ENVIRONMENTAL SOIL CHEMISTRY

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CHEMISTRY OF SOIL ORGANIC MATTER

Similar to the inorganic components of soil, soil organic matter (SOM) plays a significant role in affecting the chemistry of soils. Despite extensive and important studies, the structure and chemistry of SOM is still not well understood. Moreover, because of its variability and close relationship with clay minerals and metal oxides the chemistry and reactions it undergoes with metals and organic chemicals are complex. In this chapter, background discussions on SOM content and function in soils and its composition, fractionation, structure, and intimate association with inorganic soil components will be covered. Additionally, environmentally important reactions between SOM and metals and organic contaminants will be discussed. For further in-depth discussions on these topics the reader is referred to the suggested readings at the end of this chapter.

INTRODUCTION

Humus and SOM can be thought of as synonyms, and include the total organic compounds in soils excluding undecayed plant and animal tissues, their "partial decomposition" products, and the soil biomass (Stevenson, 1982). Humus includes humic substances (HS) plus resynthesis products of microorganisms which are stable and a part of the soil. Common definitions and terminology for these are given in Table 3.1.

Soil organic matter contents range from 0.5 to 5% on a weight basis in the surface horizon of mineral soils to 100% in organic soils (Histosols). In

TABLE 3.1. Definitions of Soil Organic Matter (SOM) and Humic Substances[a]

Term	Definition
Organic residues	Undecayed plant and animal tissues and their partial decomposition products.
Soil biomass	Organic matter present as live microbial tissue.
Humus	Total of the organic compounds in soil exclusive of undecayed plant and animal tissues, their "partial decomposition" products, and the soil biomass.
Soil organic matter	Same as humus.
Humic substances	A series of relatively high-molecular-weight, brown- to black-colored substances formed by secondary synthesis reactions. The term is used as a generic name to describe the colored material or its fractions obtained on the basis of solubility characteristics. These materials are distinctive to the soil (or sediment) environment in that they are dissimilar to the biopolymers of microorganisms and higher plants (including lignin).
Nonhumic substances	Compounds belonging to known classes of biochemistry, such as amino acids, carbohydrates, fats, waxes, resins, and organic acids. Humus probably contains most, if not all, of the biochemical compounds synthesized by living organisms.
Humin	The alkali insoluble fraction of soil organic matter or humus.
Humic acid	The dark-colored organic material which can be extracted from soil by various reagents and which is insoluble in dilute acid.
Fulvic acid	The colored material which remains in solution after removal of humic acid by acidification.
Hymatomelanic acid	Alcohol soluble portion of humic acid.

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Mollisols of the prairie regions, SOM may be as high as 5% while in sandy soils, e.g., those of the Atlantic Coastal Plain of the United States, the content is often $< 1\%$. Even at these low levels, the reactivity of SOM is so high that it has a pronounced effect on soil chemical reactions.

Some of the general properties of SOM and its effects on soil chemical and physical properties are given in Table 3.2. It improves soil structure, water-holding capacity, aeration, and aggregation. It is an important source of macronutrients such as N, P, and S and of micronutrients such as B and Mo. It also contains large quantities of C which provides an energy source for soil macroflora and microflora. The C/N ratio of soils is about 10–12:1; the quantity of soil C, $30-50 \times 10^{14}$ kg, is greater than that found in other reservoirs on the earth's surface such as atmospheric CO_2, biomass, and fresh water, but it is minute compared to the ocean sediments that contain approximately $200{,}000 \times 10^{14}$ kg of C (Stevenson, 1982).

Soil organic matter has a high specific surface (as great as 800–900 $m^2\ g^{-1}$) and a CEC that ranges from 150 to 300 $cmol\ kg^{-1}$. Thus, the majority of a surface soil's CEC is in fact attributable to SOM. Due to the high specific surface and CEC of SOM, it is an important sorbent of plant macronutrients and micronutrients, heavy metal cations, and organic materials such as pesticides. The uptake and availability of plant nutrients, particularly micronu-

TABLE 3.2. General Properties of Soil Organic Matter and Associated Effects in the Soil[a]

Property	Remarks	Effect on soil
Color	The typical dark color of many soils is caused by organic matter.	May facilitate warming.
Water retention	Organic matter can hold up to 20 times its weight in water.	Helps prevent drying and shrinking. May significantly improve the moisture-retaining properties of sandy soils.
Combination with clay minerals	Cements soil particles into structural units called aggregates.	Permits exchange of gases. Stabilizes structure. Increases permeability.
Chelation	Forms stable complexes with Cu^{2+}, Mn^{2+}, Zn^{2+}, and other polyvalent cations.	May enhance the availability of micronutrients to higher plants.
Solubility in water	Insolubility of organic matter is because of its association with clay. Also, salts of divalent and trivalent cations with organic matter are insoluble. Isolated organic matter is partly soluble in water.	Little organic matter lost by leaching.
Buffer action	Organic matter exhibits buffering in slightly acid, neutral, and alkaline ranges.	Helps to maintain a uniform reaction in the soil.
Cation exchange	Total acidities of isolated fractions of humus range from 300 to 1400 cmol kg^{-1}.	May increase the CEC of the soil. From 20 to 70% of the CEC of many soils (e.g., Mollisols) is due to organic matter.
Mineralization	Decomposition of organic matter yields CO_2, NH_4^+, NO_3^-, PO_4^{3-}, and SO_4^{2-}.	A source of nutrient elements for plant growth.
Combines with organic chemicals	Affects bioactivity, persistence and biodegradability of pesticides and other organic chemicals.	Modifies application rate of pesticides for effective control.

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trients such as Cu and Mn, and the effectiveness of herbicides are greatly affected by SOM. For example, manure additions can enhance micronutrient availability in alkaline soils where precipitation of the micronutrients at high pH reduces their availability. The complexation of low-molecular-weight SOM components such as fulvic acids (FA) with metals such as Al^{3+} and Cd^{2+} can decrease the uptake of metals by plants and their mobility in the soil profile.

EFFECTS OF SOIL FORMATION FACTORS ON SOM CONTENTS

The quantity of soil organic matter in a soil depends on the five soil forming factors first espoused by Jenny (1941)—time, climate, vegetation, parent material, and topography. These five factors determine the equilibrium level of

SOM after a period of time. Of course, these factors vary for different soils and thus SOM accumulates at different rates and, therefore, in varying quantities.

The accumulation rate of SOM is usually rapid initially, declines slowly, and reaches an equilibrium level varying from 110 years for fine-textured parent material to as high as 1500 years for sandy materials. The equilibrium level is attributed to: organic acids that are produced which are resistant to microbial attack, the stability of humus due to its interactions with polyvalent cations and clays, and low amounts of one or more essential nutrients such as N, P, and S which limit the quantity of stable humus that can be synthesized by soil organisms (Stevenson, 1982).

Climate is an extremely important factor in controlling SOM contents because it affects the type of plant species, the amount of plant material produced, and the degree of microbial activity. A humid climate causes a forest association, while a semiarid climate creates grassland associations. Soils formed under grass usually have the highest SOM content, while desert, semidesert, and tropical soils have the lowest quantities of SOM. However, tropical soils often contain high quantities of HS even though they are highly weathered. This is due to the formation of complexes between the HS and inorganic constituents such as quartz, oxides, and amorphous materials (organo–inorgano complexes) that are quite stable. In a complexed form the HS are less susceptible to microbial attack (Stevenson, 1982).

Vegetation also plays a profound role on SOM contents. Grassland soils, as mentioned above, are higher in SOM than forest soils. This is due to greater amounts of plants being produced in grassland settings, inhibition in nitrification that preserves N and C, higher humus synthesis which occurs in the rhizosphere, and the high base content of grassland soils which promotes NH_3 fixation by lignin (Stevenson, 1982).

The main effect of parent material on SOM content is the manner in which it affects soil texture. Clay soils have higher SOM contents than sandy soils. The type of clay mineral is also important. For example, montmorillonite, which has a high adsorption affinity for organic molecules, is very effective in protecting nitrogenous materials from microbial attack (Stevenson, 1982).

Topography, or the lay of the landscape, affects the content of SOM via climate, runoff, evaporation, and transpiration. Moist and poorly drained soils are high in SOM since organic matter degradation is lessened due to the anaerobic conditions of wet soil. Soils on north-facing slopes, which are wetter and have lower temperatures, are higher in SOM than soils on south-facing slopes, which are hotter and drier (Stevenson, 1982; Bohn *et al.*, 1985).

Cultivating soils also affects the content of SOM. When soils are first cultivated, SOM usually declines. In soils that were cultivated for corn production, it was found that about 25% of the N was lost in the first 20 years, 10% in the second 20 years, and 7% during the third 20 years (Jenny *et al.*, 1948). This decline is not only due to less plant residues, but also to improved aeration resulting from cultivation. The improved aeration results in increased microbial activity and lower amounts of humic materials. Wetting and drying of the soil also causes increased respiration which reduces the amount of SOM (Stevenson, 1982).

