* (Sanchez et al. 1982)

g = Gleyic, oxygen deficiency
d = (Dry Month) Duration of the dry period
e = Low effective cation exchange capacity = CEC_{eff}
h, a, c = Acidity within 50 cm of the soil surface: h = degree of Al saturation; a = Al toxicity; c = katteklei, jarosite acid sulfate soil
i = High P fixation by iron
v = Vertic, strong Vertisol properties
k = Low K reserves
b = Basic reaction, alkaline soil pH
‘ = Gravel and stones
% = Slope percentage, slope inclination

crops is required]. Therefore, the FCC allows a characterization of the soil according to its problems caused by soil fertility as well as any required soil improvement measures.

11.5.3 Land Capability Classification (LCC)

The **Land Capability Classification** was developed by the USDA and evaluates soils (including the relief) primarily for agricultural use (Klingebiel and Montgomery 1981). Eight classes represent the highest systematic level, whereby soils assigned to the first four classes (I–IV) are described as being usable as arable land. Soils falling in the remaining four classes (V–VIII) are only suitable for pasture or forestry use (Fig. 11.10). The assessment of soils usable as arable land is performed according to the potentials and limitations for sustainable production of climatically adapted crops in the observed region. Soils that can only be used as pasture or for forestry are then subdivided according to the risk of soil degradation in the event of improper cultivation and utilization measures. Depending on the type of use restrictions, subclasses can still be formed within the eight classes.

The soil properties that are used for evaluation in the *Land Capability Classification* are the water storage capacity, depth to bedrock, rock content, structure and workability of the soil, permeability of the subsoil, hydromorphism, erosion sensitivity, salinity, alkalinity and nutrient supply. Added to this are terrain characteristics such as slope inclination and flooding risk. Depending on the data, relative restrictions or

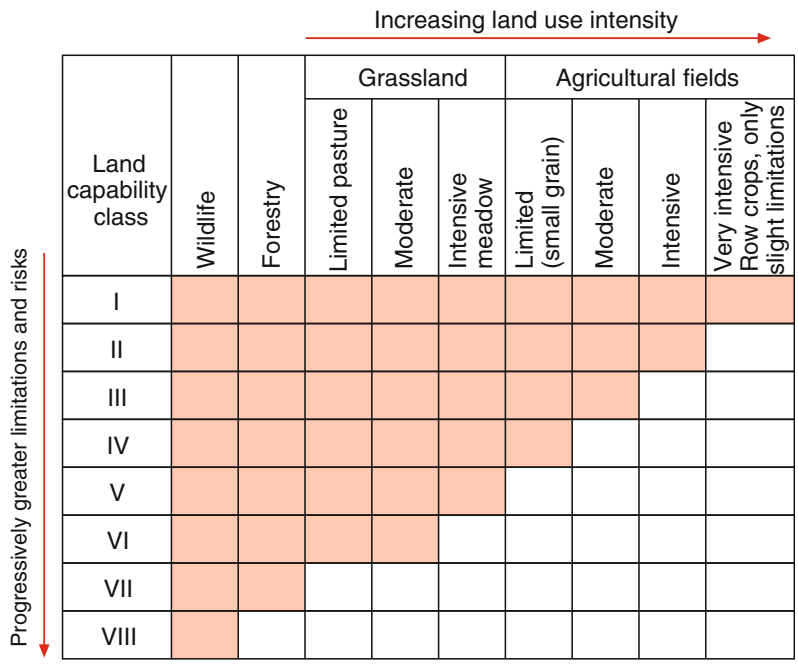

Fig. 11.10 Relationship between the LCC classes and suitability for use in rainfed agriculture. *Shaded area* suitable, *unshaded area* unsuitable

even absolute threshold values are defined for the individual soil properties, which determine the assignment of a soil to one of the eight classes (Fig. 11.10). Conclusions can be made from the evaluation results on the general suitability of the soil for agricultural use, the type of restrictions, and in particular, soil conservation or improving measures. For example, a soil with a classification of III would indicate significant restrictions in the air and water supply (w = wetness), which necessitate special amelioration measures.

The advantage of the LCC over the FCC lies in the possibility of assigning soils to a suitable type of use. On the other hand, the evaluation of soil properties with regard to the extent of their limiting effect is generally based on relative, experience-based assessments.

11.5.4 Land Suitability Classification (LSC)

Since 1950, the FAO has been striving to enable improved site utilization in the poor regions of the world. In doing so, it was realized that pure science is incapable of helping farmers if specific local features of the product, the markets, the nutritional habits, and the social dependencies are not taken into account. That is why basic patterns of evaluation methods were developed, which, in addition to soil evaluation, also include socio–economic concerns (Fig. 11.11). The areas are processed either one after another or in parallel. Over the course of time, the parallel working method has prevailed because it is faster, and all specialists can exchange information during the process, even if no one already has a final result. The LSC common today is an important ecological and production-related technical part of land evaluation.

