18

SOILS AND CHEMICAL POLLUTION

> ***Black and portentous this humor prove, unless good counsel may the cause remove . . .***
> —*W. Shakespeare,* Romeo and Juliet

The soil is a primary recipient by design or accident of a myriad of waste products and chemicals used in modern society. It has always been convenient to "throw things away," and the soil has been the recipient of most of these things. Every year millions of tons of these products from a variety of sources—industrial, domestic, and agricultural—find their way onto the world's soils. Once these materials enter the soil, they become part of biological cycles that affect all forms of life. One of the challenges facing humankind is to better understand how wastes affect these cycles and, in turn, the well-being of all plant and animal life.

In previous chapters we highlighted the enormous capacity of soils to accommodate added organic and inorganic chemicals. Tons of organic residues and animal manures are broken down by soil microbes each year (Chapter 12), and large quantities of inorganic chemicals are fixed or bound tightly by soil minerals (Chapter 14). But we also learned of the limits of the soil's capacity to accommodate these chemicals, and we have seen the disastrous effects on environmental quality when these limits are exceeded.

We have seen how soil processes affect the accommodation and release of waste products. For example, the production and sequestering of greenhouse gases, such as nitrous oxide, methane, and carbon dioxide (see, e.g., Sections 12.11 and 13.9), are very much influenced by soil processes. Other nitrogen- and sulfur-containing gases coming from domestic and industrial sources, as well as from the soil, acidify the atmosphere, and come to earth in acid rain (see, e.g., Section 9.6). Mismanaged irrigation projects result in the accumulation of salts, especially in arid-region soils (see Section 10.3).

We have also seen how fertilizer and manure applications that leave excess quantities of nutrients in the soil can result in the contamination of ground and surface waters with nitrates (Section 13.8) and phosphates (Section 14.2). The eutrophication of ponds, lakes, and even slow-moving rivers is evidence of these nutrient buildups. Huge "animal factories" for meat and poultry production produce mountains of manure that must be disposed of without loading the environment with unwanted chemicals and with pathogens that are harmful to humans and other animals (Section 16.5).

In this chapter we will focus on chemicals that contaminate and degrade soils, including some whose damage extends to water, air, and living things. The brief review of soil pollution is intended as an introduction to the nature of the major pollutants, their reactions in soils, and alternative means of managing, destroying, or inactivating them.

18.1 TOXIC ORGANIC CHEMICALS

Modern industrialized societies have developed thousands of synthetic organic compounds for thousands of uses. An enormous quantity of organic chemicals is manufactured every year—about 60 million Mg in the United States alone. Included are plastics and plasticizers, lubricants and refrigerants, fuels and solvents, pesticides and preservatives. Some are extremely toxic to humans and other life. Through accidental leakage and spills or through planned spraying or other treatments, synthetic organic chemicals can be found in virtually every corner of our environment—in the soil, in the groundwater, in the plants, and in our own bodies.

Environmental Damage from Organic Chemicals

Some of these organic compounds are relatively inert and harmless, but others are biologically damaging even in very small concentrations. Those that find their way into soils may inhibit or kill soil organisms, thereby undermining the balance of the soil community (see Section 11.15). Other chemicals may be transported from the soil to the air, water, or vegetation, where they may be contacted, inhaled, or ingested by any number of organisms. It is imperative, therefore, that we control the release of organic chemicals and that we learn of their fate and effects once they enter the soil.

Organic chemicals may enter the soil as contaminants in industrial and municipal organic wastes applied to or spilled on soils, as components of discarded machinery, in large or small lubricant and fuel leaks, and as pesticides applied to terrestrial ecosystems.

While some pesticides are meant to be applied to soils, most reach the soil because they have missed the insect or plant leaf that was the target of the application. When pesticides are sprayed in the field, most of the chemical misses the target organism. For pesticides aerially applied to forests, about 25% reaches the tree foliage and far less than 1% reaches a target insect. About 30% may reach the soil, while about half of the chemical applied is likely to be lost into the atmosphere or in runoff water.

Pesticides are probably the most widespread organic pollutants associated with soils. In the United States, pesticides are used on some 150 million ha of land, three-fourths of which is agricultural land. Soil contamination by other organic chemicals is usually much more localized. We will therefore emphasize the pesticide problem.

The Nature of Pesticides

Pesticides are chemicals that are designed to kill pests (that is, any organism that the pesticide user perceives to be damaging). Since the offending organisms may be plants (weeds), insects, fungi, nematodes, or rats, pesticides include different compounds designated as *herbicides, insecticides, fungicides, nematocides, rodenticides,* and so on.

Some 600 chemicals in about 50,000 formulations are used to control pests. They are used extensively in all parts of the world. About 350,000 Mg of organic pesticide chemicals are used annually in the United States, with similar amounts used in Western Europe and Asia. Although the total amount of pesticides used has remained relatively constant or even dropped since the 1980s, formulations in use today are generally more potent, so that smaller quantities are applied per hectare to achieve toxicity to the pest.

BENEFITS OF PESTICIDES. Pesticides have provided many benefits to society. They have helped control mosquitoes and other vectors of such human diseases as yellow fever and malaria. They have protected crops and livestock against insects and diseases. Without the control of weeds by chemicals called *herbicides,* conservation tillage (especially no-tillage) would be much more difficult to adopt; much of the progress made in controlling soil erosion probably would not have come about without herbicides. Also, pesticides reduce the spoilage of food as it moves from farm fields to distant dinner tables.

COSTS OF PESTICIDES. However, pesticides should not be seen as a panacea or as indispensable. Some farmers produce profitable yields without the use of pesticides. Even with the almost universal use of pesticides, insects, diseases, and weeds still cause the loss of one-third of the crop production in the United States, about the same proportion of crops lost to these pests in the 1940s, before many pesticides were in use. And while the benefits to society from pesticides are great, so are the costs (Table 18.1).

TABLE 18.1 Total Estimated Environmental and Social Cost from Pesticide Use in the United States

The death of an estimated 60 million wild birds may represent an additional substantial cost in lost revenues from hunters, bird watchers, and so forth.

Type of impact	*Cost, $ million/yr*
Public health impacts	787
Domestic animal deaths and contamination	30
Loss of natural enemies	520
Cost of pesticide resistance	1400
Honeybee and pollination losses	320
Crop losses	942
Fishery losses	24
Groundwater contamination and cleanup costs	1800
Cost of government regulations to prevent damage	200
Total	6023

From Pimental, et al. (1992). © American Institute of Biological Sciences.

Designed to kill living things, many of these chemicals are potentially toxic to organisms other than the pests for which they are intended. Some are detrimental to nontarget organisms, such as beneficial insects and certain soil organisms. Those chemicals that do not quickly break down may be biologically magnified as they move up the food chain. For example, as earthworms ingest contaminated soil, the chemicals tend to concentrate in the earthworm bodies. When birds and fish eat the earthworms, the pesticides can build up further to lethal levels. The near extinction of certain birds of prey (including the bald eagle) during the 1960s and 1970s called public attention to the sometimes devastating environmental consequences of pesticide use. More recently, evidence is mounting suggesting that human endocrine (hormone) balance may be disrupted by the minute traces of some pesticides found in water, air, and food.

18.2 KINDS OF PESTICIDES

Pesticides are commonly classified according to the target group of pest organisms: (1) *insecticides,* (2) *fungicides,* (3) *herbicides* (weed killers), (4) *rodenticides* and (5) *nematocides.* In practice, all find their way into soils. Since the first three are used in the largest quantities and are therefore more likely to contaminate soils, they will be given primary consideration. Figure 18.1 shows that most pesticides contain aromatic rings of some kind, but that there is great variability in pesticide chemical structures.