COMPOSITION OF SOM

The main constituents of SOM are C(52–58%), O(34–39%), H(3.3–4.8%), and N(3.7–4.1%). As shown in Table 3.3 the elemental composition of HA from several soils is similar. Other prominent elements in SOM are P and S. Research from Waksman and Stevens (1930) showed that the C/N ratio is around 10. The major organic matter groups are lignin-like compounds and proteins with other groups, in decreasing quantities, being hemicellulose, cellulose, and ether and alcohol soluble compounds. While most of these constituents are not water soluble, they are soluble in strong bases.

Soil organic matter consists of nonhumic and humic substances. The nonhumic substances have recognizable physical and chemical properties and consist of carbohydrates, proteins, peptides, amino acids, fats, waxes, and low-molecular-weight acids. These compounds are attacked easily by soil microorganisms and persist in the soil only for a brief time.

Humic substances can be defined as "a general category of naturally occurring, biogenic, heterogeneous organic substances that can generally be characterized as being yellow to black in color, of high molecular weight (MW), and refractory" (Aiken *et al.*, 1985b). Humic substances can be subdivided into humic acid (HA), fulvic acid (FA), and humin. Definitions of HS are classically based on their solubility in acid or base (Schnitzer and Khan, 1972) as will be discussed later in the section on fractionation of SOM.

Several mechanisms have been proposed to explain the formation of soil HS (Fig. 3.1). Selman Waksman's classical theory, the so-called lignin theory, was that HS are modified lignins that remain after microbial attack (pathway 4 of Fig. 3.1). The modified lignins are characterized by a loss of methoxyl (OCH_3) groups and the presence of *o*(ortho)-hydroxyphenols and oxidation of aliphatic side chains to form COOH groups. These lignins undergo more modifications and then result in first HA and then FA. Pathway 1, which is not considered significant, assumes that HS form from sugars (Stevenson, 1982).

The contemporary view of HS genesis is the polyphenol theory (pathways 2 and 3 in Fig. 3.1) that involves quinones (Fig. 3.2). In pathway 3 (Fig. 3.1) lignin is an important component of HS creation, but phenolic aldehydes and

TABLE 3.3. The Elementary Composition of Humic Acids from Different Soils[a]

	Percentage				Ratio		
Soil	**C**	**H**	**N**	**O**	**C/N**	**C/H**	**O/H**
A[b]	52.39	4.82	3.74	39.05	14.0	10.9	8.1
B	57.47	3.38	3.78	35.37	15.2	17.0	10.4
C	58.37	3.26	3.70	34.67	15.7	17.9	10.6
D	58.56	3.40	4.09	33.95	14.3	17.2	10.0

[a] From Kononova (1966).

[b] Soils A, B, C, and D represent soils of varying genesis, taxonomy, and physicochemical properties.

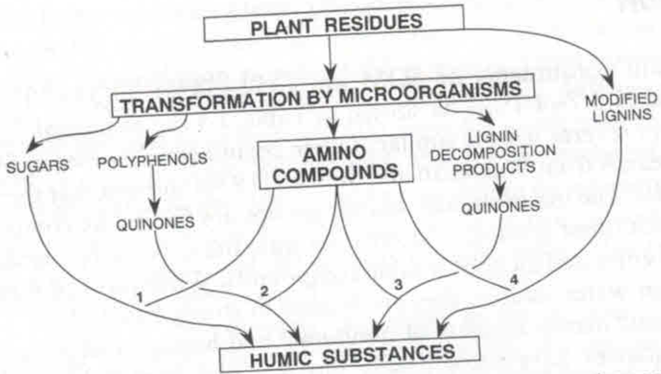


FIGURE 3.1. Mechanisms for the formation of soil humic substances. Amino compounds synthesized by microorganisms are seen to react with modified lignins (pathway 4), quinones (pathways 2 and 3), and reducing sugars (pathway 1) to form complex dark-colored polymers. From F. J. Stevenson (1982), "Humus Chemistry." Copyright 1982 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

acids that are released from lignin during microbial attack enzymatically are altered to quinones, which polymerize in the absence or presence of amino compounds to form humic-like macromolecules. Pathway 2 (Fig. 3.1) is analogous to pathway 3 except the polyphenols are microbially synthesized from nonlignin C sources, e.g., cellulose, and oxidized by enzymes to quinones and then to HS (Stevenson, 1982).

While the polyphenol theory is currently in vogue to explain the creation of HS, all four pathways may occur in all soils. However, one pathway is usually prominent. For example, pathway 4, the lignin pathway, may be primary in poorly drained soils while the polyphenol pathways (2 and 3) may predominate in forest soils (Stevenson, 1982).

Humic acids are extremely common. According to Szalay (1964) the amount of C in the earth as humic acids (60×10^{11} Mg) exceeds that which

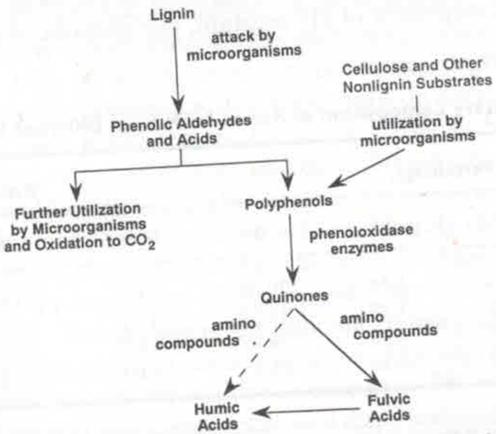


FIGURE 3.2. Schematic representation of the polyphenol theory of humus formation. From F. J. Stevenson (1982), "Humus Chemistry." Copyright 1982 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

occurs in living organisms (7×10^{11} Mg). Humic acids are found in soils, waters, sewage, compost heaps, marine and lake sediments, peat bogs, carbonaceous shales, lignites, and brown coals. While they are not harmful, they are not desirable in potable water (Stevenson, 1982).

One of the problems in studying humin is that it is not soluble. Thus methods that do not require solubilization are necessary. Carbon-13 (^{13}C) nuclear magnetic resonance (NMR) spectroscopy has greatly assisted in the study of humin since the high content of mineral matter in humin is not a factor. Humin is similar to HA. It is slightly less aromatic (organic compounds that behave like benzene, Aiken *et al.*, 1985b) than HA, but it contains a higher polysaccharide content (Wright and Schnitzer, 1961; Acton *et al.*, 1963; Schnitzer and Khan, 1972).

The amounts of nonhumic and humic substances in soils differ. The amount of lipids can range from 2% in forest soil humus to 20% in acid peat soils. Protein may vary from 15 to 45% and carbohydrates from 5 to 25%. Humic substances may vary from 33 to 75% of the total SOM with grassland soils having higher quantities of HA and forest soils having higher amounts of FA (Stevenson, 1982).

There are a multitude of paths that HS can take in the environment (Fig. 3.3). Water is obviously the most important medium that affects the transport of HS. A host of environmental conditions affect HS, ranging from oxic to anoxic environments, and from particulate to dissolved HS. Additionally, the time range that HS remain in the environment is wide. It can range from weeks and months for HS in surface waters of lakes, streams, and estuaries to hundreds of years in soils and deep aquifers (Aiken *et al.*, 1985b).

Humic substances range in diameter from 1 to 0.001 μm. While HA fit into this size range some of the lower-molecular weight FA are smaller. Humic substances are hydrophilic and consist of globular particles which in aqueous solution contain hydration water. Stevenson (1982) notes that HS are thought of as coiled, long-chain molecules or two- or three-dimensional cross-linked

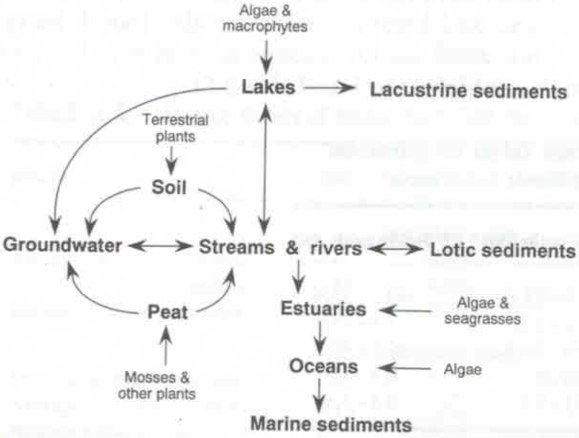


FIGURE 3.3. Diagram of the many possible environmental flowpaths of humic substances. From Aiken, G. R., McKnight, D. M., Wershaw, R. L., and MacCarthy, P. *In* "Humic Substances in Soil, Sediments, and Water" (G. R. Aiken, D. M. McKnight, and R. L. Wershaw, eds.), pp. 1–9. Copyright © 1985 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

macromolecules whose negative charge is primarily derived from ionization of acidic functional groups, e.g., carboxyls.

The average molecular weight of HS may range from 500 to 5000 for FA to 3000–1,000,000 for HA (Stevenson, 1982). Soil HA have higher molecular weights than aquatic HA. The molecular weight measurements depend on pH, concentration, and ionic strength.

The lack of reproducibility in analytical methods makes the study of HS difficult and exacerbates the task of deriving a precise elemental composition. Table 3.4 shows the average elemental composition for HA and FA. Based on these data, mean formulae of $C_{10}H_{12}O_5N$ for HA and $C_{12}H_{12}O_9N$ for FA, disregarding S, could be derived. The major elements composing HA and FA are C and O. The C content varies from 41 to 59% and the O content varies from 33 to 50%. Fulvic acids have lower C (41 to 51%) but higher O (40 to 50%) contents than HA. Percentages of H, N, and S vary from 3 to 7, 1 to 4, and 0.1 to 4%, respectively. Humic acids tend to be higher in N than FA, while S is somewhat higher in FA.