The Land Suitability Classification (FAO 1976) was created to establish a globally applicable framework for site evaluation in terms of agricultural production. In contrast to the above-mentioned classification systems, the LSC attempts to include the overall site complexity (climate, relief, soil) in the evaluation. Furthermore, the evaluation framework creates the opportunity to perform the site evaluation for precisely defined types of use or for individual crops. This corresponds to the principle of differing adaptability of plants to the site; however, it can lead to different evaluations of one and the same site, depending on the type of use or crop being considered.

In the simplest case, the evaluation method compares the properties of the site with the requirements of a crop. In doing so, both **climatic** (precipitation regime, thermal conditions, atmospheric moisture, solar radiation) as well as **edaphic site properties** (water and air regimes, nutrient regime/supply, salinity and alkalinity) are taken into account. Each site characteristic is evaluated according to whether and to which extent they represent a constraint for the considered crop. In the qualitative site evaluation, the sites are classified into **suitability classes** (Fig. 11.12), whereby differentiations can be

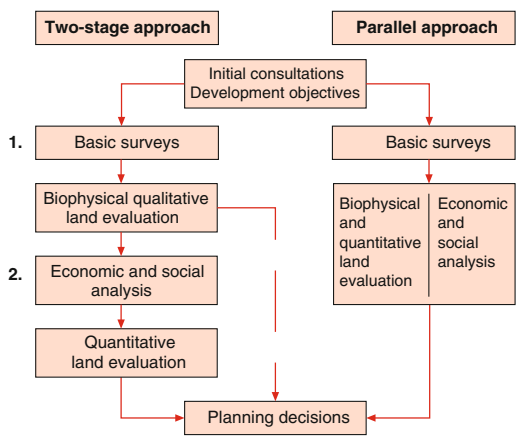

Fig. 11.11 Representation of both methods in land use planning according to the *Land Suitability Classification*

Order	Class	Category subclass	Unit
S Suitable	S1 S2 S3 etc.	S2m S2e S2me etc.	S2e-1 S2e-2 etc.
Phase SC: Conditionally suitable	Sc2	Sc2m	
N Not suitable	N1 N2	N1m N1e etc.	

Fig. 11.12 Structure and suitability classification of the land evaluation (FAO 1976)

made according to the climatic and edaphic suitability. This is determined by the most limiting climatic or edaphic site factor. The suitability class provides information about the degree of suitability of a site for a specific crop as well as about the type and extent of the restrictions. For example, the suitability class S3cf for wheat describes sites that are only moderately (S3) suitable for wheat cultivation due to their climatic (c) and soil chemical (f: fertility) properties.

The advantage of the LSC is that it explicitly includes the climate as a decisive site factor in the soil evaluation, so strictly speaking, it represents a site evaluation, and that it offers the possibility of evaluating the site in terms of its suitability for specific land utilization types or crops. This requires precise knowledge of the specific requirements of the use being evaluated.

11.5.5 Agro-Ecological Zones

The ***Agro-Ecological Zones Project*** was also developed and implemented by the FAO (1978) to establish basic principles for the planning and development of the agricultural potential in developing countries. This study resulted in a land suitability classification for 20 widespread crops in rainfed agriculture for two cropping intensities as well as further development of the methodology. The evaluation system is based on the comparison between specific plant requirements and the climate and soil properties. Four suitability classes are defined, which are associated with the expected yield. Very well suited are sites where more than 80 % of the maximum yield is achieved, suitable are sites with a yield performance between 40 and 80 %, marginally suitable are those between 20 and 40 %, and not suitable are sites with a less than 20 % yield performance. In the evaluation process, first the climatic requirements of the plants are defined and combined with the agroclimatic zones, which are classified according to the length of the growing period (duration of the water availability and temperature). Subsequently, the climate zones suitable for a crop are compared with the soil evaluation. The soil evaluation is performed based on the FAO '*Soil Map of the World*' at a scale of 1:5,000,000, and is subdivided into three suitability levels depending on the type and extent of the growth-restricting soil properties. The prior climatic evaluation is modified according to the soil suitability. With good soil suitability, the evaluation remains the same; with moderate suitability the evaluation is reduced one level, and with no suitability, the sites are altogether unsuitable.

11.5.6 Soil Quality Assessment

The **Soil Quality Assessment** is a new group of methods for soil evaluation that originated in the USA. Until now, different definitions, guidelines and instructions have been given in the various publications on soil quality. In general, however, soil quality is defined as the capacity of a specific kind of soil to perform functions within the boundaries of a natural or managed ecosystem. It focuses on sustainable plant and livestock production, maintaining or improving water and ambient air quality, and supporting human health and general living conditions. Soil quality can therefore be modified on the long term by changing the land use. It can be reduced (degraded) or it can also be improved. The orientation of a land use system towards sustainability can be verified by evaluating the soil quality. Even if the procedure and the definition still remains unclear in some cases, it is still a significant change that here, for the first time in an American-international system, not only the soil productivity is evaluated but rather also the functions in the environmental system. The Soil Quality Assessment evaluates five basic functions of the soil (USDA-NRCS 2001).