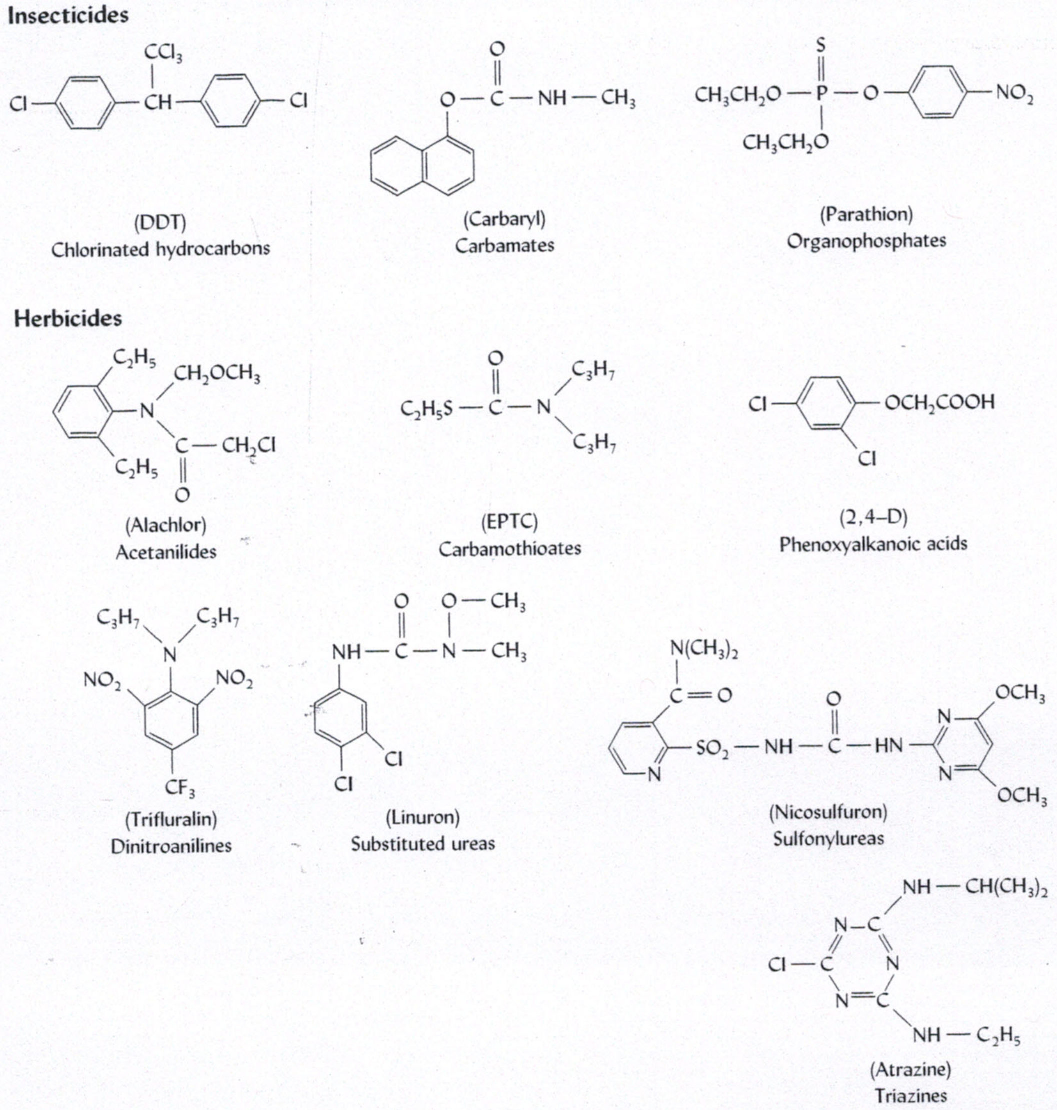
Insecticides

Most of these chemicals are included in three general groups. The *chlorinated hydrocarbons,* such as DDT, were the most extensively used until the early 1970s, when their use was banned or severely restricted in many countries due to their low biodegradability and persistence, as well as their toxicity to birds and fish.

The *organophosphate* pesticides are generally biodegradable, and thus less likely to build up in soils and water. However, they are extremely toxic to humans, so great care must be used in handling and applying them. The *carbamates* are considered least dangerous because of their ready biodegradability and relatively low mammalian toxicity. However, they are highly toxic to honeybees and other beneficial insects and to earthworms.

Fungicides

Fungicides are used mainly to control diseases of fruit and vegetable crops and as seed coatings to protect against seed rots. Some are also used to protect harvested fruits and vegetables from decay, to prevent wood decay, and to protect clothing from mildew. Organic materials such as the thiocarbamates and triazoles are currently in use.



Insecticides

(DDT)
Chlorinated hydrocarbons

(Carbaryl)
Carbamates

(Parathion)
Organophosphates

Herbicides

(Alachlor)
Acetanilides

(EPTC)
Carbamothioates

(2,4–D)
Phenoxyalkanoic acids

(Trifluralin)
Dinitroanilines

(Linuron)
Substituted ureas

(Nicosulfuron)
Sulfonylureas

(Atrazine)
Triazines

FIGURE 18.1 Structural formulae of representative compounds in 10 classes of widely used pesticides. Carbaryl, DDT, and parathion are insecticides; the other compounds shown are herbicides. The widely differing structures result in a great variety of toxicological properties and reactions in the soil.

Herbicides

The quantity of herbicides used in the United States exceeds that of the other two types of pesticides combined. Starting with 2,4-D (a chlorinated phenoxyalkanoic acid), dozens of chemicals in literally hundreds of formulations have been placed on the market (see Figure 18.1). These include the *triazines,* used mainly for weed control in corn; *substituted ureas;* some *carbamates;* the relatively new *sulfonylureas,* which are potent at very low rates; *dinitroanilines;* and *acetanilides,* which have proved to be quite mobile in the environment. As one might expect, this wide variation in chemical makeup provides an equally wide variation in properties. Most herbicides are biodegradable, and most of them are relatively low in mammalian toxicity. However, some are quite toxic to fish and perhaps to other wildlife. They can also have deleterious effects on beneficial aquatic vegetation that provides food and habitat for fish and shellfish.

Nematocides

Although nematocides are not widely used, some of them are known to contaminate soils and the water draining from treated soils. For example, some carbamates used as nematocides are quite soluble in water, are not adsorbed by the soil, and consequently leach downward and into the groundwater.

18.3 BEHAVIOR OF ORGANIC CHEMICALS IN SOIL[1]

Once they reach the soil, organic chemicals, such as pesticides or hydrocarbons, move in one or more of seven directions (Figure 18.2): (1) they may vaporize into the atmosphere without chemical change; (2) they may be absorbed by soils; (3) they may move downward through the soil in liquid or solution form and be lost from the soil by leaching; (4) they may undergo chemical reactions within or on the surface of the soil; (5) they may be broken down by soil microorganisms; (6) they may wash into streams and rivers in surface runoff; and (7) they may be taken up by plants or soil animals and move up the food chain. The specific fate of these chemicals will be determined at least in part by their chemical structures, which are highly variable.

Volatility

Organic chemicals vary greatly in their volatility and subsequent susceptibility to atmospheric loss. Some soil fumigants, such as methyl bromide (now banned from most uses), were selected because of their very high vapor pressure, which permits them to penetrate

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[1] For reviews on organic chemicals in the soil environment, see Sawhney and Brown (eds.) (1989) and Pierzynski, et al. (1994); for pesticides, see Cheng (ed.) (1990).

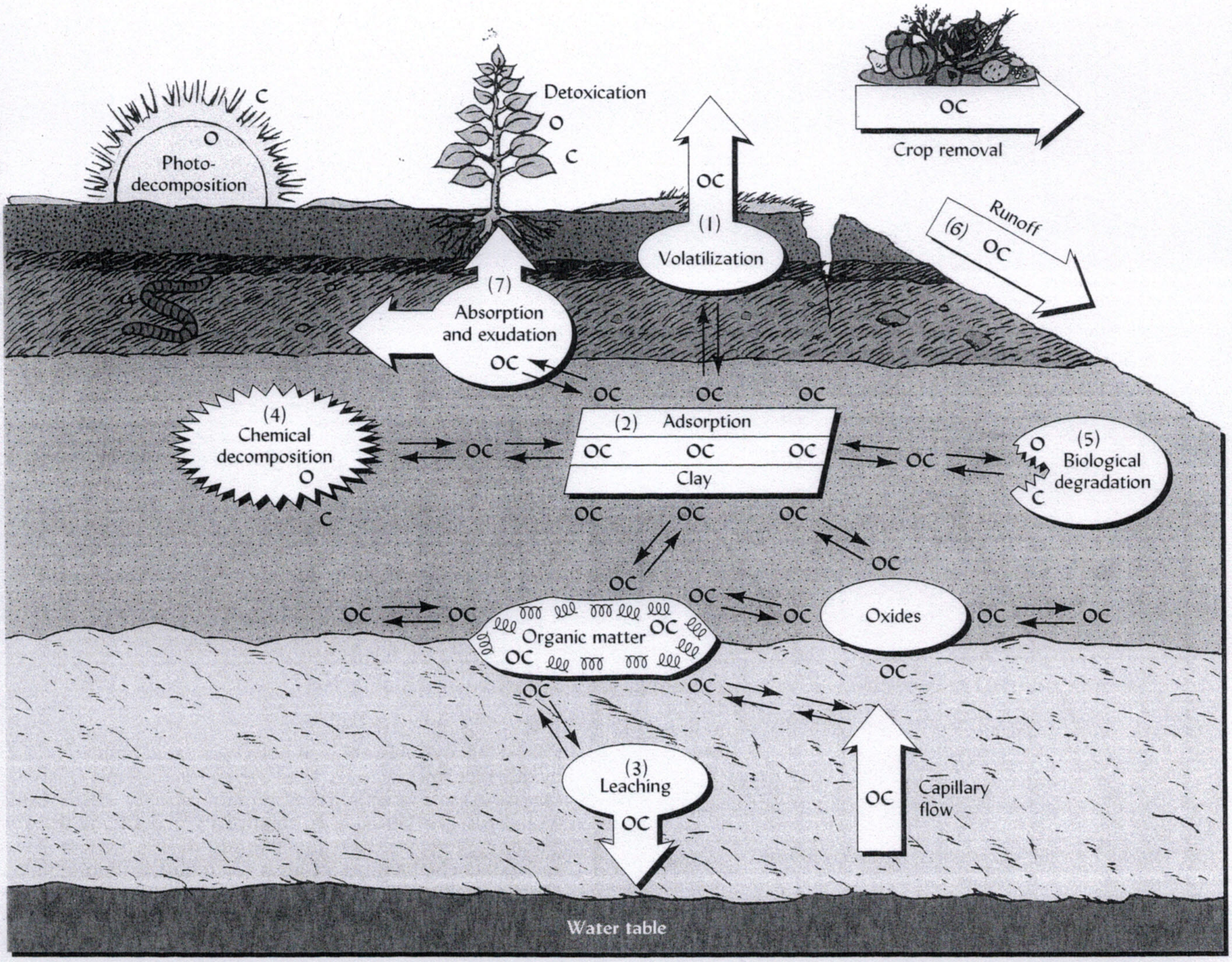

FIGURE 18.2 Processes affecting the dissipation of organic chemicals (OC) in soils. Note that the OC symbol is split up by decomposition (both by light and chemical reaction) and degradation by microorganisms, indicating that these processes alter or destroy the organic chemical. In transfer processes, the OC remains intact. [From Weber and Miller (1989)]

soil pores to contact the target organisms. This same characteristic encourages rapid loss to the atmosphere after treatment, unless the soil is covered or sealed. A few herbicides (e.g., trifluralin) and fungicides (e.g., PCNB) are sufficiently volatile to make vaporization a primary means of their loss from soil. The lighter fractions of crude oil (e.g., gasoline and diesel) and many solvents vaporize to a large degree when spilled on the soil.