Schnitzer and Khan (1972) have studied HS from arctic, temperate, subtropical, and tropical soils. They found ranges of 54–56% for C, 4–5% for H, and 34–36% for O. Neutral soils tend to have narrow ranges of C, H, and O, while acid soils show broader ranges, and particularly higher O contents. Table 3.5 shows the elemental composition of HS from a number of organic soils.

Atomic ratios of H/C, O/C, and N/C can be useful in identifying types of HS and in devising structural formulas (Table 3.6). Based on the information in Table 3.6 it appears that the O/C ratio is the best indicator of humic types. Soil HA O/C ratios are about 0.50 while FA O/C ratios are 0.70.

A number of methods can be used to quantitate the functional groups of HS, particularly the acidic groups. The main acidic groups are carboxyl (R—C=O—OH) and acidic phenolic OH groups (presumed to be phenolic OH), with carboxyls being the most important group (Table 3.7). The total acidities of FA are higher than those for HA (Table 3.8). Smaller amounts of alcoholic OH, quinonic, and ketonic groups are also found. Fulvic acids are high in carboxyls, while alcoholic OH groups are higher in humin than in FA or HA and carbonyls are highest in FA (Table 3.8).

TABLE 3.4. Average Values for Elemental Composition of Soil Humic Substances[a]

	Humic acids (%)	Fulvic acids (%)
Carbon	53.8–58.7	40.7–50.6
Hydrogen	3.2–6.2	3.8–7.0
Oxygen	32.8–38.3	39.7–49.8
Nitrogen	0.8–4.3	0.9–3.3
Sulfur	0.1–1.5	0.1–3.6

[a] From Steelink, C. *In* "Humic Substances in Soil, Sediments, and Water" (G. R. Aiken, D. M. McKnight, and R. L. Wershaw, eds.), pp. 457–476. Copyright © 1985 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

TABLE 3.5. Elemental Composition of Humic Substances from Various Organic Soils with Standard Errors of the Means[a]

Organic soils	Number of samples	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Sulfur (%)	Oxygen (%)
				Humins		
Florida mucks[b]	11	57.8 ± 0.6	4.7 ± 0.2	2.9 ± 0.1	0.4 ± 0.1	34.2 ± 0.6
				Humic acids		
Florida mucks[b]	11	57.0 ± 0.3	4.5 ± 0.2	3.3 ± 0.1	0.4 ± 0.1	34.8 ± 0.3
Florida mucks[c]	11	56.5 ± 0.5	5.9 ± 0.1	3.9 ± 0.2	1.0 ± 0.0	32.7 ± 0.6
Sackville peats[d]	2	53.3 ± 0.8	5.6 ± 0.1	4.0 ± 0.3	1.5 ± 0.2	35.8 ± 0.8
Sackville mucks[d]	2	49.6 ± 0.1	5.2 ± 0.3	3.4 ± 0.5	0.8 ± 0.1	41.1 ± 0.8
				Fulvic acids		
Florida mucks[b]	11	54.5 ± 1.3	5.3 ± 0.4	1.9 ± 0.2	0.8 ± 0.2	37.6 ± 1.1
Sackville peats[d]	2	44.7 ± 1.1	6.7 ± 0.9	3.4 ± 0.1	1.2 ± 0.2	44.2 ± 2.2
Sackville mucks[d]	2	42.6 ± 0.1	6.8 ± 1.0	3.3 ± 0.3	1.2 ± 0.1	46.3 ± 1.3

C higher
N

O higher

[a] From Mathur, S. P., and Farnham, R. S. *In* "Humic Substances in Soil, Sediments and Water" (G. R. Aiken, D. M. McKnight, and R. L. Wershaw, eds.), pp. 53–85. Copyright © 1985 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

[b] From Zelazny and Carlisle (1974).

[c] From Volk and Schnitzer (1973).

[d] From Preston *et al.* (1984).

TABLE 3.6. Atomic Ratios of Elements in Soil Humic and Fulvic Acids[a]

Source	H/C	O/C	N/C	References
		Soil fulvic acids		
Average of many samples	1.4	0.74	0.04	Schnitzer and Khan (1978)
Average of many samples	0.83	0.70	0.06	Ishiwatari (1975)
Average of many samples	0.93	0.64	0.03	Malcolm *et al.* (1981)
		Soil humic acids		
Average of many samples	1.0	0.48	0.04	Schnitzer and Khan (1978)
Average of many samples	1.1	0.50	0.02	Ishiwatari (1975)
Neutral soils, average	1.1	0.47	0.06	Hatcher (1980)
Aldrich humic acid	0.8	0.46	0.01	Steelink *et al.* (1989)
Amazon HA/FA	0.97	0.57	0.04	Leenheer (1980)

O/C ≐ 0.7

O/C = 0.5

[a] From Steelink, C. *In* "Humic Substances in Soil, Sediments, and Water" (G. R. Aiken, D. M. McKnight, and R. L. Wershaw, eds.), pp. 457–476. Copyright © 1985 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

TABLE 3.7. Some Important Functional Groups of SOM[a]

Functional group	Structure
	Acidic groups
Carboxyl	$R-C{=}O(-OH)$[b]
Enol	$R-CH{=}CH-OH$
Phenolic OH	$Ar-OH$[b]
Quinone	$Ar{=}O$
	Neutral groups
Alcoholic OH	$R-CH_2-OH$
Ether	$R-CH_2-O-CH_2-R$
Ketone	$R-C{=}O(-R)$
Aldehyde	$R-C{=}O(-H)$
Ester	$R-C{=}O(-OR)$
	Basic groups
Amine	$R-CH_2-NH_2$
Amide	$R-C{=}O(-NH-R)$

[a] Adapted from F. J. Stevenson (1982), "Humus Chemistry." Copyright 1982 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc. and Thurman (1985) with permission of Kluwer Academic Publishers.

[b] R is an aliphatic (a broad category of carbon compounds having only a straight, or branched, open chain arrangement of the constituent carbon atoms; the carbon–carbon bonds may be saturated or unsaturated; Aiken *et al.*, 1985a) backbone and Ar is an aromatic ring.

The chemical structures of some of the amino acids found in soils are shown in Table 3.9. The quantities of amino acids found in HS extracted from tropical soils are given in Table 3.10. High levels of amino acid nitrogen were found in HA, FA, and humin. There are high distributions of acidic and some neutral amino acids, particularly glycine, alanine, and valine.

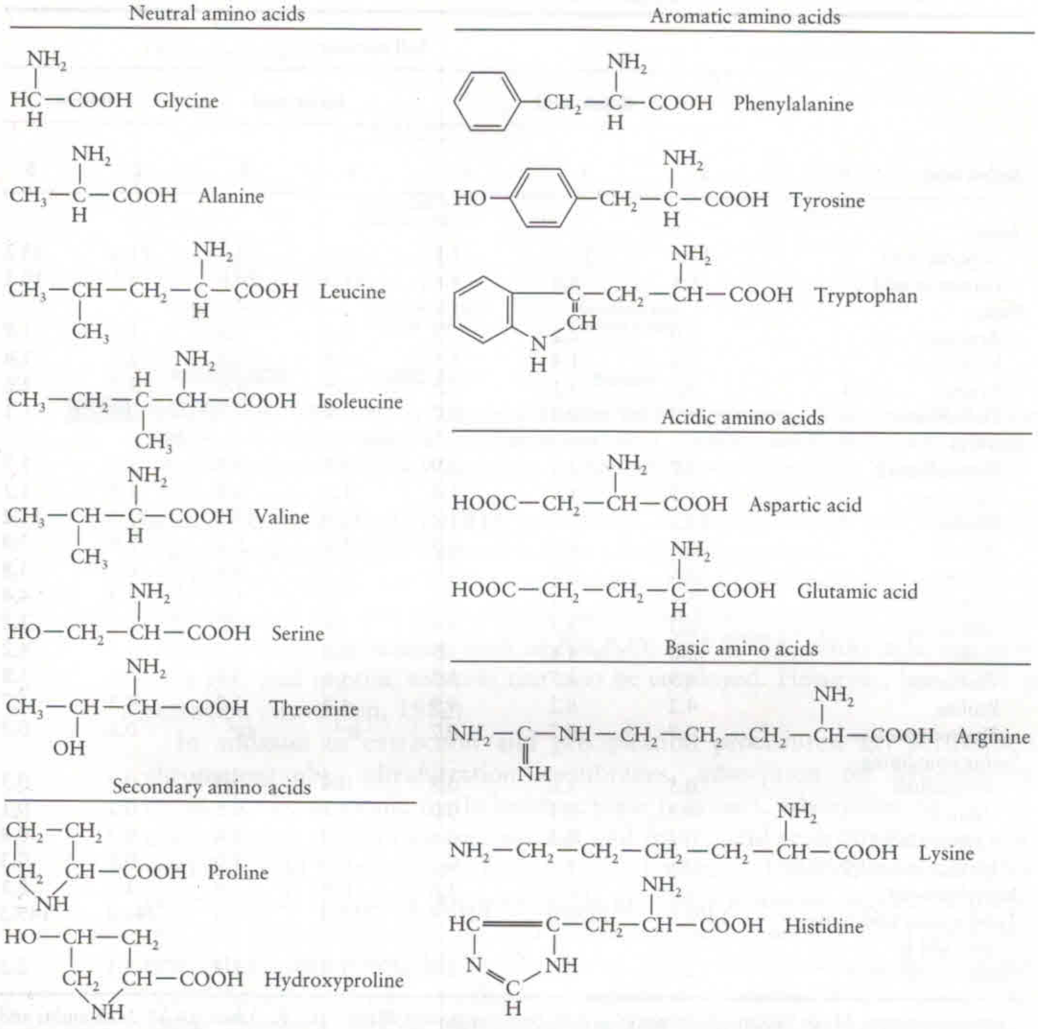
Humic substances also contain small amounts of nucleic acids and their derivatives, chlorophyll, and chlorophyll-degradation products, phospholipids, amines, and vitamins. The nucleic acids include DNA and RNA. They can be identified by the nature of the pentose sugar, i.e., deoxyribose or ribose, respectively (Stevenson, 1982).