1. Regulation of **water movement**.
   Soils control what happens with precipitation and irrigation water. The influence that a soil has on the water balance is an important aspect of the *Soil Quality Assessment*.
2. Long-term conservation of the **flora and fauna**.
   The diversity and productivity of organisms is very strongly dependent on soil functions.

3. **Filtering and transformation potential** for **pollutants**.
   The mineralogical composition of the soil and the microorganisms in the soil are responsible for the filtering, buffering, decomposition, immobilization and detoxification of organic and inorganic substances in the soil.
4. **Nutrient cycle**.
   Carbon, nitrogen, phosphorus and many other nutrients are stored and transformed in the soil and become part of the cycle.
5. **Preservation of the soil structure**.
   On the one hand, soils must have a stable structure in order to be able to carry structures or streets. On the other hand, they hold real archaeological treasures, which are connected to human life.

The *Soil Quality Assessment* is performed similar to the *Land Suitability Classification*. It can therefore be assumed that different soils have a different natural soil quality. However, with a given soil quality, the possibility exists that the soil will be sustainably managed, that the soil quality will be degraded or even aggraded, meaning that its quality increases.

With this method, a specific set of indicators is selected. These indicators then each receive a measurement and these measured values are associated with an index. For the soil quality index, all individual index values are added, divided by the number of values, and then multiplied by 10. In contrast to the previous Storie index, an **addition method** has been selected in this case. The evaluation is based on a data set that must be recorded from the soils. To be able to evaluate this data, it must then be correlated with corresponding uses or soil functions. The so-called **minimum dataset** plays an important role in the discussion. In doing so, an attempt is made to be able to assess the quality of a soil with the least possible observations or measured values. In this minimum dataset, 12–15 parameters are used, from soil organic matter through water holding capacity all the way to potentially mineralizable nitrogen. The significant constraints with the soil quality concept so far are that there is no standardization for soil quality indicators. In addition, the functional relationships between the soil quality indicators and the soil quality rating are still open. Despite these uncertainties, the soil quality assessment has still grown in significance in recent years because it includes the participative interests of users and also includes economic assessments.

11.6 Soil Information Systems

The traditional method for passing on soil information is the **soil map**. A soil map contains a topographical base with a scale from 1:1000 to 1:5,000,000. The map defines soil units, which are areas in which specific characteristic soils predominate and have a uniform structure. These areas are colored with a specific color or a symbol. There is usually a legend for these symbols. The **legend** assigns the areas to specific soil classification units. The legend can also contain additional specific explanations about the parent rock and relief. A soil survey report is often published along with the map. The **soil survey report** explains the characteristics of the various soil units. Above all, it ensures that the areal information is converted to 3-dimensional information by outlining the characteristics of the different horizons of a soil. While the legends are often soil type legends, the survey reports provide information on the soil including the substrate (German: soil form, US: soil family), on their history and on their threats as well as on their suitability for use. Derived maps are also often included in modern map series. These **derived maps** portray simple levels for the **suitability for use**, e.g. for wheat and vine, specific threats, e.g. erodibility, or certain functions, such as groundwater recharge or heavy metal buffering. A textbook example for such a soil information system based on one map is the **Soil Map of the World** (1974). In Germany, there are soil maps for all federal states. These maps are mostly compiled at a scale of 1:25,000. In some federal

states, there are also soil maps going down to a scale of 1:5000, which are able to provide precise information on individual parcels of land. Inversely, there are also soil maps in many federal states with a scale of 1:50,000. A series of maps for Germany and the European Union with a scale of 1:200,000 is being produced.

With the progress of electronic information systems, modern soil information systems are based on the availability of the soil data on the Internet. One such Internet-based soil information system is the **NIBIS** (Lower Saxony Soil Information System). All soil maps, associated information and many applied derived maps are stored in this information system. This information is then readily accessible. It can be cut, reduced or enlarged as desired, whereby the user can rapidly gain an overview of the existing map coverage and extract specific information.

The next generation of soil information systems is based on the SOTER system. This soil and terrain digital database enables the user to go back to the primary data, and to a limited extent, to also personally influence the evaluation. The SOTER system is a geographical information system. At first, a digital topographical model is available, which often also includes an elevation model. The respective SOTER region is hierarchically organized into **terrain units**, which are mostly areas delimited by their geological/geomorphological properties, **terrain components**, which are simple relief units, and **soil components**, which are the soil units. There is also a soil database for this map. In this way, specific soil information can be retrieved for each area, or all of the soils investigated in an area can be retrieved with their analytical data. The third element in the SOTER system consists of the rules and standards, which enables the linking of data with specific target parameters. For example, a derivation of the plant-available water, the depth to bedrock or the soil organic matter stock. Frequently, there are derived maps already in the SOTER database intended for certain important applications, such as e.g. suitability for cultivation of maize or the risk of wind erosion. What is new is that such applications can be supplemented at any time by activating certain functions or by adding certain assignment criteria. Local or regional application systems have been developed in many countries of the world based on the SOTER scheme. A significant advantage of this system is that here, new insights or additional data can be easily integrated into the system. A similar new system is SLISYS (*Soil and Land Information System*), which was developed for Baden-Württemberg.