The assumption that disappearance of pesticides from soils is evidence of their breakdown is questionable. Some chemicals lost to the atmosphere are known to return to the soil or to surface waters with the rain.

Adsorption

The adsorption of organic chemicals by soil is determined largely by the characteristics of the compound and of the soils to which they are added. Soil organic matter and high-surface-area clays tend to be the strongest adsorbents for some compounds (Figure 18.3), while oxide coatings on soil particles strongly adsorb others. The presence of certain functional groups, such as —OH, —NH_2, —NHR, —$CONH_2$, —COOR, and —$^+NR_3$, in the chemical structure encourages adsorption, especially on the soil humus. Hydrogen bonding (see Sections 5.1 and 8.5) and protonation [adding of H^+ to a group such as an —NH_2 (amino) group] probably promotes some of the adsorption. Everything else being equal, larger organic molecules with many charged sites are more strongly adsorbed.

Some organic chemicals with positively charged groups, such as the herbicides diquat and paraquat, are strongly adsorbed by silicate clays. Adsorption by clays of some pesticides tends to be pH-dependent (Figure 18.4), with maximum adsorption occurring at low pH levels, which encourages protonation. Adding an H^+ ion to functional groups (e.g., —NH_2) yields a positive charge on the herbicide, resulting in greater attraction to negatively charged soil colloids.

Leaching and Runoff

The tendency of organic chemicals to leach from soils is closely related to their solubility in water and their potential for adsorption. Some compounds, such as chloroform and phenoxyacetic acid, are a million times more water-soluble than others, such as DDT and PCBs, which are quite soluble in oil but not in water. High water-solubility favors leaching losses.

Strongly adsorbed molecules are not likely to move down the profile (Table 18.2). Likewise, conditions that encourage such adsorption will discourage leaching. Leaching

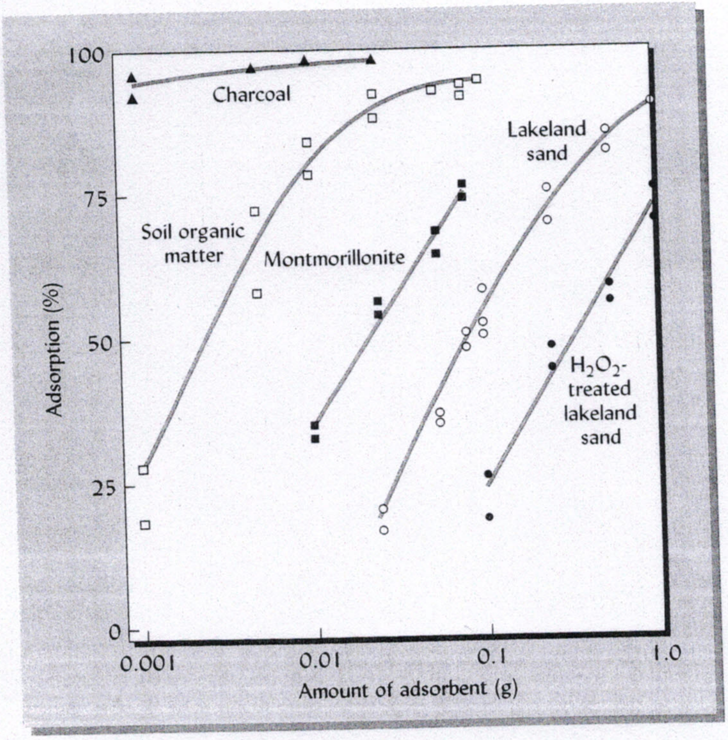

FIGURE 18.3 Adsorption of polychlorinated biphenyl (PCB) by different soil materials. The Lakeland sand (Typic Quartzipsamments) lost much of its adsorption capacity when treated with hydrogen peroxide to remove its organic matter. The amount of soil material required to adsorb 50% of the PCB was approximately 10 times as great for montmorillonite (a 2:1 clay mineral) as for soil organic matter, and 10 times again as great for H_2O_2-treated Lakeland sand. Later tests showed that once the PCB was adsorbed, it was no longer available for uptake by plants. Note that the amount of soil material added is shown on a log scale. [From Strek and Weber (1982)]

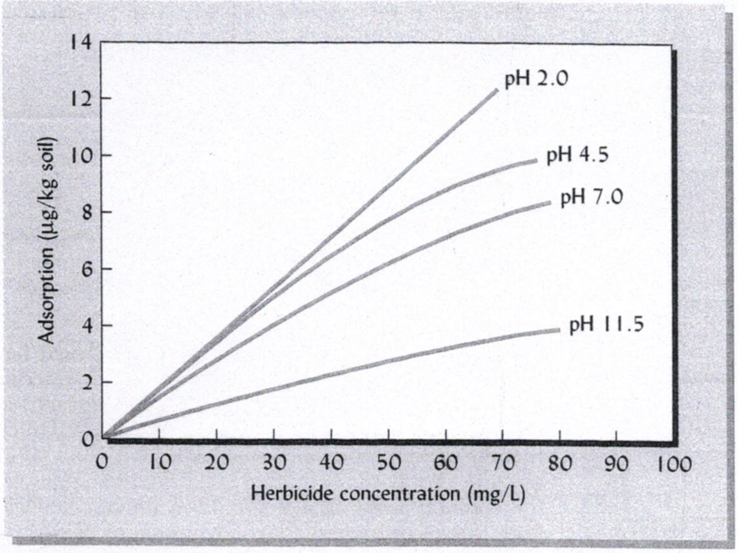

FIGURE 18.4 The effect of pH of kaolinite on the adsorption of glyphosate, a widely used herbicide (Brand name Roundup®). [Reprinted with permission from J. S. McConnell and L. R. Hossner, *J. Agric. Food Chem.* 33:1075–78 (1985); copyright 1985 American Chemical Society]

is apt to be favored by water movement, the greatest leaching hazard occurring in highly permeable, sandy soils that are also low in organic matter. Periods of high rainfall around the time of application of the chemical promote both leaching and runoff losses (Table 18.3). With some notable exceptions, herbicides seem to be somewhat more mobile than most fungicides or insecticides, and therefore are more likely to find their way to groundwater supplies and streams (Figure 18.5).

TABLE 18.2 **The Degree of Adsorption of Selected Herbicides**

Weakly adsorbed herbicides are more susceptible to movement in the soil than those that are more tightly adsorbed.

Common name or designation	*Trade name*	*Adsorptivity to soil colloids*
Dalapon	Dowpon	None
Chloramben	Amiben	Weak
Bentazon	Basagran	Weak
2,4-D	Several	Moderate
Propachlor	Ramrod	Moderate
Atrazine	AAtrex	Strong
Alachlor	Lasso	Strong
EPTC	Eptam	Strong
Diuron	Karmex	Strong
Paraquat	Paraquat	Very strong
Trifluralin	Treflan	Very strong
DCPA	Dacthal	Very strong

Selected data from DMI (1981).

TABLE 18.3 **Surface Runoff and Leaching Losses (Through Drain Tiles) of the Herbicide Atrazine from a Clay Loam Lacustrine Soil (Alfisols) in Ontario, Canada**

The herbicide was applied at 1700 g/ha in late May. The data are the average of three tillage methods. Note that the rainfall for May and June is related to the amount of herbicide lost by both pathways.

	Atrazine loss, g/ha				
Year of study	*Surface runoff loss*	*Drainage water loss*	*Total dissolved loss*	*Percent of total applied, %*	*Rainfall, May–June, mm*
1	18	9	27	1.6	170
2	1	2	3	0.2	30
3	51	61	113	6.6	255
4	13	32	45	2.6	165

Data abstracted from Gaynor, et al. (1995).

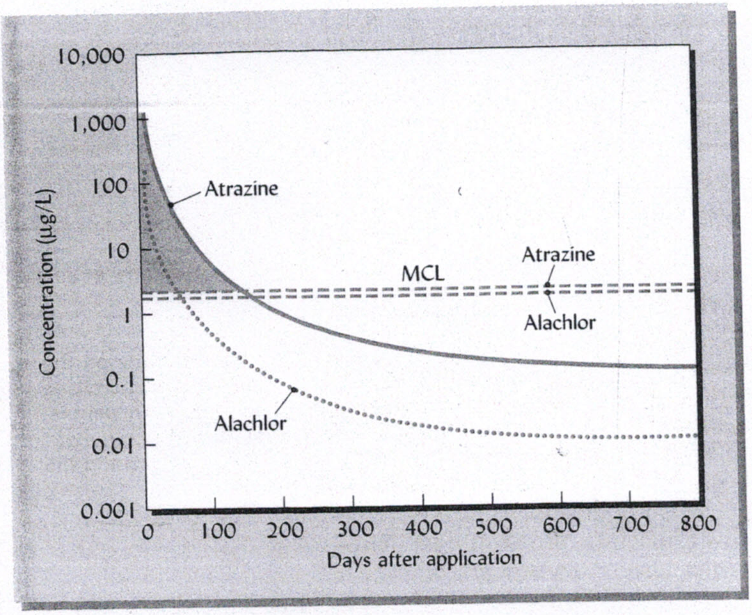

FIGURE 18.5 Concentration of two widely used herbicides, atrazine and alachlor, in the runoff from watersheds in Ohio planted to corn, along with the allowed Maximum Contaminant Level (MCL) for drinking water. Note that the concentration far exceeds the MCL, especially for atrazine, during the first 50 to 100 days after application. If this runoff is not diluted with less-contaminated water, it would not be suitable for consumption by downstream users. [Redrawn from Shipitalo, et al. (1997)]

Contamination of Groundwater

Experts once maintained that contamination of groundwater by pesticides occurred only from accidents such as spills, but it is now known that many pesticides reach the groundwater from normal agricultural use. Since many people (e.g., 40% of Americans) depend on groundwater for their drinking supply, leaching of pesticides is of wide concern. Table 18.4 lists some of the 46 pesticides found in a national survey of well waters in the United States. The concentrations are given in parts per billion (see Box 18.1). In some cases, the amount of pesticide found in the drinking water has been high enough to raise long-term health concerns.