TABLE 3.8. Functional Groups in Humic Substances from 11 Florida Muck Samples ($cmol\ kg^{-1}$), with Standard Errors of the Means[a]

	Total acidity	Carboxyls	Phenolic OH	Alcoholic OH	Carbonyls
Humins	510 ± 20	200 ± 20	310 ± 20	360 ± 30	260 ± 20
Humic acids	720 ± 40	310 ± 20	420 ± 30	130 ± 30	130 ± 10
Fulvic acids	860 ± 40	400 ± 20	460 ± 20	80 ± 20	430 ± 10

[a] From Zelazny and Carlisle (1974), with permission.

TABLE 3.9. Chemical Structures of Some Protein Amino Acids Found in Soils[a]



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FRACTIONATION OF SOM

Before one can suitably study SOM, it must be separated from the inorganic soil components. Fractionation of SOM lessens the heterogeneity of HS so that physical and chemical techniques can be used to study their structure and molecular properties (Hayes and Swift, 1978). The classical fractionation scheme (Fig. 3.4) involves precipitation of HS by adjustment of pH and salt concentrations, addition of organic solvents, or addition of metal ions.

TABLE 3.10. Relative Molar Distribution of Amino Acids in Humic Substances (α-Amino Acid Nitrogen of Each Amino Acid × 100/Total Amino Acid Nitrogen) from Several Tropical Soils[a,b]

	Soil number[c]						
	Humic acid			Fulvic acid		Humin	
Amino acid	2	3	5	2	5	2	5
Acidic							
Aspartic acid	13.0	11.7	11.8	26.1	23.1	11.8	23.2
Glutamic acid	8.5	8.8	8.6	15.0	20.9	8.2	10.1
Basic							
Arginine	2.0	2.2	2.3	0.5	0.3	1.9	1.9
Histidine	2.3	1.4	1.5	0.9	0.2	2.1	1.4
Lysine	3.3	3.1	3.5	1.9	1.4	2.7	2.6
Ornithine	0.7	0.8	0.7	0.9	0.7	0.6	1.1
Neutral							
Phenylalanine	3.2	3.3	2.9	1.3	0.9	2.9	1.7
Tyrosine	1.5	1.6	1.4	1.2	0.2	1.5	1.2
Glycine	11.2	10.9	11.1	12.6	13.5	13.1	11.2
Alanine	7.6	8.5	8.3	7.4	9.1	8.9	7.9
Valine	5.4	6.2	5.9	4.1	3.6	6.0	3.8
Leucine	5.1	5.8	5.1	3.0	1.7	5.3	4.4
Isoleucine	3.3	3.5	3.5	1.8	1.7	3.0	2.2
Serine	5.0	4.8	4.9	5.2	4.3	5.7	4.2
Threonine	4.9	4.7	5.2	4.4	3.9	5.3	3.8
Proline	4.2	6.2	4.9	4.4	3.3	4.2	2.7
Hydroxyproline	0.7	0.7	0.7	tr[d]	tr[d]	0.8	0.3
Sulfur-containing							
Methionine	0.5	1.0	0.8	0.4	0.3	0.7	0.3
Cystine	0.3	0.1	0.2	0.1	0.2	0.1	0.1
Cysteic acid	0.4	0.5	0.6	1.7	3.4	0.3	0.8
Methionine sulphoxide	0.6	0.2	0.3	0.1	1.0	0.2	0.3
Miscellaneous[e]	1.7	0.9	1.6	0.9	2.9	1.6	2.1
Total amino acid nitrogen (μM g^{-1})	1496.0	1476.0	1856.0	775.0	587.0	346.4	149.5
Amino sugar ratio[f]	1.3	1.3	1.3	1.2	1.4	3.5	2.5

[a] From Schnitzer, M. *In* "Humic Substances in Soil, Sediments, and Water" (G. R. Aiken, D. M. McKnight, and R. L. Wershaw, eds.), pp. 303–325. Copyright © 1985 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

[b] Reprinted from Sowden, F. J., Griffith, S. M., and Schnitzer, M. (1976). The distribution of nitrogen in some highly organic tropical volcanic soils. *Soil. Biol. Biochem.* 8, 55–60, with kind permission from Elsevier Science Ltd., The Boulevard, Langford Lane, Kidlington 0X5 1GB, U.K.

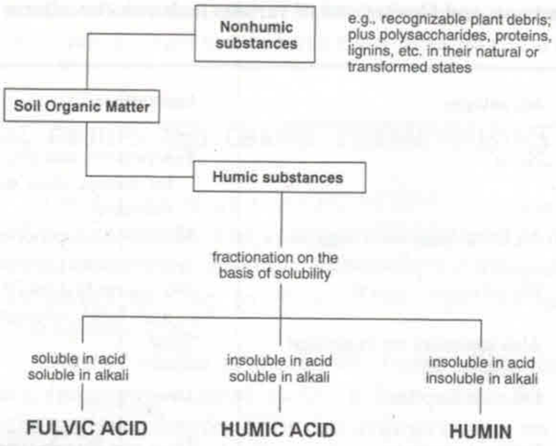
[c] Numbers represent different soils.

[d] tr, Trace.

[e] Includes allo-isoleucine, α-NH_2-butyric acid; 2-4-diaminobutyric acid, diaminopimelic acid, β-alanine, ethanolamine, and unidentified compounds.

[f] Ratio of glucosamine/galactosamine.

Alkali extraction, usually with 0.1–0.5 *M* NaOH and Na_2CO_3 solutions, is based on solubility principles. Humic acid is soluble in alkali (base) and insoluble in acid while FA is soluble in both alkali and acid. Hymatomelanic acid is the alcohol soluble portion of HA, and humin is not soluble in alkali or



① NaOH → humin
② HCl

FIGURE 3.4. Fractionation of soil organic matter and humic substances. From Hayes, M. H. B. and Swift, R. S. *In* "The Chemistry of Soil Constituents" (D. J. Greenland and M. H. B. Hayes, eds.), pp. 179–230. Copyright 1978 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

acid. After extraction, the HA precipitate is usually frozen and thawed to remove water and then freeze-dried for subsequent analysis.

However, alkali extractions can dissolve silica, contaminating the humic fractions, and dissolve protoplasmic and structural components from organic tissues. Milder extractants, such as $Na_4P_2O_7$ and EDTA, dilute acid mixtures with HF, and organic solvents can also be employed. However, less SOM is extracted (Stevenson, 1982).

In addition to extraction and precipitation procedures, gel permeation chromatography, ultrafiltration membranes, adsorption on hydrophobic resins (XAD, nonionic methylmethacrylate polymer), adsorption on ion exchange resins, adsorption on charcoal and Al_2O_3, and centrifugation are also used for SOM fractionation (Buffle, 1984; Thurman, 1985). New electrophoretic methods including polyacrylamide gel electrophoresis, isoelectric focusing, and isotachophoresis are also promising techniques for SOM fractionation (Hayes and Swift, 1978). The use of XAD resins is considered by many researchers to be the best method to fractionate or isolate HS (Thurman *et al.*, 1978; Thurman, 1985). The advantages and limitations of various isolation procedures for HS are given in Table 3.11.

SOM STRUCTURE

While we know the elemental and functional group compositions of HS, definitive knowledge of the basic "backbone structure" is still an enigma. Many structures have been proposed and each of them is characterized by similar functional groups and the presence of aliphatic and aromatic components. Based on a variety of techniques and analyses Schulten and Schnitzer (1993) have proposed a structure for HA (Fig. 3.5). Oxygen is present as carboxyls, phenolic and alcoholic hydroxyls, and carboxylic esters and ethers, while nitrogen is present as heterocyclic structures and as nitriles. The elemental composition of the HA structure in Fig. 3.5 is $C_{308}H_{328}O_{90}N_5$; it has a

TABLE 3.11. **Advantages and Limitations of Various Isolation Procedures for Humic Substances**[a]

Method	Advantages	Limitations
Precipitation	None	Fractionates sample, not specific for humus, slow with large volumes
Freeze concentration	All DOC (dissolved organic carbon) concentrated	Slow, tedious procedure, concentrates inorganics
Liquid extraction	Visual color removal	Not quantified by DOC, slow with large volumes
Ultrafiltration	Also separates by molecular weight	Slow
Strong anion-exchange	Efficient sorption	Does not desorb completely
Charcoal	Efficient sorption	Does not desorb completely
Weak anion-exchange	Adsorbs and desorbs efficiently	Resin bleeds DOC
XAD resin	Adsorbs and desorbs efficiently	Resin must be cleaned to keep DOC bleed low

[a] From Thurman (1985). Reprinted by permission of Kluwer Academic Publishers.

molecular weight of 5540 Da and an elemental analysis of 66.8% C, 6.0% H, 26.0% O, and 1.3% N.