In the future, the further development of such information systems will find increasing use for developing policies or political consulting. Thereby, the topographical and pedological land information still remains of great importance. The quality of the database is also decisive. In addition, simulation models (e.g. EPIC) can also be integrated into these systems, which then enable direct user requests. **Decision support systems** must have a user-friendly interface. Then it is possible, for example, to predict the effect of increased fertilization on plant growth and to depict it on a map. Further important applications for such decision supports systems would be, for example, the change in the groundwater recharge due to increasing surface sealing and increasing erosion rates caused by high proportions of root crop cultivation. Here, it is important that the creation of decision making tools remains in the hands of experts and that the probability of errors also continues to be assessed by specialists. The future acceptance of pedological findings in society very strongly depends on its clear accessibility, so that the development of decision support systems seems essential.

A global consortium has been formed aiming to create a new digital soil map of the world using state-of-the-art and emerging technologies for soil mapping and predicting soil properties at fine resolution. This new global soil map will be supplemented by interpretation and functionality options to assist better decision-making in a range of global issues like food production and hunger eradication, climate change, and environmental degradation. This is an initiative of the Digital Soil Mapping Working Group of the International Union of Soil Sciences IUSS (from Global Soil Map.net). This approach will collect a huge amount of data and aims to construct

simple soil property maps without using any soil classification, but offering the possibility of calculating derived properties (Minasny and McBratney 2010).

11.7 Soil Protection

11.7.1 Reasons for Soil Protection

The realization that the soil resources on Earth are finite only happened recently. When large-scale deforestation first began in Central Europe in the Younger Stone Age and agriculture boasted its first great revolution, **soil resources** seemed endless. The area used depended only on the available labor. All around, there was enough room to expand. However, land became scarce in Europe early in modern times, as testified by the large peatland cultivations and the diking of coastal landscapes in the Netherlands and Northern Germany. But the emigrants of the 18th and 19th Century found immeasurable quantities of land resources in North and South America as well as in Australia. Today these resources are utilized everywhere, all the way to the edge of the deserts, up to the inaccessible high-altitude mountains and all the way to the ocean. When Mao made his way with a huge mass of people to find new land in Western China about 60 years ago, all they found was barren, dry, alkalized or even saline land. It took one more generation, until the 1960s and '70s, when the *Club of Rome* and the FAO as well as the European Council drew the attention of the public to the finite nature of soil resources with its Soil Charter in 1972.

Still today, the most important function of soils worldwide is for food production, and it will also remain so in the 21st Century. For this reason, soil protection in an industrial society must focus especially on this function. Since the area of soils of each country and on Earth is altogether finite, the demands of different uses on the soils will no longer be completely met on a regional and global level. The recent tendencies to produce more and more energy crops can only underline the necessity for wise land use that is capable of feeding the increasing world population.

Soils are also natural bodies, and as such, are four-dimensional sections of the upper Earth's crust, where rocks, water, air and organisms coexist. These soils are very diverse and complex bodies, which always consist of different phases and exhibit an internal order (structure). Soils have often developed, under the influence of natural factors and human activities, over the course of long periods of time. They are therefore archives of natural and cultural history, which are hardly reparable. There are two reasons why soils are worth protecting:

1. Because soils must be preserved as natural bodies and
2. Because of their importance (functions) in the ecological balance and for society.

Criteria for the conservation of natural bodies are the **diversity**, the **scarcity** and the **reproducibility** of soils to be particularly protected. Thereby it is decisive that the preservation of soils as natural bodies can only be sensible if the matter turnover of the landscape is also taken into account. They are to be preserved as parts of ecosystems. For ecological and technical functions of the soil, the **degree of capability**, i.e. the level of its potential, is the most essential criterion for conservation value.

11.7.2 Protection of the Natural Body

If soils are to be preserved as natural bodies, then it is necessary that the areas (landscapes) are protected. The simple preservation of a soil profile for illustration cannot be considered to be sufficient, since certain space must be available especially for further investigation. Furthermore, a **minimum area** is required to preserve the dynamics of a soil, so that e.g. populations of soil organisms can be sustained, or as can be seen in the example of a bog, the peat body must be large enough so that it can regulate its own water balance. It would be desirable that not only very rare soils, but rather also the regular, wide-spread

soils are preserved under nature-orientated conditions, since the increasing intensity of use often results in the loss of their natural properties. Soils can serve as geological documentation even without human intervention, e.g. if they became covered by volcanic eruptions, landslides or through flooding and therefore constitute **fossil soils**. These fossil soils provide information about the respective time period and its characteristics, during which they participated in soil development on the Earth's surface. Elsewhere, we find **relic soils**, which still exist today on the Earth's surface, but have characteristics that e.g. no longer correspond to the climate conditions in Central Europe, such as red and sometimes ferralitic weathered soils in karst landscapes that developed in the Tertiary period. Finally, **natural bodies of soil** are often also sites of **natural beauty**, meaning that the observation of the soil surface or particularly the soil profile often holds exceptionally esthetic information through the various distributions of substances, such as quartz, iron oxides and organic matter. This information must also be kept preserved for posterity. This thought is promoted through the campaign "Soil of the Year/Day of the Soil", which draws public attention to a particularly remarkable soil.