Chemical Reactions

Upon contacting the soil, some pesticides undergo chemical modification independent of soil organisms. For example, iron cyanide compounds decompose within hours or days if exposed to bright sunlight. DDT, diquat, and the triazines are subject to slow photodecomposition in sunlight. The triazine herbicides (e.g., atrazine) and organophosphate insecticides (e.g., malathion) are subject to hydrolysis and subsequent degradation. While the complexities of molecular structure of the pesticides suggest different mechanisms of breakdown, it is important to realize that degradation independent of soil organisms does in fact occur.

Microbial Metabolism

Biochemical degradation by soil organisms is the single most important method by which pesticides are removed from soils. Certain polar groups on the pesticide molecules, such as —OH, —COO^-, and —NH_2, provide points of attack for the organisms.

DDT and other chlorinated hydrocarbons, such as aldrin, dieldrin, and heptachlor, are very slowly broken down, persisting in soils for 20 or more years. In contrast, the organophosphate insecticides, such as parathion, are degraded quite rapidly in soils, apparently by a variety of organisms (Figure 18.6). Likewise, the most widely used herbicides, such as 2,4-D, the phenylureas, the aliphatic acids, and the carbamates, are readily attacked by a host of organisms. Exceptions are the triazines, which are slowly degraded, primarily by chemical action. Most organic fungicides are also subject to microbial decomposition, although the rate of breakdown of some is slow, causing troublesome residue problems.

TABLE 18.4 Pesticides Present in Groundwater from Normal Agricultural Use

Note the wide range in concentrations which are considered to be risky to health. The great majority of wells sampled were uncontaminated, but when pesticides were detected they were often near or above the health-advisory level.

		Level found, parts per billion		
Pesticide	*Use*[a]	*Median level found*[b]	*Maximum level found*	*Health-advisory level*[c]
Alachlor	H	1	113	
Aldicarb	I	9	315	10
Atrazine	H	1	40	3
Bromacil	H	9	22	90
Carbofuran	I	5	176	40
Cyanazine	H	0.4	7	10
2,4-D (2,4 Dichlorophenoxyacetic acid)	H	1	50	70
DBCP[d]	FUM	0.01	0.02	—
DCPA	H	109	1040	4000
Dinoceb[d]	H, I, F	1	37	7
EDB	F	1	14	—
Fonofos	I	0.1	0.9	10
Malathion	I	42	53	200
Metolachlor	H	0.4	32	100
Metribuzin	H	1	7	200
Oxamyl	I	4	395	200
Trifluran	H	0.4	2.2	5

Data from General Accounting Office (1991).

[a] H = herbicide; I = insecticide; F = fungicide; FUM = fumigant.

[b] Fifty percent above and 50% below this value.

[c] Health-advisory level is the concentration that is suspected of causing health problems over a 70-year lifetime. Blank means no advisory level has been set.

[d] Most uses of this pesticide have been banned in the United States.

Plant Absorption

Pesticides are commonly absorbed by higher plants. This is especially true for those pesticides (e.g., systemic insecticides and most herbicides) that must be taken up in order to perform their intended function. The absorbed chemicals may remain intact inside the plant, or they may be degraded. Some degradation products are harmless, but others are even more toxic to humans than the original chemical that was absorbed. Understandably, society is quite concerned about pesticide residues found in the parts of plants that people eat, whether as fresh fruits and vegetables or as processed foods. The use of pesticides and the amount of pesticide residues in food are strictly regulated by law to ensure human safety. Despite widespread concerns, there is little evidence that the small amounts of residues permissible in foods by law have had any ill effects on public health. However, routine testing by regulatory agencies has shown that about 1 to 2% of the food samples tested contain pesticide residues above the levels permissible.

Persistence in Soils

The persistence of chemicals in soils is a summation of all the reactions, movements, and degradations affecting these chemicals. Marked differences in persistence are the rule (see Figure 18.6). For example, organophosphate insecticides may last only a few days in soils. The widely used herbicide 2,4-D persists in soils for only two to four weeks. PCBs, DDT, and other chlorinated hydrocarbons may persist for 3 to 20 years or longer (Table 18.5). The persistence times of other pesticides and industrial organics fall generally between the extremes cited. The majority of pesticides degrade rapidly enough to prevent buildup in soils having normal annual applications. Those that resist degradation have a greater potential to cause environmental damage.

Continued use of the same pesticide on the same land can increase the rate of microbial breakdown of that pesticide. Apparently, having a constant food source allows a population build up of those microbes equipped with the enzymes needed to break down the compound. This is an advantage with respect to environmental quality and is

BOX 18.1 CONCENTRATIONS AND TOXICITY OF CONTAMINANTS IN THE ENVIRONMENT

As analytical instrumentation becomes more sophisticated, contaminants can be detected at much lower levels than was the case in the past. Since humans and other organisms can be harmed by almost any substance if large enough quantities are involved, the subject of toxicity and contamination must be looked at *quantitatively*. That is, we must ask *how much*, not simply *what*, is in the environment. Many highly toxic (meaning harmful in very small amounts) compounds are produced by natural processes and can be detected in the air, soil, and water—quite apart from any activities of humans.

The mere presence of a natural toxin or a synthetic contaminant may not be a problem. Toxicity depends on (1) the *concentration* of the contaminant, and (2) the level of *exposure* of the organism. Thus, low concentrations of certain chemicals that would cause no observable effect by a single exposure (e.g., one glass of drinking water) may cause harm (e.g., cancer, birth defects) to individuals exposed to these concentrations over a long period of time (e.g., three glasses of water a day for many years).

Regulatory agencies attempt to estimate the effects of long-term exposure when they set standards for no-observable-effect levels (NOEL) or health-advisory levels (see Table 18.4). Some species and individuals within a species will be much more sensitive than others to any given chemical. Regulators attempt to consider the risk to the most susceptible individual in any particular case. For nitrate in groundwater, this individual might be a human infant whose entire diet consists of infant formula made with the contaminated water. For DDT, the individual at greatest risk might be a bird of prey that eats fish that eat worms that ingest lake sediment contaminated with DDT. For a pesticide taken up by plants from the soil, the individual at greatest risk might be an avid gardener who eats vegetables and fruits mainly from the treated garden over the course of a lifetime.

It is important to get a feel for the meaning of the very small numbers used to express the concentration of contaminants in the environment. For instance, in Table 18.4, the concentrations are given in parts per billion (ppb). This is equivalent to micrograms per kilogram or µg/kg. In water this would be µg/L. To comprehend the number 1 *billion* imagine a billion golf balls: lined up, they would stretch completely around the earth. One bad ball out of a billion (1 ppb) seems like an extremely small number. On the other hand, 1 ppb can seem like a very large number. Consider water contaminated with 1 ppb of cyanide, a very toxic substance consisting of a carbon and a nitrogen atom linked together. If you drank just *one drop* of this water, you would be ingesting over 2 *trillion* molecules of cyanide:

$$\frac{6.023 \times 10^{23}\ \text{molecules}}{1\ \text{mol}} \times \frac{1\ \text{mol}}{27\ \text{g HCN}} \times \frac{1\ \text{g HCN}}{10^{6}/\mu\text{g HCN}} \times \frac{1\ \mu\text{g HCN}}{\text{L}} \times \frac{\text{L}}{10^{3}\ \text{cm}^{3}} \times \frac{\text{cm}^{3}}{10\ \text{drops}} = \frac{2.2 \times 10^{12}\ \text{molecules}}{\text{drop}}$$

In the case of cyanide, the molecules in this drop of water would probably not cause any observable effect. However, for other compounds, this many molecules may be enough to trigger DNA mutations or the beginning of cancerous growth. Assessing these risks is still an uncertain business.

a principle sometimes applied in environmental cleanup of toxic organic compounds, but the breakdown may become sufficiently rapid to reduce a pesticide's effectiveness.

18.4 EFFECTS OF PESTICIDES ON SOIL ORGANISMS

Since pesticides are formulated to kill organisms, it is not surprising that some of these compounds are toxic to specific soil organisms. At the same time, the diversity of the soil organism population is so great that, excepting a few fumigants, most pesticides do not kill a broad spectrum of soil organisms.

Fumigants

Fumigants are compounds used to free a soil of a given pest, such as nematodes. These compounds have a more drastic effect on both the soil fauna and flora than do other pesticides. For example, 99% of the microarthropod population is usually killed by the fumigants DD and vampam, and it may take as long as two years for the population to fully recover. Fortunately, the recovery time for the microflora is generally much less.