The main reason that the basic structure of HS is still not fully understood is largely due to the heterogeneity and complexity of HS. If HS could be separated into their pure components, major advances in SOM chemistry could be

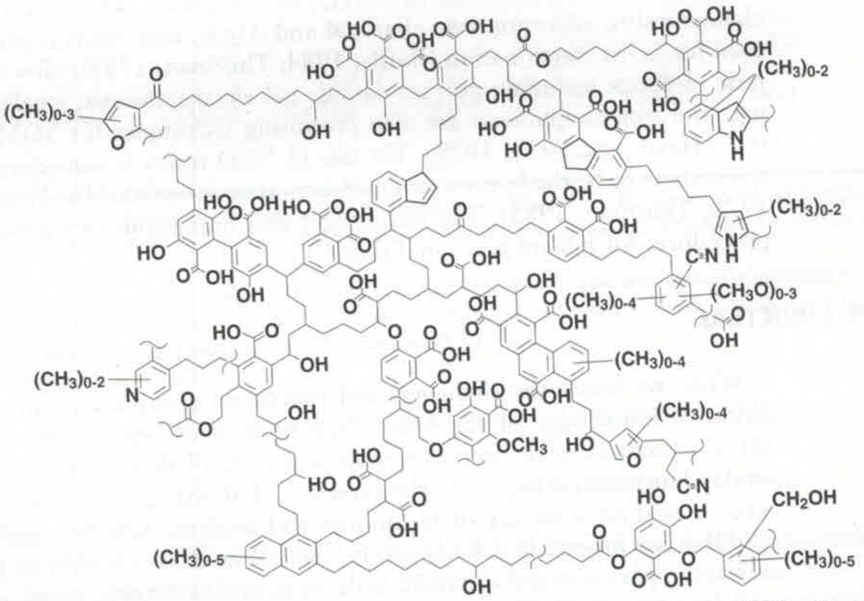


FIGURE 3.5. Schematic of humic acid structure. From Schulten and Schnitzer (1993), with permission from Springer-Verlag.

made. Such advances have been made in protein and other biopolymer chemistry where pure forms have been isolated (MacCarthy and Rice, 1985).

FUNCTIONAL GROUPS AND CHARGE CHARACTERISTICS

The surface areas and CEC of SOM, as given earlier, are higher than those of clay minerals. The role that SOM plays in the retention of ions is indeed significant, even in soils where the SOM content is very low. It has been estimated that up to 80% of the CEC of soils is due to organic matter (Stevenson, 1982).

Organic matter is a variable charge soil component. Since its point of zero charge (pzc), defined as the pH at which the colloidal particle has no net charge (see Chapter 5 for discussions on points of zero charge), is low, about 3, SOM is negatively charged at pH values greater than 3. As pH increases, the degree of negative charge increases due to the deprotonation or dissociation of H^+ from functional groups.

The major acidic functional groups are carboxyls ($pK_a < 5$), quinones that may dissociate as readily as carboxyl groups and have as low a pK_a, phenolic OH groups, and enols (Table 3.7). Since carboxyl and phenolic groups can deprotonate at pHs common in many soils, they are major contributors to the negative charge of soils. It has been estimated that up to 55% of the CEC from SOM is due to carboxyl groups (Broadbent and Bradford, 1952) while about 30% of the CEC of SOM up to pH 7 is due to the quinonic, phenolic, and enolic groups. Neutral and basic functional groups important in SOM are also given in Table 3.7.

Two seminal papers (Helling *et al.*, 1964; Yuan *et al.*, 1967) in the scientific literature clearly established the importance of SOM in contributing to the CEC of a soil. Helling *et al.* (1964) measured the CEC of 60 Wisconsin soils at pH values between 2.5 and 8, and by multiple correlation analysis determined the contributions of OM and clay at each pH, and the variation in CEC of each as pH changed (Table 3.12). Based on these studies, Helling *et al.* (1964) concluded that the CEC of the clay fraction changed much less as pH increased

TABLE 3.12. Contribution of Organic Matter and Clay Fractions to Soil Cation Exchange Capacity as Influenced by pH

Buffer pH	Clay fraction (cmol kg^{-1} clay)	Organic fraction (cmol kg^{-1} SOM)	% of CEC due to SOM
2.5	38	36	19
3.5	45	73	28
5.0	54	127	37
6.0	56	131	36
7.0	60	163	40
8.0	64	215	45

Note. Adapted from data of Helling *et al.* (1964), with permission.

compared to the CEC of the SOM fraction. They attributed this to the dominance of permanent charge of the clay fraction, primarily composed of montmorillonite and vermiculite, which would increase little with increase in pH. The small increases in CEC of the clay fraction were attributed to the dissociation of edge functional groups on the kaolinite surfaces as pH increased.

However, the CEC of the organic fraction of the soils increased dramatically with pH—from 36 cmol kg^{-1} at pH 2.5 to 215 cmol kg^{-1} at pH 8.0. This was due to the dissociation of H^+ from functional groups of the SOM. At pH 2.5, 19% of the CEC was due to SOM, while at pH 8.0 SOM accounted for 45% of the total CEC.

The importance of SOM in sandy soils to the cation exchange capacity is shown in Table 3.13. From 66.4 to 96.5% of the CEC of these soils was due to SOM.

Soil organic matter is a major contributor to the buffering capacity of soils. A typical titration curve of peat HA and soil HA is shown in Fig. 3.6. As base is added pH increases, illustrating the large buffering capacity of HS that is apparent over a wide pH range and the weak acid characteristics of HS. Most buffer curves of HS from acid soils have a pK_a of about 6. The titration curve (Fig. 3.6) can be divided into three zones. Zone I, the most acid region, represents dissociation of carboxyl groups, while Zone III represents dissociation of phenolic OH and other very weak acid groups. Zone II is an intermediate region attributed to a combination of dissociation of weak carboxyl and very weak acid groups (Stevenson, 1982).

TABLE 3.13. Contribution of Organic Matter and Clay to the Cation Exchange Capacities of Sandy Soils[a]

		Relative contribution (%)	
Soil group	Average CEC (cmol kg^{-1})	SOM	Clay
Entisols			
Psamments	5.26	74.9	25.1
Aquipsamments	3.84	86.8	15.2
Quartipsamments	5.63	75.7	24.3
Acid family	3.83	78.7	21.3
Nonacid family	4.21	95.4	4.6
Phosphatic family	10.58	77.4	22.6
Inceptisols			
Aquepts and Umbrepts	8.17	69.2	30.8
Mollisols			
Aqualls	12.93	66.4	33.6
Spodosols			
Aquods	5.53	96.5	3.5
All soils	6.77	76.1	23.9

[a] Adapted from Yuan, T. L., Gammon, N., Jr., and Leighty, R. G. (1967). Relative contribution of organic and clay fractions to cation-exchange capacity of sandy soils from several groups. *Soil Sci.* 104, 123–128. Used with permission of Williams and Wilkins.

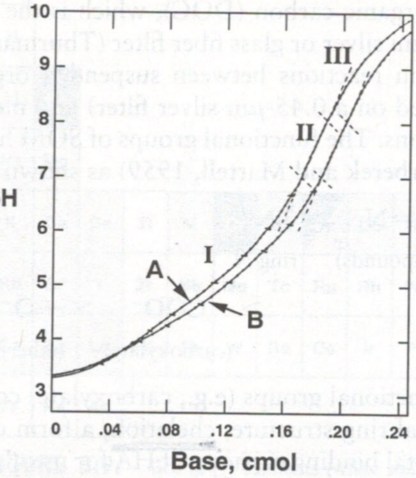


FIGURE 3.6. Titration of a peat (A) and soil (B) humic acid. The small wavy lines on the curves indicate endpoints for dissociation of weak acid groups having different but overlapping dissociation constants. From F. J. Stevenson (1982), "Humus Chemistry." Copyright 1982 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

The weak acid character of SOM is ascribed to complexation with free metals, such as Al^{3+}, Fe^{3+}, and Cu^{2+}, and hydroxy-Al and hydroxy-Fe materials. Thus, important functional groups such as carboxyls are not always found as free groups in soils but are complexed with metals (Martin and Reeve, 1958).