11.7.3 Soil Functions and Potentials

All soils that are found on the surface have specific functions in the matter budget of the landscape. Their function in the water balance is clear, where they primarily serve as an intermediate storage for evaporation, groundwater recharge and runoff. But they also serve important functions in the carbon balance or in other nutrient or energy balance, even without serving an actual use. Furthermore, soils have the inherent property of being able to perform additional functions immediately or at a later point in time. These not yet utilized but existing functions are called **soil potentials**. The variety of existing soil potentials can be subdivided into three groups, first according to their biotic functions, which can principally be used sustainably, and are maintained mainly in the organic matter and nutrient cycle as well as through the energy input from the sun and from the earth's interior. Even the **abiotic functions** of air purification and water extraction can be sustainably managed. In contrast, the exploitation of raw materials already requires soil destruction. Even simply the use of so–called **areal functions** always results in contamination/degradation, lasting adverse effects or even the destruction of existing soils (Table 11.6).

Table 11.6 Overview of the potentials of the soils, which can serve functions for the ecological balance or society

(A) *Biotic potentials*
1. Habitat for soil biota 2. Food and feed production 3. Materials production 4. Energy production 5. Genetic resource 6. Transformation potential
(B) *Abiotic potentials*
7. Air filter 8. Filter and buffer in the water cycle 9. Raw material deposit
(C) *Areal potentials*
10. Load capacity (development potential) 11. Traffic route 12. Deposit (landfill) 13. Recreation

11.7.4 German Federal Soil Protection Act

After soil scientists worldwide had been demanding since 1970 that legal measures be taken to protect the soils, the German Federal Government came up with a soil protection concept in 1985. It was only in 1991 that the first soil protection act worldwide was passed in the state of Baden-Württemberg. In 1998, the law for the protection against harmful soil change and for the remediation of contaminated sites, in short the **Federal Soil Protection Act** (BBodSchG), was published. This law has now been effective since 03.01.1999.

The first part of the law deals with **'General Regulations':**

§ 1 states: "The purpose of this **law** is to ensure and restore the **functions** of the soil on the long term. To do so, harmful soil deterioration is to be prevented, the soil and contaminated sites as well as the resulting watercourse pollution are to be remediated and precautions are to be taken against adverse effects on the soil. In case of effects on the soil, impacts on its natural functions as well as its function as an archive of natural and cultural history should be avoided as much as possible."—The law stipulates the safeguarding of soil functions, preventative soil protection, and remediation of existing and prevention of future soil contaminations.

In § 2, the **terminology** is explained and the **soil functions** are defined, and the terms '**contaminated sites**' and '**suspected contaminated sites**' are introduced.

§ 2 (2) states: "Within the meaning of this law, the soil fulfils

1. **Natural functions as**
   (a) The basis of life and habitat for humans, animals, plants and soil organisms,
   (b) A component of the ecological balance, in particular with its water and nutrient cycles,
   (c) A decomposition, exchange and restoration as well as new formation medium for matter impacts due to its filtering, buffering and transforming properties, particularly also in terms of groundwater protection,
2. **Functions as** an archive of **natural and cultural history** as well as
3. **Utilization functions** as
   (a) Raw material deposit,
   (b) Area for settlement and recreation,
   (c) Site for agricultural and forestry use,
   (d) Site for other economic and public uses, traffic, supply and disposal."

Contaminated sites are subdivided into **former waste deposal sites** (sites where waste is treated, stored or dumped) and **abandoned industrial sites** (sites where hazardous materials were handled). Within the meaning of the law, suspected contaminated sites are former waste disposal site and abandoned industrial sites, where there is suspicion of harmful soil change.

In the second part of the Federal Soil Protection Act, the governing 'Principles and Obligations' are presented, among others, the "**Obligations to avert danger**" (§ 4). § 4 (1) explains that "…anyone, who has an impact on the soil should behave in such a manner that harmful soil change is not induced." The term **harmful soil change** represents a central concept of the law and constitutes an impact or damage to one or several soil functions. According to § 4 (3), "…those causing a harmful soil change or contaminated site as well as their universal legal successor (…) are obligated to remediate the soil and contaminated sites as well as contaminations caused by harmful soil change or contaminated sites in such a way that there are no lasting hazards, significant disadvantages or significant disruptions for individual or public welfare." With this definition, the "**polluter pays principle**" is incorporated in the German Federal Soil Protection Act and a remediation obligation is established. Furthermore, in accordance with § 4 (3) "…other protective and restrictive measures" can be prescribed and therefore also a **use restriction** for agriculture and forestry land use. However when such use restrictions are prescribed, then a reasonable economic compensation can be granted [§ 10 (2)] under certain conditions, depending on the federal state law. As per § 5, directives on the '**desealing**' of soils can be implemented. § 6 prescribes the legal regulations for the '**application and introduction of materials on or into the soil**' …" regarding the pollutant content and other properties of the materials to be used". § 7 established a '**precautionary obligation**' "…against the development of harmful soil change". § 8 states that **precautionary values** as well as **trigger values** and **action values** can be defined to create guidelines for precautions towards harmful soil change and for an assessment of already existing