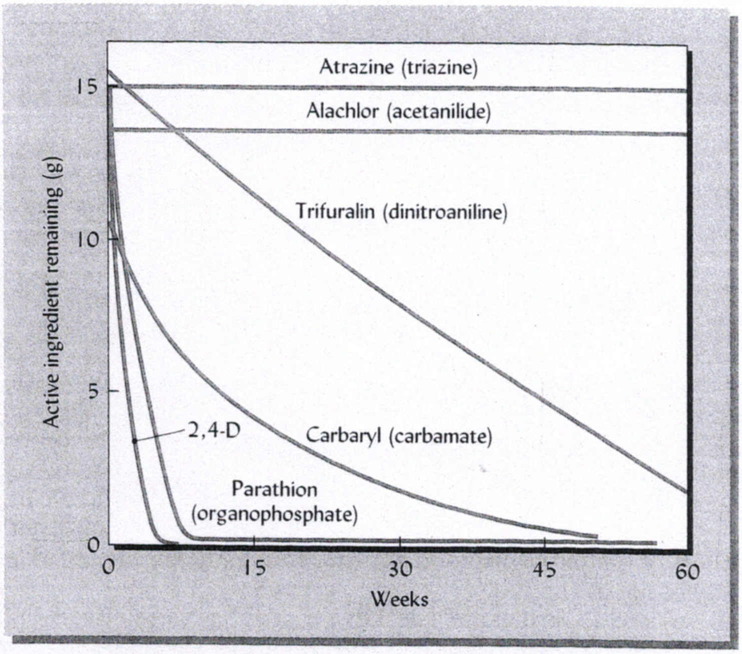

FIGURE 18.6 Degradation of four herbicides (alachlor, atrazine, 2,4-D, and trifuralin) and two insecticides (parathion and carbaryl), all of which are used extensively in the Midwest of the United States. Note that atrazine and alachlor are quite slowly degraded, whereas parathion and 2,4-D are quickly broken down. [Reprinted with permission from R. G. Krueger and J. N. Seiber, *Treatment and Disposal of Pesticide Wastes,* Symposium Series 259; copyright 1984 American Chemical Society]

Fumigation reduces the number of species of both flora and fauna, especially if the treatment is repeated, as is often the case where nematode control is attempted. At the same time, the total number of bacteria is frequently much greater following fumigation than before. This increase is probably due to the relative absence of competitors and predators following fumigation and to the carbon and energy sources left by dead organisms for microbial utilization.

Effects on Soil Fauna

The effects of pesticides on soil animals varies greatly from chemical to chemical and from organism to organism. Nematodes are not generally affected, except by specific fumigants. Mites are generally sensitive to most organophosphates and to the chlorinated hydrocarbons, with the exception of aldrin. Springtails vary in their sensitivity to both chlorinated hydrocarbons and organophosphates, some chemicals being quite toxic to these organisms.

EARTHWORMS. Fortunately, many pesticides have only mildly depressing effects on earthworm numbers, but there are exceptions. Among insecticides, most of the carbamates (carbaryl, carbofuran, aldicarb, etc.) are highly toxic to earthworms. Among the herbi-

TABLE 18.5 Common Range of Persistence of a Number of Organic Compounds

Risks of environmental pollution are highest with those chemicals with greatest persistence.

Organic chemical	*Persistence*
Chlorinated hydrocarbon insecticides (e.g., DDT, chlordane, and dieldrin)	3–20 yr
PCBs	2–10 yr
Triazine herbicides (e.g., atrazine and simazine)	1–2 yr
Benzoic acid herbicides (e.g., amiben and dicamba)	2–12 mo
Urea herbicides (e.g., monuron and diuron)	2–10 mo
Vinyl chloride	1–5 mo
Phenoxy herbicides (2,4-D and 2,4,5-T)	1–5 mo
Organophosphate insecticides (e.g., malathion and diazinon)	1–12 wk
Carbamate insecticides	1–8 wk
Carbamate herbicides (e.g., barban and CIPC)	2–8 wk

cides, simazine is more toxic than most. Among the fungicides, benomyl is unusually toxic to earthworms. The concentrations of pesticides in the bodies of the earthworms are closely related to the levels found in the soil (Figure 18.7). Thus, earthworms can magnify the pesticide exposure of birds, rodents, and other creatures that prey upon them.

Pesticides have significant effects on the numbers of certain predators and, in turn, on the numbers of prey organisms. For example, an insecticide that reduces the numbers of predatory mites may stimulate numbers of springtails, which serve as prey for the mites (Figure 18.8). Such organism interaction is normal in most soils.

Effects on Soil Microorganisms

The overall levels of bacteria in the soil are generally not too seriously affected by pesticides. However, the organisms responsible for nitrification and nitrogen fixation are sometimes adversely affected. Insecticides and fungicides affect both processes more than do most herbicides, although some of the latter can reduce the numbers of organisms carrying out these two reactions. Recent evidence suggests that some pesticides can enhance biological nitrogen fixation by reducing the activity of protozoa and other organisms that are competitors or predators of the nitrogen-fixing bacteria. These findings illustrate the complexity of life in the soil.

Fungicides, especially those used as fumigants, can have marked adverse effects on soil fungi and actinomycetes, thereby slowing down the humus formation in soils. Interestingly, however, the process of ammonification is often stimulated by pesticide use.

The negative effects of most pesticides on soil microorganisms are temporary, and after a few days or weeks, organism numbers generally recover. But exceptions are common enough to dictate caution in the use of the chemicals. Care must be taken to apply them only when alternate means of pest management are not available.

This brief review of the behavior of organic chemicals in soils reemphasizes the complexity of the changes that take place when new and exotic substances are added to our environment. Our knowledge of the soil processes involved certainly reaffirms the necessity for a thorough evaluation of potential environmental impacts prior to approval and use of new chemicals for extensive use on the land.

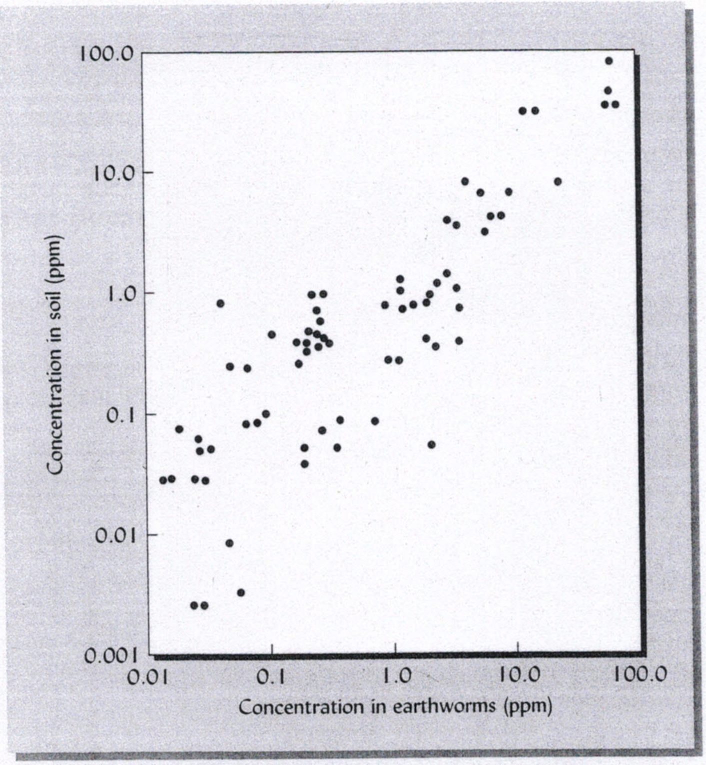

FIGURE 18.7 Effect of concentration of pesticides in soil on their concentration in earthworms. Birds eating the earthworms at any level of concentration would further concentrate the pesticides. [Data from several sources gathered by Thompson and Edwards (1974); used with permission of Soil Science Society of America]

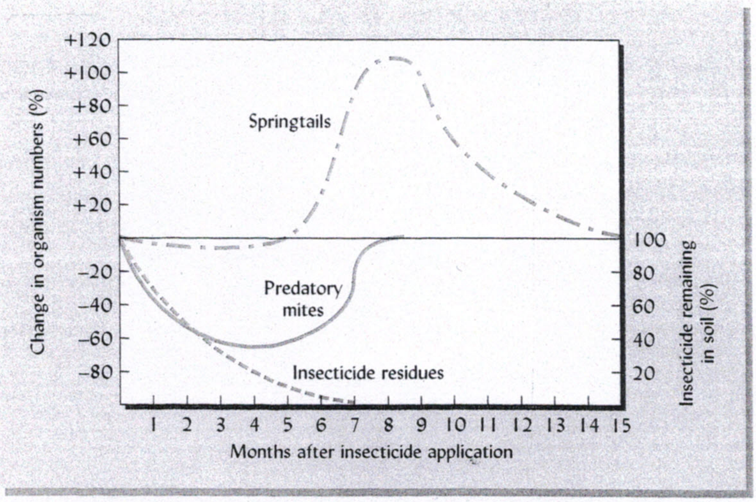

FIGURE 18.8 The direct effect of insecticide on predatory mites in a soil and the indirect effect of reducing mite numbers on the population of springtails (tiny insects) that serve as prey for the mites. [Replotted from Edwards (1978); used with permission of Academic Press, Inc., London]

18.5 REGIONAL VULNERABILITY TO PESTICIDE LEACHING

The vulnerability to leaching of pesticides to the groundwater varies greatly from one area to another. Highest vulnerability occurs in regions with high rainfall, an abundance of sandy soils, and intensive cropping systems that involve high usage of those types of pesticides that are not adsorbed by the soil particles. Table 18.6 shows the results of one study set up to measure the vulnerability of different regions of the United States to the leaching of pesticides and nitrates. Note the high average vulnerability score for the southern Atlantic Coast area where sandy soils are prominent, and where highly intensive cropping systems (fruits and vegetables) are used. Likewise, vulnerability for leaching is high in the corn belt, where much of the land is under continuous corn production with its high herbicide and fertilizer nitrogen use.