HUMIC SUBSTANCE–METAL INTERACTIONS

The complexation of metal ions by SOM is extremely important in affecting the retention and mobility of metal contaminants in soils and waters. Several different types of SOM–metal reactions can occur (Fig. 3.7). These include

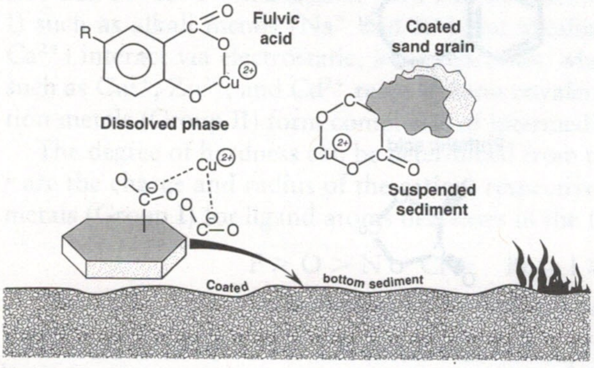


FIGURE 3.7. Complexation of metal ions by organic matter in suspended sediment, bottom sediment, colloidal and dissolved phases. From Thurman (1985). Reprinted by permission of Kluwer Academic Publishers.

reaction between dissolved organic carbon (DOC), which is the organic carbon passing through a 0.45-μm silver or glass fiber filter (Thurman, 1985) and metal ions, and complexation reactions between suspended organic matter (SOC, organic carbon retained on a 0.45-μm silver filter) and metal ions and bottom sediment and metal ions. The functional groups of SOM have different affinities for metal ions (Charberek and Martell, 1959) as shown below;

$$\underset{\text{(enolate)}}{-O^-} > \underset{\text{(amine)}}{-NH_2} > \underset{\text{(azo compounds)}}{-N{=}N-} > \underset{\text{ring N}}{\backslash N /} > \underset{\text{(carboxylate)}}{COO^-} > \underset{\text{(ether)}}{-O^-} > \underset{\text{(carbonyl).}}{-C{=}O}$$

If two or more organic functional groups (e.g., carboxylate) coordinate the metal ion, forming an internal ring structure, chelation, a form of complexation, occurs (Fig. 3.8). The total binding capacity of HA for metal ions is about 200–600 μmol g^{-1}. About 33% of this total is due to retention on cation complexing sites. The major complexing sites are carboxyl and phenolic groups.

Factors Affecting Metal–Complexant (Ligand) Interactions

The types of interactions between metal ions and complexants such as inorganic (anions) and organic (e.g., carboxyl and phenolic groups of SOM) ligands (a ligand is an atom, functional group, or molecule that is attached to the central atom of a coordination compound) can be predicted based on: (1) the hydrolysis properties of elements, and (2) the concept of "hardness" and "softness" of metals and electron-donor atoms of complexing sites (Buffle and Stumm, 1994).

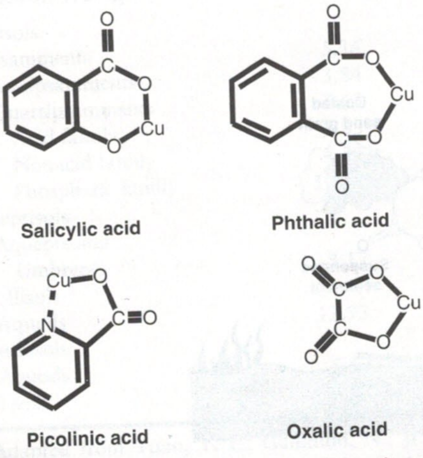


FIGURE 3.8. Chelation of metal ions by organic compounds. From Thurman (1985). Reprinted by permission of Kluwer Academic Publishers.

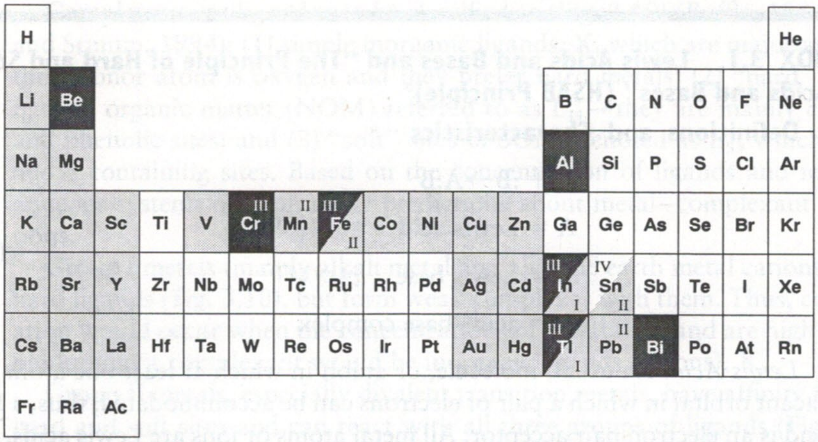


FIGURE 3.9. Group (1) elements (white squares), Group (2) elements (dark shaded squares), and Group (3) elements (light shaded squares). Group Elements (1), (2), and (3) are defined in text. Reprinted with permission from Buffle and Stumm (1994). Copyright Lewis Publishers, an imprint of CRC Press, Boca Raton, Florida.

Hydrolysis Properties

Inorganic elements in the periodic table can be divided into three groups based on their reactions with OH^- or O^{2-} (Fig. 3.9). Group 1 elements form nondissociated oxocomplexes (e.g., SO_4^{2-}, PO_4^{3-}) and oxyacids (e.g., $As(OH)_3$). Group 2 elements are highly hydrolyzed but can also occur as hydrated cations (e.g., Fe(III)), and Group 3 elements do not have very stable hydroxo complexes even at high pH (e.g., Ca^{2+}, Zn^{2+}). The major ligand in water is OH^-; ligands other than OH^- will combine only with Group 3 elements and to some extent with Group 2, but not at all with Group 1 elements.

Hard and Soft Characteristics

Elements can also be classified based on their hard and soft characteristics (see Box 3.1 for a discussion of hard and soft elements). Hard cations (Group I) such as alkali metals (Na^+ and K^+) and alkaline earth metals (Mg^{2+} and Ca^{2+}) interact via electrostatic, ionic reactions, while soft cations (Group III) such as Cu^{2+}, Zn^{2+}, and Cd^{2+} react to form covalent bonds (Box 3.1). Transition metals (Group II) form complexes of intermediate strength.

The degree of hardness can be determined from the term Z^2/r, where Z and r are the charge and radius of the cation, respectively. The preference of hard metals (Group I) for ligand atoms decreases in the following order.

$$\underbrace{F > O > N \sim Cl >}_{\text{hard donor atoms}} \quad \underbrace{Br > I > S}_{\text{soft donor atoms}}$$

This order is reversed for soft metal ions (Group III). Thus the hard donor atoms such as F and O prefer hard metal ions while the soft donor atoms such as I and S prefer soft metal ions (Box 3.1).

BOX 3.1. Lewis Acids and Bases and "The Principle of Hard and Soft Acids and Bases" (HSAB Principle)[a]

Definitions and Characteristics

$$
\begin{aligned}
&A + {:}B \rightarrow A{:}B\\
&A = \text{Lewis acid} \quad \text{acceptor}\\
&{:}B = \text{Lewis base} \quad \text{donor}\\
&A{:}B = \text{acid–base complex}
\end{aligned}
\tag{3.1a}
$$

Lewis Acid. An atom, molecule, or anion in which at least one atom has a vacant orbital in which a pair of electrons can be accommodated; thus, a Lewis acid is an electron pair acceptor. All metal atoms or ions are Lewis acids. Most cations are Lewis acids. In Eq. (3.1a) above, when A is a metal ion, B is referred to as a ligand. Lewis acids are coordinated to Lewis bases or ligands.

Lewis Base. An atom, molecule, or ion which has at least one pair of valence electrons which are not being shared in a covalent bond; thus, a Lewis base is an electron pair donor. Most anions are Lewis bases.

Hard Acid. The acceptor atom is of high positive charge and small size, and does not have easily excited outer electrons. A hard acid is not polarizable and associates with hard bases through ionic bonds.

Soft Acid. The acceptor atom is of low positive charge and large size, and has several easily excited outer electrons. A soft acid is polarizable and prefers soft bases through covalent bonds.

Hard Base. The donor atom is of low polarizability and high electronegativity, is hard to reduce, and is associated with empty orbitals of high energy and thus is unaccessible.

Soft Base. The donor atom is of high polarizability and low electronegativity, is easily oxidized, and is associated with empty, low-lying orbitals.

Classification of Lewis Acids and Bases

Lewis acids	Lewis bases
Hard acids: Group I metals[b]	Hard bases
H^+, Li^+, Na^+, K^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Fe^{3+}, Al^{3+}, Sc^{3+}	H_2O, OH^-, F^-, PO_4^{3-}, SO_4^{2-}, Cl^-, CO_3^{2-}, ClO_4^-, NO_3^-
Transition acids: Group II metals	Transition bases
Cr^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}	Br^-, NO_2^-, N_2
Soft acids: Group III metals	Soft bases
Ag^+, Au^+, Tl^+, Cu^+, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Sn^{2+}	I^-, CN^-, CO

[a] Adapted from Pearson (1963, 1968) and Buffle and Stumm (1994).

[b] Refers to metal groups in text discussion of hard and soft characteristics of elements.