soil contaminations. With the '**German Federal Soil Protection and Contaminated Sites Directive** (BBodSchV)' from July 16th, 1999 as the sublegal framework for the German Federal Soil Protection Act, such values are defined for a series of organic and inorganic pollutants (see Chap. 10). Although the list of values is still incomplete and may still require some corrections, it is a positive beginning for an evaluation of chemical soil contaminations to be carried out according to uniform standards in Germany. This list is recently being improved and expanded. The regulatory framework also prescribes the testing methods to be used, which are largely internationally standardized. Furthermore, § 9 of the German Federal Soil Protection Act authorizes the responsible authorities, upon presenting indications for harmful soil change or contaminated sites, to implement a '**risk assessment and investigation warrant**'.

The **third part** of the German Federal Soil Protection Act contains '**additional provisions for contaminated sites**' such as their surveying, remediation planning and monitoring.

In the fourth part, '**agricultural land use**' is addressed. The fulfillment of the precautionary obligation (§ 7) with agricultural land use is achieved in accordance with § 17 (1) through '**Good Agricultural Practices**'. According to § 17 (2), this included "…the long-term safeguarding of soil fertility and the quality/productivity of the soil as a natural resource. The basic principles of good agricultural practices include, in particular, that

1. Soil tillage is to be generally adapted to the site and performed under consideration of the weather conditions,
2. The soil structure is preserved or improved,
3. Soil compaction is avoided as much as possible, particularly by considering the soil texture, soil moisture and the soil pressure caused by implements used for agricultural practices.
4. Soil erosion is avoided as much as possible by adapting the use to the site, in particular under consideration of the slope inclination, the water and wind conditions as well as the ground cover.
5. The nature-conserving structural elements of the arable field are preserved, especially hedges, copses, greened field margins and field terraces, which are necessary to protect the soil.
6. The biological activity of the soil is preserved or promoted by adequate crop rotation, and
7. The site-typical humus content of the soil is preserved, in particular through sufficient additions of organic matter or through the reduction of the tillage intensity."

The contents of a series of the principles of "Good Agricultural Practices" outlined in the law must still be defined or specified. The individual Federal States are responsible for the implementation of the German Federal Soil Protection Act, which have passed subsequent State soil protection laws and have established soil protection authorities for this purpose. According to the legal regulations for the purification of air and water, soil is now protected by federal law and subordinate state laws as the third environmental medium.

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Appendix

A.1 Classification of Geological Formations

See references at the end of appendix.

A.2 Symbols, Conversion Factors

A.2.1 Abbreviations

~	Approximately
AEC	Anion exchange capacity
Al_o, Al_l, Al_a	Oxalate-soluble, NaOH-soluble and exchangeable Al
ANC	Acid neutralization capacity
BBodSchG	German Federal Soil Protection Act (Bundes-Bodenschutzgesetz)
BBodSchV	German Soil Protection and Contaminated Sites Ordinance (Bundes-Bodenschutz- und Altlastenverordnung)
BNC	Base-neutralizing capacity
BS_{pot}	Base saturation (formerly: V value), measured at pH > 7
BS_{eff}	Base saturation, based on the CEC_{eff}
BS_{Na}, BS_{Mg}	Na or Mg saturation
CEC	Cation exchange capacity
CEC_{pot}, CEC_{eff}	Potential, effective CEC
C_p	Pyrophosphate-extractable C
D	Diffusion coefficient
DIBAEX	Distribution based extrapolation
DOM	Dissolved organic matter
d_B	Bulk density (g cm^{-3})
E, Eh	Redox potential in (V) related to standard hydrogen electrode
EC	Electr. conductivity
ED	Effective dose
ESP	Exchangeable sodium percentage
ESR	Exchangeable sodium ratio
FAME	Factorial application method
FAO	Food and Agriculture Organisation of the United Nations in Rome
Fe_o, Fe_d, Fe_p	Oxalate-, dithionite- or pyrophosphate-soluble Fe
Fs	Fine soil, fine earth
FC	Field capacity
Fr. M., FM	Fresh matter
ESS	Equilibrium soil solution
GS	Ground surface
GWS	Groundwater surface
IBU (IUSS)	International Union of Soil Science (Internationale Bodenkundliche Gesellschaft (Union))
ISRIC	International Soil Reference and Information Centre
I-TEq	International toxicity equivalents (for dioxins and Furans)
K_{DOC}	Sorption coefficient for dissolved organic matter
K_S	Sorption coefficient according to Freundlich
K_{oc}	Distribution coefficient, standardized for SOC content
K_{ow}	Distribution coefficient octanol-water