It should be pointed out, however, that these regional data may mask localized areas of vulnerability. For example, in arid regions of the mountain states are found irrigated areas of intensive vegetable crop production that may involve considerable leaching of both pesticides and nitrates. Likewise, application of some water-soluble pesticides may result in leaching into the groundwater even though the soil may not be coarse in texture. This suggests the site-specific nature of pesticide hazards.

TABLE 18.6 **Average Cropland Leaching Vulnerability Scores for Pesticides and Nitrates in Different Regions of the United States**

The scores are based on the kinds and amounts of pesticides used in an area and potential for leaching from the soils in each region. The higher the score, the more vulnerable the areas are for leaching of these chemicals. Note the very high leaching vulnerability for pesticides in the southern Atlantic states, the corn belt and the Delta states.

	Comparative leaching vulnerability (average = 100)	
Area	*Pesticides*	*Nitrates*
Northeast	26	39
Southern Atlantic Coast	420	151
Appalachia	90	153
Lake states	74	76
Corn belt	156	336
Delta states	109	120
Northern Plains	45	47
Southern Plains	22	39
Mountain states	15	10
Pacific Coast	44	29
Average	100	100

Calculated from data in Kellogg, et al. (1994).

18.6 REMEDIATION OF SOILS CONTAMINATED WITH ORGANIC CHEMICALS

Soils contaminated with organic pollutants are found throughout the world. The wide areas contaminated with organic pesticides are best addressed by reducing the amounts of pesticides used and by using less toxic, less mobile, and more rapidly degradable compounds. In a reasonable time, the soil ecosystem should be able to recover its function and diversity through *self remediation.*

Perhaps of greater significance, however, are the sites around centers of population where, through the decades, organic wastes from industrial and domestic processes have been dumped on soils. The levels of such *acute contamination* are often sufficiently high that plant growth is restrained or even prevented. Pollutants move into the groundwater and make the drinking water unfit for human consumption. Fish and wildlife are often decimated. Because of public concerns, industry and government are spending billions of dollars annually to clean up (remediate) these contaminated soils. We shall consider a few of the methods they use.

Physical and Chemical Methods

The most widespread methods of soil remediation involve physical and/or chemical treatment of the soil, either in place (*in situ*) or by moving the soil to a treatment site (*ex situ*). Ex situ treatment may involve excavating the soil to treatment bins where it may be incinerated to drive off volatile chemicals and to destroy others that are decomposed upon being heated. Water-soluble and volatile chemicals may also be removed by pushing or pulling air or water through the soil by vacuum extraction or leaching. Such treatments are usually quite efficient but are very expensive, especially if large quantities of soil are involved.

In situ treatments are usually preferred if viable technologies are available. The soil is left in its natural condition, thereby reducing excavation and treatment costs and providing greater flexibility in future land use. The contaminants are either removed from the soil (*decontamination*) or are sequestered (*bound up*) in the soil matrix (*stabilized*). Decontamination in situ involves some of the same techniques of water flushing, leaching, and vacuum extraction used in ex situ processes. Water treatment is not effective, however, with nonpolar compounds that are repelled by water. To help remove such compounds, scientists and engineers have sprayed onto the soil surface or have injected into the soil compounds called *surfactants*. As these move downward in the soil, they solubilize organic contaminants, which can then be pumped out of the soil as in the water washing systems.

ORGANOCLAYS. Certain surfactants may also be used to immobilize or stabilize soil contaminants. They are positively charged and through cation exchange can replace metal cations on soil clays. For example, one group of such surfactants, quaternary ammonium compounds (QACs), have the general formula $(CH_3)_3NR^+$, where R is an organic alkyl or aromatic group. The positive charges on QACs stimulate cation exchange by reactions such as the following, using a monovalent exchangeable cation such as K as an example:

$$\underset{\text{Untreated clay}}{\boxed{\text{Micelle}}\ K^+} + \underset{\text{QAC}}{(CH_3)_3NR^+} \rightarrow \underset{\text{Organoclay}}{\boxed{\text{Micelle}}\ (CH_3)_3NR^+} + K^+$$

The resulting products, known as *organoclays*, have properties quite different from the untreated clays. They attract rather then repel nonpolar organic compounds. Thus, the injection of a QAC into the zone of groundwater flow can stimulate the formation of organoclays and thereby immobilize soluble organic groundwater contaminants, holding them until they can be degraded (Figure 18.9).

DISTRIBUTION COEFFICIENTS K_D. As we learned in Section 8.16, the degree of sorption of organic compounds by soil colloids is commonly indicated by the coefficient of distribution K_d between the sorbed and solution portions of the organic compound.

$$K_d = \frac{\text{mg contaminant/kg soil}}{\text{mg contaminant/L solution}}$$

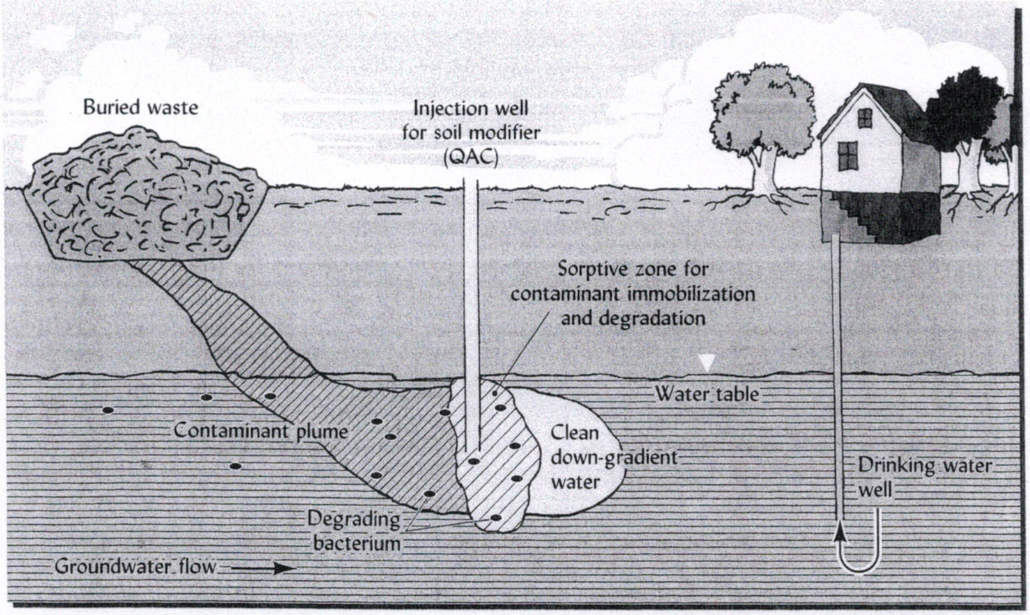

FIGURE 18.9 How a combination of a quatenary ammonium compound (QAC), hexadecyltrimethylammonium, and bioremediation by degrading bacteria could be used to hold and remove an organic contaminant. The pollutant is moving into groundwater from a buried waste site. The QAC reacts with soil clays to form organoclays and soil organic matter complexes that adsorb and stabilize the contaminant, giving microorganisms time to degrade or destroy it. [Redrawn from Xu, et al. (1997)]

The K_d for untreated clays is very low because the clays are hydrophilic (water-loving) and their adhering water films repel the hydrophobic, nonpolar organic compounds. In contrast, organoclays sorb the contaminants, leaving little in the soil solution, thereby reducing their movement into the groundwater and eventually into streams or drinking water. Consequently, the K_d values of organic contaminants on organoclays are commonly 100 to 200 times those measured on the untreated clays. Table 18.7 shows K_d values for some common organic contaminants on organoclays and indicates the very high sorbing power of the newly created sorbants. Their tenacity is complemented by the very strong complexation of organic compounds by soil organic matter. Organoclays thus offer promising mechanisms for holding organic soil pollutants until they can be destroyed by biological or physicochemical processes.

Bioremediation[2]

For many heavily contaminated soils there is a biological alternative to incineration, soil washing, and landfilling—namely, **bioremediation.** Simply put, this technology uses enhanced plant and/or microbial action to degrade organic contaminants into harmless metabolic products. Petroleum constituents, including the more resistant polyacrylic aromatic hydrocarbons (PAHs), as well as several synthetic compounds, such as pentachlorophenol and trichloroethylene, can be broken down, primarily by soil bacteria. In some cases, advantage is taken of organisms currently in the soil. In others, microbes specifically selected for their ability to remove the contaminants are introduced into the soil zones known to be polluted. For example, a bacterium has been identified recently that can detoxify perchloroethene (PCE), a common, highly toxic groundwater pollutant that is suspected of being a carcinogen.[3] The organism expedites the removal of the four chlorines from the PCE, producing ethylene, a gas that is relatively harmless to humans.

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[2] For reviews of this topic, see Alexander (1994) and Skipper and Turco (1995).

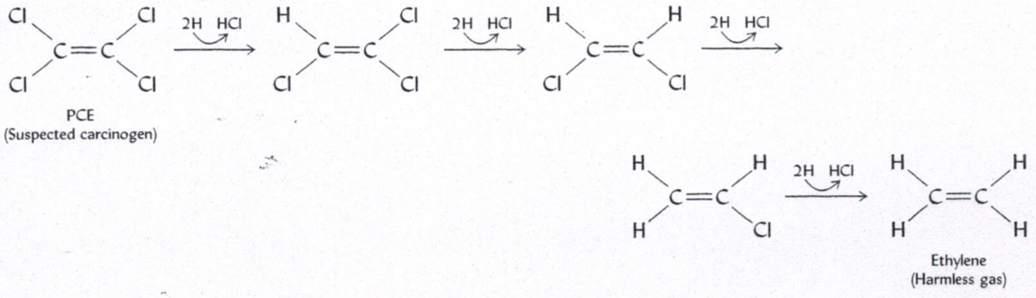
[3] See Maymo-Gatell, et al. (1997).