Complexants or ligands can be classified as (Fig. 3.10) (Buffle, 1984; Buffle and Stumm, 1994): (1) simple inorganic ligands, X, which are major anions—their donor atom is oxygen and they prefer hard metals; (2) "hard" sites of natural organic matter (NOM) referred to as L_H—they are mainly carboxyl and phenolic sites; and (3) "soft" sites of SOM, denoted as L_S, which are N- and S-containing sites. Based on the concentration of ligands and metals in aqueous systems one can make predictions about metal–complexant interactions.

Group I metals (mainly alkali metal and alkaline earth metal cations) prefer hard ligands (Fig. 3.10), but form weak complexes with them. Thus, complexation would occur when the concentrations of metal or ligand are high and the predominant complexant would be inorganic ligands (anions), X.

Group II metals, especially divalent transition metals, have affinity for both hard and soft sites and can react with all three groups of ligands (Fig. 3.10). These metals will compete for L_H sites with metals from Group 1, which are less strongly bound but at higher concentrations, and for L_S sites with Group III metals, which are at lower concentrations but more strongly bound.

Group III metals have greater affinity for soft sites (L_S) than for hard sites (L_H) or X ligands.

Determination of Stability Constants of Metal–HS Complexes

The determination of stability constants for HS–metal complexes provides information on the affinity of the metal for the organic ligand, and they also provide valuable insights into the fate of heavy metals in the environment. Box 3.2 outlines how stability constants are calculated. Stability constants can be determined using potentiometric titration, chromatography, ultrafiltration, equilibrium dialysis, ion specific electrodes (ISE), differential pulse anodic stripping voltammetry (DPASV), fluorescence spectrometry, and modeling

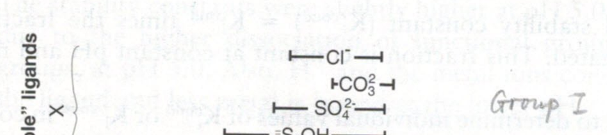


FIGURE 3.10. Ranges of concentrations of ligands or complexing sites in natural freshwaters. ≡S—OH refers to inorganic solid surface sites. —COOH and —OH refer to total concentrations of carboxyl and phenolic sites in natural organic matter. N_{org}, S_{org} refer to total concentrations of organic nitrogen and sulfur. Reprinted from Buffle (1984), by courtesy of Marcel Dekker, Inc.

BOX 3.2. Determination of Stability Constants for Metal–HS Complexes

The complexation reaction between a metal ion M and the ith deprotonated ligand (L_i) or binding site in a multiligand mixture at constant pH can be written as (Perdue and Lytle, 1983)

$$M + L_i \rightleftharpoons ML_i \tag{3.2a}$$

The stability constant for this reaction can be expressed as

$$K_i^{\mathrm{cond}} = \frac{[ML_i]}{[M][L_i]}, \tag{3.2b}$$

where brackets indicate the concentration.

It is usually not possible to analytically determine L_i because of H^+ competition and the possibility that the ith metal binding ligand may bind several protons. A more realistic expression of eq. 3.2b is

$$K_i'^{\mathrm{cond}} = \frac{[ML_i]}{[M][H_{X_i}\,L_i]}, \tag{3.2c}$$

where $[H_{X_i}\,L_i]$ is the concentration of all forms of the ith ligand that are not bound to M. Both K_i^{cond} and $K_i'^{\mathrm{cond}}$ are referred to as conditional stability constants. Conditional stability constants are valid only for the conditions (i.e., pH, neutral salt concentration) stated for a particular system. By definition, the value of K_i^{cond} and $K_i'^{\mathrm{cond}}$ will change with changes in pH or neutral salt concentration. Note also that $K_i'^{\mathrm{cond}}$ is related to K_i^{cond} through the expression

$$K_i'^{\mathrm{cond}} = \frac{[ML_i]}{[M][L_i]}\;\frac{[L_i]}{[H_{X_i}\,L_i]} = K_i^{\mathrm{cond}}\,\frac{[L_i]}{[H_{X_i}\,L_i]}. \tag{3.2d}$$

The conditional stability constant ($K_i'^{\mathrm{cond}}$) = K_i^{cond} times the fraction of $[H_{X_i}\,L_i]$ not protonated. This fraction is constant at constant pH and neutral salt concentration.

It is not possible to determine individual values of K_i^{cond} or $K_i'^{\mathrm{cond}}$ in complex mixtures of ligands, such as often occurs with natural systems. Rather, average K_i^{cond} ($\overline{K}^{\mathrm{cond}}$) or $K_i'^{\mathrm{cond}}$ ($\overline{K}'^{\mathrm{cond}}$) values are determined from experimental data,

$$\overline{K}^{\mathrm{cond}} = \frac{\sum\limits_i [ML_i]}{[M]\sum\limits_i [L_i]} = \frac{\sum\limits_i K_i^{\mathrm{cond}}[L_i]}{\sum\limits_i [L_i]} \tag{3.2e}$$

$$\overline{K}'^{\mathrm{cond}} = \frac{\sum\limits_i [ML_i]}{[M]\sum\limits_i [H_{X_i}\,L_i]} = \frac{\sum\limits_i K_i'^{\mathrm{cond}}[H_{X_i}\,L_i]}{\sum\limits_i [H_{X_i}\,L_i]}$$

$$= \frac{(C_M - [M])}{[M](C_L - C_M + [M])}, \tag{3.2f}$$

where C_M and C_L are stoichiometric concentrations of metal and total ligand, respectively. Note that as before $\overline{K}'^{\,cond}$ is related to $\overline{K}^{cond}$ through an expression similar to eq. (3.2d)

$$\overline{K}'^{\,cond} = K^{cond}\,\frac{\sum_i [L_i]}{\sum_i [H_{X_i}\,L_i]}. \qquad (3.2g)$$

The values of $K'^{\,cond}$ stability constants are the easiest to determine experimentally, and are the most common values that are published in the scientific literature. Their dependence on the total concentration of metal and ligand present in a given system (Eq. 3.2f), however, reinforces the fact that these are conditional stability constants and are only valid for the environmental conditions under which they were determined. Application of the concept of stability constants for metal-HS complexes requires using average stability constants determined under similar environmental conditions.

(Scatchard method). For more details on these methods the reader should consult Buffle (1984) and Thurman (1985).

Stability constants are affected by the source of the HS and extraction or isolation procedure employed, concentration of HS, ionic strength (see Chapter 4) of the solution, temperature, pH, method of analysis of the complex, and method of data manipulation and stability constant calculation (Thurman, 1985).

Schnitzer and Hansen (1970) calculated conditional stability constants (K_i^{cond}) for metal–FA complexes, based on continuous variations and ion exchange equilibrium methods, and found that the order of stability was $Fe^{3+} > Al^{3+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Pb^{2+} > Ca^{2+} > Zn^{2+} > Mn^{2+} > Mg^{2+}$. The stability constants were slightly higher at pH 5.0 than at pH 3.5, which is due to the higher dissociation of functional groups, particularly carboxyl groups, at pH 5.0. Also, H^+ and the metal ions compete for binding sites on the ligand and less metal is bound at the lower pH.

Effect of HS–Metal Complexation on Metal Transport

The complexation of HS with metals can beneficially as well as deleteriously affect the fate of metals in soils and waters. The speciation (see Chapter 4) of metals can be affected by these complexes as well as oxidation–reduction reactions (see Chapter 8). For example, HA can act as a reducing agent and reduce Cr(VI), the more toxic form of Cr, to Cr(III). As a Lewis hard acid, Cr(III) will form a stable complex with the carboxyl groups on the HA, further limiting its availability for plant or animal uptake.

Humic substances can serve as carriers of toxic metals, forming complexes that are stable and enhance transport of toxic metals in waters. In water treatment scenarios, these stable, soluble complexes can diminish the removal effectiveness of heavy metals from leachate waters of hazardous waste sites when precipitation techniques are employed as a remediation technique (Manahan, 1991). Additionally, the efficiency of membrane processes (reverse osmosis) and resin processes (ion exchange) that are used to treat the leachate waters is diminished. On the other hand, the binding of heavy metals to HS can enhance biological treatment of inorganic contaminants by reducing the toxicity of the heavy metals to the microbes. Additionally, inorganic anions such as phosphate and cyanide can be removed from water as well by mixed ligand complexation.

Effect of HS–Al^{3+} Complexes on Plant Growth

The importance of HS–Al^{3+} complexes on plant growth is illustrated in studies that have shown that crops often grow well on soils with a pH of < 4 in the surface horizon (Evans and Kamprath, 1970; Thomas, 1975). Organic matter contents of the surface horizons, which were enhanced due to no-tillage practices, were fairly high (4–5%). Exchangeable Al^{3+} (Al^{3+} bound electrostatically on soil colloids such as clay minerals and SOM) and the activity of Al^{3+} (see Chapter 4 for a discussion of ion activity) in the soil solution were low.