H.-P. Blume et al., *Scheffer/Schachtschabel Soil Science*, DOI 10.1007/978-3-642-30942-7

Lime	$CaCO_3$ equivalent
LD	Lethal dose
M	Molar; metal
Mn_d	Dithionite soluble Mn
NATO/CCMS	North Atlantic Treaty Organization/Committee on the Challenges of Modern Society
ODOE	Optical density of oxalate extract (mobile humus)
OM, SOM	Organic matter
PAW	Plant-available water
P_{ret}	Phosphate retention
PAH	Polycyclic aromatic hydrocarbons
PCB	Polychlorinated biphenyls
PCDD	Polychlorinated dibenzodioxins
PCDF	Polychlorinated dibenzofurans
p*e*	Electron concentration
pH	pH ($CaCl_2$)
ppmv	Parts per million, in general related to the volume
PV	Pore volume in % (f = fine pores < 0.2 μm, m = medium-sized pores 0.2−10 μm, c = coarse pores > 10 μm, vc = very coarse pores > 50 μm ∅)
P_v	Phosphorus soluble in 30 % HCl at 100 °C
PWP	Permanent wilting point
SAR	Sodium adsorption ratio
SOC	Soil organic carbon
SV	Substance volume (T = clay, U = silt, fS = fine sand, mS = medium sand, cS = coarse sand, X = gravel and stones)
t	Total content (as a subscript, e.g. Al_t)
TRB	Base reserves (exchangeable + mineral Ca + Mg + K + Na in $cmol_c\ kg^{-1}$)
TRD	Tolerable resorbed dose
m_D	Dry matter
USDA	United States Department of Agriculture
US EPA	United States Environmental Protection Agency
WHO	World Health Organization
WRB	World Reference Base for Soil Resources
WC	Water column

A.2.2 Conversion Factors for Fertilizers

$P \cdot 2.291 \rightarrow P_2O_5$; $P_2O_5 \cdot 0.436 \rightarrow P$
$K \cdot 1.205 \rightarrow K_2O$; $K_2O \cdot 0.830 \rightarrow K$
$Mg \cdot 1.658 \rightarrow MgO$; $MgO \cdot 0.603 \rightarrow Mg$
$Ca \cdot 1.399 \rightarrow CaO$; $CaO \cdot 0.715 \rightarrow Ca$

See Table A.1.

Table A.1 Geological time scale

Formation/ Period	Epoch/Series	Age (10^6 a)	Series and levels (incomplete)	Examples of landscape development and climate in Central Europe
Cenozoic Era				
	Holocene Q_2		(see Tab. 12-2)	Floodplains, perimarine marshes, peatlands
		0.012	Weichselian-Würmian-Wisconsin ice age	
QUATERNARY Q	Upper...	0.126	Eemian interglacial Saalenian-Rissian ice age	Laach lake volcanoes Boulder marls, glacial till
	Middle...		Holsteinian interglacial Elsterian-Mindelian ice age	Cold desert Loess, dune sand, periglacial gravel
	Pleistocene Q_1		Cromer (ice age and interglacial)	Cold steppe, tundra
		0.78 1.80	Günzian and Danube ice ages Multiple cold and warmer periods	**Paleosols** Temperate humid
	Calabrian Gelasian...	**2.58**		
	Neogene N	5.3 23	Pliocene Miocene	Volcanoes (Kaiserstuhl, Hegau, Eifel, Vogelsberg) Mediterranean, semi-humid to arid
TERTIARY	Paleogene P	34 56	Oligocene Eocene Paleocene	Harz uprise, Upper Rhine Valley Graben Alpine orogeny Lignite coal Tropical, humid
		66		
Mesozoic MZ				
	Upper K_2		Maastrichtian Campanian Santonian Coniacian Turonian Cenomanian	Oldest surface soils (Eifel, Hunsrück, Swabian Alb) First flowering plants Tropical, humid
CRETACEOUS K		**100**		
	Lower K_1		Albian Aptian Barrêmian Hauterivian Valangian Berriasian	North German marine sea South German and mountains Continental Tropical, humid
		145		
	Upper J_3		Tithonian Kimmeridgian	Jurassic sea/saurian, corals, ammonites Rhenish Island
JURASSIC J	Middle J_2 Lower J_1	164 174	Oxfordian Callovian/Bathonian/Bajozian/ Aalenian Toarcian/Pliensbachian/ Sinemurian/Hettangian	Vindelicic continent Tropical to subtropical
		201		
	Upper (Keuper)		Rhätian Norian Carnian } T_3	Germanic basin subtrop. desert
			Ladinan } T_2	Wadil-ike streams, salt lakes, calcretes Alpine sea Subtropical
TRIASSIC T		**237**		Middle Trassic sea (Muschelkalk)

(continued)

Table A.1 (continued)