TABLE 18.7 The Organic Level After Treating Clays Varying in Cation Exchange Capacity with an Quaternary Ammonium Compound (QAC) to Form Organoclays, and The Sorption Coefficients K_d of Five Organic Compounds on These Organoclays

High K_d values suggest high retention of the pollutants and low concentration in the soil solution. Note the low tendency for kaolinite and illite to form organoclays, and the variability in sorption coefficients of the different compounds.

Clay	*CEC of untreated clay, cmol/kg*	*Organic C in organoclay, %*	*K_d of organic contaminants on organoclays*				
			Benzene	*Toluene*	*Ethylbenzene*	*PropylBenzene*	*Naphthalene*
Illite	24	2.5	39	77	156	—	1270
Vermiculite	80	16.4	68	169	448	1618	1387
Smectite (high charge)	130	23.0	184	319	583	1412	4818
Kaolinite	4	1.0	3	7	21	—	—

Data from Jaynes and Boyd (1997).



PHYTOREMEDIATION.[4] Higher plants have also been found to participate in bioremediation, a process termed **phytoremediation.** For years, plant-based systems have been used for the removal of municipal wastewater contaminants. More recently, this concept has been extended to industrial pollutants and to the removal of shallow groundwater pollutants of all kinds, both organic and inorganic. Many plant species, domesticated and wild, have been used in phytoremediation. Prairie grasses can stimulate the degradation of petroleum products, including the PAHs, and spring wildflower plants in Kuwait were recently found to degrade the hydrocarbons in oil spills. Fast-growing hybrid poplars can remove ammunition compounds, such as trinitrotoluene (TNT), as well as some pesticides and excess nitrates.

Some plants can absorb and metabolize specific organic contaminants. Others release exudates from their roots that help degrade the pollutants. However, the primary agents in the plant-associated degradation of contaminants are the microorganisms associated with the rhizosphere of the plants. The plants' roots release compounds that serve as energy sources for the microbes, which, in turn, produce enzymes that can degrade the organic contaminants. As we shall see later (Section 18.10), phytoremediation is perhaps even more effective in removing heavy metals and other inorganic pollutants, including radionuclides.

Phytoremediation is particularly advantageous where large areas of soil are contaminated with only moderate concentrations of organic pollutants. However, phytoremediation also commonly takes a longer time to remove large quantities of contaminants than do the more costly engineering procedures.

BIOAVAILABILITY OF SORBED AND/OR COMPLEXED CHEMICALS. Researchers have found that some chemicals that are normally subject to microbial attack seem to be protected from such degradation when the compounds are complexed by soil organic matter or sorbed by inorganic materials. The complexation is essentially irreversible and the sorption by Fe, Al oxides or silicate clays is so tight that the compounds are only very slowly available.

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[4] For a recent review of phytoremediation, see Cunningham, et al. (1996).

Some compounds may also be trapped between the internal structural layers of some silicate clays. The bioavailability usually decreases as the soil–contaminant complex ages over time. Reduced bioavailability of the pollutants constrains their remediation by microorganisms. It also has some implications for regulatory policies, since pollutants so held are not likely to move into the groundwater or elsewhere in the environment.

NUTRIENT SUPPLEMENTATION. Bioremediation technology assists natural chemical breakdown in several ways. Usually, the soil naturally contains some bacteria or other microorganisms that can degrade the specific contaminant. But the rate of natural degradation may be far too slow to be very effective. Both growth and metabolic rate of organisms capable of using the contaminant as a carbon source are often limited by insufficient mineral nutrients, especially nitrogen and phosphorus (see Section 12.3 for a discussion of the C/N ratio in organic decomposition). Special fertilizers have been formulated and used successfully to greatly speed up the degradation process. One such fertilizer of French manufacture is an oil-in-water microemulsion of urea, lauryl phosphate, and an emulsion stabilizer. It acts not only as a supplier of nutrients, but as a surfactant that can enhance interaction between microbes and the organic contaminants.

OIL SPILL CLEANUP. The 30 or more different genera of bacteria and fungi known to degrade hydrocarbons are found in almost any soil or aquatic environment. But they may need help. The cleanup of crude oil contamination from the 1989 Exxon Valdez oil spill in Alaskan waters was a spectacular case of successful bioremediation by fertilization (Figure 18.10). A special fertilizer was sprayed on the oil-soaked beaches (Entisols). The fertilizer was formulated to be oliophilic (soluble in oil but not in water) so that it would stay with the oil and not contribute to eutrophication of Prince William Sound. Within a few weeks, and despite the cold temperatures, most of the oil in the test area was degraded. The success of bioremediation was greatest where nitrogen was most available to the microorganisms.

IN SITU TECHNIQUES. Other situations call for the use of bioremediation techniques in situ. In some cases, low soil porosity causes oxygen deficiency that limits microbial activity.

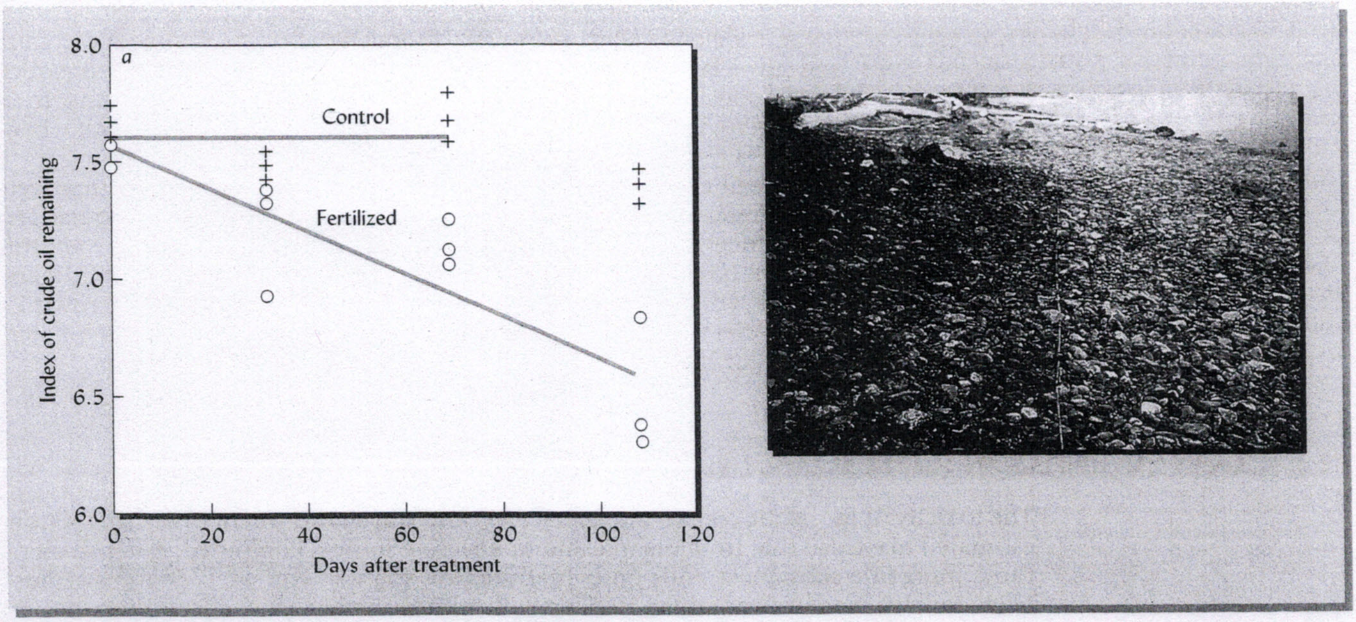

FIGURE 18.10 Bioremediation of crude oil from the Exxon Valdez oil spill off the coast of Alaska. The oil contaminating the beach soils was degraded by indigenous bacteria when an oil-soluble fertilizer containing nitrogen and phosphorus was sprayed on the beach (o data points in graph on the left). The control sections of the beach (+ data points) were left unfertilized for 70 days. By then the effect of the fertilization was so dramatic that a decision was made to treat the control sections as well. The index of oil remaining is based on natural logarithms, so each whole number indicates more than doubling of oil remaining. The photo (right) shows the clear delineation between the oil-covered control section and the fertilized parts of the beach. [Data from Bragg, et al. (1994); reprinted with permission from *Nature*, © 1994 Macmillan Magazines Limited; photo P. H. Pritchard, USEPA, Gulf Breeze, Fla.; courtesy of Pritchard, et al. (1992); reprinted by permission of Kluwer Academic Publishers]