Thomas (1975) studied HS–Al^{3+} complexation effects on plant growth with a Maury silt loam soil from Kentucky with an average pH of 6.1 and an organic matter content ranging from 5.11% in the 0- to 7.5-cm layer to 0.80% in the 37.5- to 45-cm layer. Various amounts of 0.1 *M* HNO_3 were added such that the pH of the soils was 3.10–3.30. No exchangeable H^+ was found in the soils. The relationship between organic matter percentage and exchangeable Al^{3+} at several pH values is shown in Fig. 3.11. One sees that the influence of SOM on exchangeable Al^{3+} at any given pH is greatest up to 2.5% with a smaller effect at higher SOM contents. The effect of organic matter on exchangeable Al^{3+} was greater at the lower pH values. At pH 3.5, an increase from 1 to 2% organic matter lowered exchangeable Al from 6 to 4.2 cmol kg^{-1}. These results show that even small increases in SOM result in a significant reduction in exchangeable Al^{3+} and the activity of Al^{3+} in the soil

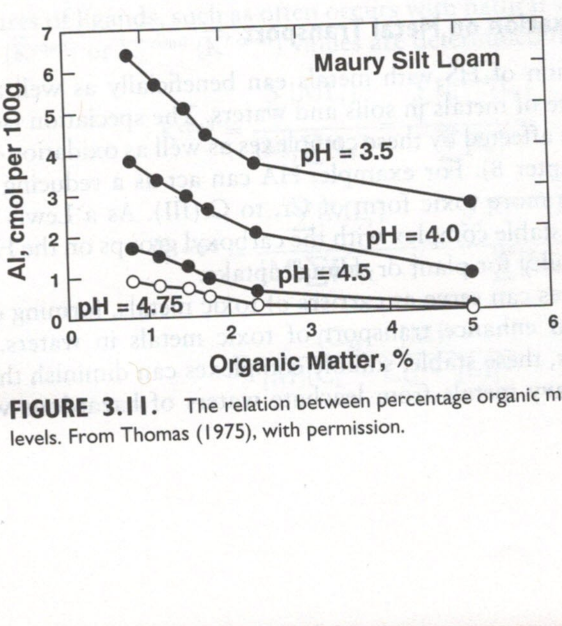


FIGURE 3.11. The relation between percentage organic matter and exchangeable Al at several pH levels. From Thomas (1975), with permission.

solution. Therefore, the lack of any deleterious effect on plant growth even at low pH may be due to the complexation of Al^{3+} with SOM and the removal of Al^{3+} and perhaps other toxic metals from the soil solution.

Effects of HS on Mineral Dissolution

Humic substances can also cause mineral dissolution. Lichens, bacteria, and fungi, which often grow on mineral surfaces, enhance this breakdown by producing organic complexing materials. At $pH > 6.5$ HA and FA can attack and degrade minerals and form water-soluble and water-insoluble metal complexes (Schnitzer, 1986). Humic acids can extract metals from galena (PbS), pyrolusite (MnO_2), calcite ($CaCO_3$), and malachite [$Cu_2(OH)_2CO_3$]. Humic acid can also extract metals from silicates (Baker, 1973), but to a lesser degree than from previously mentioned minerals. Various metal sulfides and carbonates can be solubilized by HA, including Pb(II), Zn(II), Cu(II), Ni, Fe(III), and Mn(IV). Solubilization ranges from 2100 μg for PbS to 95 μg for ZnS.

SOM–CLAY COMPLEXES

Soil organic matter complexes can also occur with clay minerals that are coated with metal oxides such as Al and Fe oxides. Useful reviews on this topic can be found in a number of sources (Mortland, 1970; Greenland, 1971; Mortland *et al.*, 1986; Schnitzer, 1986). Clays tend to stabilize SOM, and a correlation is often observed between the clay content and SOM. Some organic substances bridge soil particles together, resulting in stable aggregates. In some soils, particularly those high in humic substances, all of the clay may be coated with HS. It has been estimated that from 52 to 98% of all C in soils occurs as clay–SOM complexes (Stevenson, 1982). Even though such a complex exists, the organic surface is still reactive and can retain ions and other materials such as pesticides.

Other organic acids, organic amine cations, and amino acids can also interact with clays. Organic acids are negatively charged in the pH range of most soils but they are pH-dependently charged; some adsorption can occur through H-bonding and van der Waals forces (see definitions in next section) when the pH is below the pK_a of the acidic group, and when the organic acid is in the undissociated form. Organic materials such as proteins and charged organic cations can also be adsorbed in the interlayers of expansible layer silicates like montmorillonite.

Mechanisms of Interactions

The types of interactions involved in SOM–clay complexes include physical adsorption or interactions via van der Waals forces, electrostatic interactions (cation and anion exchange processes), cation and anion bridges whereby the polyvalent metal forms a bridge between the organic molecule and the inorganic surface to which it is bound (clay mineral–metal–HS), often referred to as coordination complexes, chemical adsorption, and H-bonding. Two or more of these mechanisms may occur simultaneously, depending on the type of organic material, the nature of the exchangeable ion on the clay surface, the surface acidity, and the moisture content of the system (Schnitzer, 1986).

Physical adsorption or retention via van der Waals forces is weak and results from changes in the electric charge density of individual atoms. An electrically positive fluctuation in one atom causes an electrically negative fluctuation in a neighboring atom, resulting in a net attractive force. Adsorption due to physical forces occurs with neutral polar and nonpolar molecules, particularly those with high molecular weight (Schnitzer, 1986).

Electrostatic bonding can occur via cation or anion exchange or protonation. The cationic property of a weakly basic organic molecule is strongly pH-dependent. Thus this mechanism is dependent on the basic character of the organic molecule, the pH of the system, the properties of the organic cation or chain length, and the type of cation on the clay surface. Sorption of HS on negatively charged clays occurs only when polyvalent metal cations such as Al^{3+}, Fe^{3+}, and Ca^{2+} are present on the clay exchanger since they can neutralize the negative charge on the clay and the charge on the deprotonated organic functional group, e.g., COO^-. Calcium is weakly held as a cation bridge and can be easily displaced, whereas Al^{3+} and Fe^{3+} are usually bound nonelectrostatically and are difficult to remove (Schnitzer, 1986). It is probably through this latter mechanism and through coordination that FA and HA are primarily retained in soils (Stevenson, 1982).

Hydrogen bonding results from linkage between two electronegative atoms through bonding with a single H^+ ion. The H^+ ion is a bare nucleus with a 1^+ charge and a propensity to share electrons with those atoms which contain an unshared electron pair such as O. The hydrogen bond is weaker than ionic or covalent bonds, but stronger than van der Waals attractive forces (Stevenson, 1982).

RETENTION OF PESTICIDES AND OTHER ORGANIC SUBSTANCES BY HUMIC SUBSTANCES

Pesticides have a strong affinity for SOM. Soil organic matter has an important effect on the bioactivity, persistence, biodegradability, leachability, and volatility of pesticides. In fact, perhaps SOM is the soil component that is most important in pesticide retention. Thus, the amount of pesticide that must be added to soils is strongly affected by the quantity of SOM.

Factors that affect the retention of pesticides by SOM are: number, type, and accessibility of HS functional groups, nature of the pesticides, properties of the soil including types and quantities of clay minerals and the other soil components, pH, exchangeable cations, moisture, and temperature (Stevenson, 1982). Bailey and White (1970) noted several properties of pesticides that affect retention and type of bonding on soil components: (1) type of the functional group, i.e., carboxyl, alcoholic hydroxyl, amine; (2) nature of the substituting group which alters the functional group, and the position of the substituting groups in relation to the functional group which may affect bonding; and (3) the presence and magnitude of unsaturation in the molecule, which affects the lyophilic and lyophobic balance. These factors determine important chemical properties such as the acidity or basicity of the compound as suggested by the pK_a of the compound.

The mechanisms by which pesticides are retained by SOM are not clearly understood. However, the pesticide may be strongly retained in the internal voids of humus molecules that are sieve-like (Khan, 1973). Adsorption of pesticides on HS occurs via ion exchange and protonation, H-bonding, van der Waals forces, ligand exchange (an organic functional group such as a carboxyl or hydroxyl displaces an inorganic hydroxyl or water molecule of a metal ion at the surface of a soil mineral such as a metal oxide, resulting in an inner-sphere complex; see discussions on ligand exchange and inner-sphere complexes in Chapter 5), and cation and water bridging. These mechanisms are discussed in detail in Koskinen and Harper (1990).

Humic substances can also combine with nonpolar organic compounds via a partitioning mechanism (see discussion in Chapter 5). This partitioning on hydrophobic SOM surfaces results from a weak solute–solvent interaction, or the low solubility or hydrophobic nature of the solute. Important hydrophobic sites on HS include fats, waxes, and resins and aliphatic side chains. Since humus has an aromatic framework and contains polar groups it may have both hydrophobic and hydrophilic sites.

Soluble humic substances can enhance the transport of pesticides in soils and into groundwaters. Fulvic acids, which have low molecular weight and high acidities and are more soluble than HA, can transport pesticides and other organic materials quite effectively. For example, the downward movement of the insecticide DDT in the organic layers of some forest soils has been ascribed to water-soluble, humic substances (Ballard, 1971)

Humic substances can also serve as reducing agents and chemically alter pesticides. The alteration is enhanced by the presence of reactive groups such as phenolic, carboxyl, enolic, heterocyclic, aliphatic-OH, and semiquinone like those contained in FA and HA. The presence of stable free radicals in HS would also indicate that they can effect chemical alterations of pesticides. The hydroxylation of the chloro-*s*-triazines is an example of nonbiological transformation of a pesticide by HS (Stevenson, 1982).

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