Formation/ Period	Epoch/Series	Age (10^6 a)	Series and levels (incomplete)	Examples of landscape development and climate in Central Europe
			Ladinian } T_2	Salt deposits Mediterranean, arid
	Middle (Muschelkalk)	247	Anisian	
				Germanic basin
			Olenekian } T_1	Semi-humid to arid, sub-tropical
	Lower (Buntsandstein)		Induan	Paleogleysols (groundwater)
		252		
Paleozoic PZ				
	Lopingian (Zechstein)	260	Changhsingian Wuchiapingian	Permian (Zechstein) sea in the North
			Capitanian	Hot deserts/salt deposits
PERMIAN R		272	Wordian	Younger red continent in the South,
	Gadalupian (Rotliegendes)		Roadian	Volcanoes
	Cisuralian		**Kungurian/Artinskian** **Sakmarian/Asselian**	
		299		
	Pennsylvanian C2		Gzehelian	Coal swamps (bryophytes, ferns, shave grass, first coni-fers)
	Upper		Kasimovian	
	Middle	323	Moscovian	
	Lower		Bashkivian	Hot humid
CARBONI-FEROUS				Varician orogeny
	Mississippian C1			Rhenish massif
	Upper		Serpukhovian	Black Forest young granites
	Middle		Viséan	
	Lower		Tournaisian	
		359		
	Upper D_3	383	Famennian/Frasnian	Devonian sea
DEVONIAN D	Middle D_2	393	Givetian/Eifelian	(fish, insects, amphibians)
	Lower D_1		Emsian/Pragian/Lochkovian	**Some on** continents (ferns)
				South Germany, magmatic intrusions
		419		
	Pridoli		Ludfordian/Gorstian	Siluvian sea
SILURIAN S	Ludlow		Homerian/Scheinwoodian	First vertebrates
	Wenlock		Telychian/Aeronian/	Plants colonize the continents
	Llandovery		Rhuddanian	Volcanism in Central Germany
		443		
	Upper	458	Hirnantian/Katian/Sandbian	Ordovician sea Greywackes
ORDOVICIAN O	Middle	470	Darwillian/Dapingian	Caledonian orogeny (gneisses and granites)
	Lower		Floian/Tremadocian	Scandinavia and Lausitz basic volcanism
		485		
	Furongian	497	Stage 10/	Marine deposits,
	Series 3	509	Jüngshanian/Paribian	basic and acidic volcanism
CAMBRIAN Cbr	Series 2	521	**Guzhangian**/Drumian/Stage 5	
	Terreneuvian		Stage 4 + 3	
			Stage 2/Fortunian	
		541		
Precambrian				
	Neo-	1000		Algae, worms, brachiopods
PROTERO-ZOIC	Meso-	1600		**First occurrence of O2 in the atmosphere**
	Paleo-	2500		Old sediments, Metamorphic rocks

(continued)

Table A.1 (continued)

Formation/ Period	Epoch/Series	Age (10^6 a)	Series and levels (incomplete)	Examples of landscape development and climate in Central Europe
		2800		
ARCHEAN	Neo- Meso- Paleo-	3200 3600		First traces of life
		4000		
HADEAN				Origins of planet Earth
		4600		

Table A.2 Timetable of late and postglacial period in Central Europe

Geological periods		Time before present (b.p.)	Climate	Vegetation, human activities, soils
Holocene	Subatlantic	Less than 2500 a	Current climate temperate humid (oceanic)	Beech, oak, spruce-forest, clearcut/deforestation since "iron age" until historic times, formation of loamy floodplain cover beds, Stagnosols
	Subboreal (late warm period)	5 720 – 2 500 a	Warmer, few dry periods (continental)	Mixed oak forest with beech and spruce, "bronze age" strong anthropogenic erosion, younger tidal sediments, transgression of Duinkerke
	Atlantic (middle warm period)	9 280 – 5 720 a	Warm, humid climatic optimum (oceanic)	Mixed oak forest, first deforestation at beginning of "younger stone age", oldest tidal sediments, transgression of Calais, Luvisols
	Boreal (early warm period)	10 700 – 9 280 a	Warm, dry (continental)	Birch - pine forest with hazel maximum, Chernozems
	Preboreal	11710 – 10700 a	Cool, temperature increase (continental)	Pine - birch period, begin of "Mesolithic period"
Late Weichselian period	Younger Dryas	12740 – 11710 a	Cold (subarctic)	Tundra (cold steppe) with birch end of "Paleolithic period"
Upper pleistocene	Alleroed	13410 – 12740 a	Temperate (continental)	Open forest with birch and pine, last eruption of "Laacher Lake" volcano
	Older Dryas	13600 – 13410 a	Cold (subarctic)	Open tundra
	Boelling	13730 – 13600 a	Temperate (continental)	Birch (pine)
	Oldest Dryas	16000 – 13730 a	Cold (arctic)	Tundra without trees
	End of the Weichselian/ Wuermian/ Wisconsin-ice age (around 16 000 a b. p.) with Pommerian ice-push and Mecklenburg phase			

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Index

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B

C

G

H

M

P

Q

R

T

U