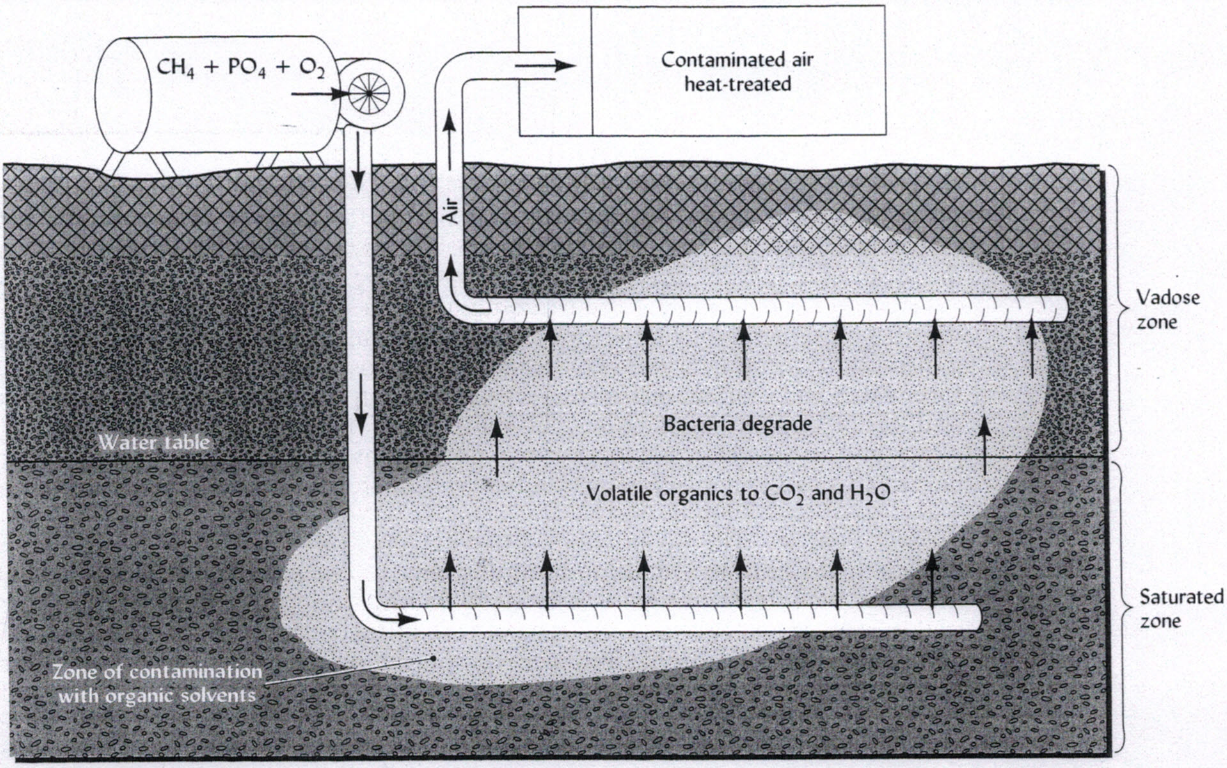

FIGURE 18.11 In situ bioremediation of soil and groundwater contaminated with volatile organic solvents at an industrial site in Georgia. The methane-air-phosphorus mixture was pumped *intermittently* into the soil through slotted pipes, while another pipe "vacuumed" air out of the soil. The air and nutrients stimulated the growth of certain bacteria which, when the methane was taken away, turned to the solvent for a carbon source. It was estimated that the bioremediation technology would cut the time to clean up the site from more than 10 years to less than 4, saving $1.6 million in costs. [Redrawn from Hazen (1995)]

Techniques are being developed that use in situ bioremediation to clean up oxygen-deficient soils and associated groundwater contamination. For example, organic-solvent-contaminated soils have been bioremediated (Figure 18.11) by piping in a mixture of air (for oxygen), methane (to act as a carbon source to stimulate specific bacteria), and phosphorus (a nutrient that is needed for bacteria growth).

Some success has been achieved by inoculating contaminated soils with improved organisms that can degrade the pollutant more readily than can the native population. Although genetic engineering may prove useful in making "superbacteria" in the future, most inoculation has been achieved with naturally occurring organisms. Organisms isolated from sites with a long history of the specific contamination or grown in laboratory culture on a diet rich in the pollutant in question tend to become acclimated to metabolizing the target chemical.

18.7 CONTAMINATION WITH TOXIC INORGANIC SUBSTANCES[5]

The toxicity of inorganic contaminants released into the environment every year is now estimated to exceed that from organic and radioactive sources combined. A fair share of these inorganic substances ends up contaminating soils. The greatest problems most likely involve mercury, cadmium, lead, arsenic, nickel, copper, zinc, chromium, molybdenum, manganese, selenium, fluorine, and boron. To a greater or lesser degree, all of these elements are toxic to humans and other animals. Cadmium and arsenic are extremely poisonous; mercury, lead, nickel, and fluorine are moderately so; boron, cop-

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[5] For a review of this subject, see Kabata-Pendias and Pendias (1992).

TABLE 18.8 **Sources of Selected Inorganic Soil Pollutants**

Chemical	*Major uses and sources of soil contamination*	*Organisms principally harmed*[a]	*Human health effects*
Arsenic	Pesticides, plant desiccants, animal feed additives, coal and petroleum, mine tailings, and detergents	H, A, F, B	Cumulative poison, possibly cancer
Cadmium	Electroplating, pigments for plastics and paints, plastic stabilizers, batteries, and phosphate fertilizers	H, A, F, B, P	Heart and kidney disease, bone embrittlement
Chromium	Stainless steel, chrome-plated metals, pigments, refractory brick manufacture, and leather tanning	H, A, F, B	Mutagenic; also essential nutrient
Copper	Mine tailings, fly ash, fertilizers, windblown copper-containing dust, and water pipes	F, P	Rare; essential nutrient
Lead	Combustion of oil, gasoline, and coal; iron and steel production; and solder on water-pipe joints	H, A, F, B	Brain damage, convulsions
Mercury	Pesticides, catalysts for synthetic polymers, metallurgy, and thermometers	H, A, F, B	Nerve damage
Nickel	Combustion of coal, gasoline, and oil; alloy manufacture; electroplating; batteries; and mining	F, P	Lung cancer
Selenium	High Se geological formations and irrigation wastewater in which Se is concentrated	H, A, F, B	Rare; loss of hair and nail deformities; essential nutrient
Zinc	Galvanized iron and steel, alloys, batteries, brass, rubber manufacture, mining, and old tires	F, P	Rare; essential nutrient

[a] H = humans, A = animals, F = fish, B = birds, P = plants.

Data selected from Moore and Ramamoorthy (1984) and numerous other sources.

per, manganese, and zinc are relatively lower in mammalian toxicity. Although the metallic elements (which exclude fluorine and boron) are not all, strictly speaking, "heavy" metals, for the sake of simplicity this term is often used in referring to them. Table 18.8 provides background information on the uses, sources, and effects of some of these elements.

Sources and Accumulation

There are many sources of the inorganic chemical contaminants that can accumulate in soils. The burning of fossil fuels, smelting, and other processing techniques release into the atmosphere tons of these elements, which can be carried for miles and later deposited on the vegetation and soil. Lead, nickel, and boron are gasoline additives that are released into the atmosphere and carried to the soil through rain and snow.

Borax is used in detergents, fertilizers, and forest fire retardants, all of which commonly reach the soil. Superphosphate and limestone, two widely used amendments, usually contain small quantities of cadmium, copper, manganese, nickel, and zinc. Cadmium is used in plating metals and in the manufacture of batteries. Arsenic was for many years used as an insecticide on cotton, tobacco, fruit crops, lawns, and as a defoliant or vine killer. Some of these mentioned elements are found as constituents in specific organic pesticides and in domestic and industrial sewage sludge. Additional localized contamination of soils with metals results from ore-smelting fumes, industrial wastes, and air pollution.

Some of the toxic metals are being released to the environment in increasing amounts, while others (most notably lead, because of changes in gasoline formulation) are decreasing. All are daily ingested by humans, either through the air or through food, water, and—yes—soil.

Concentration in Organism Tissue

Irrespective of their sources, toxic elements can and do reach the soil, where they become part of the food chain: soil→plant→animal→human (Figure 18.12). Unfortunately, once the elements become part of this cycle, they may accumulate in animal and human body tissue to toxic levels. This situation is especially critical for fish and other wildlife and for humans at the top of the food chain. It has already resulted in restrictions on the use of certain fish and wildlife for human consumption. Also, it has become necessary to curtail the release of these toxic elements in the form of industrial wastes.

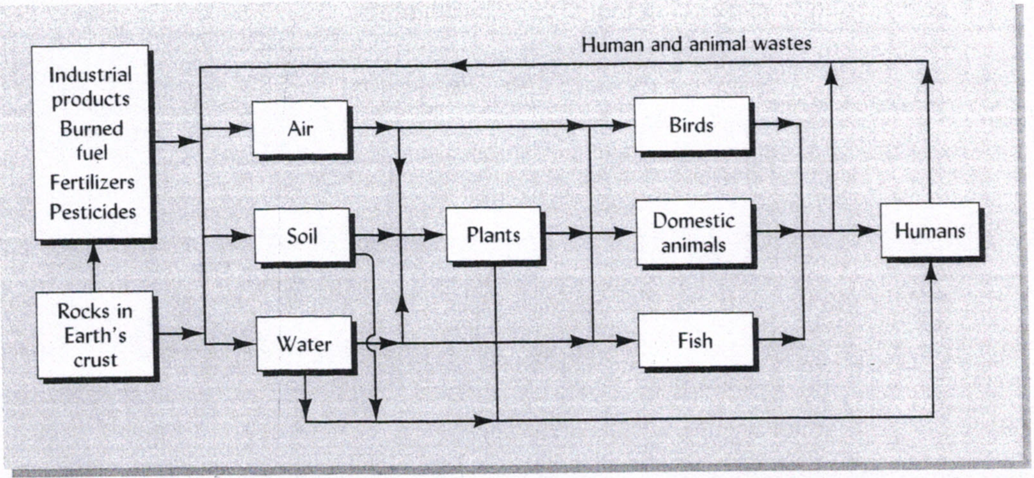


FIGURE 18.12 Sources of heavy metals and their cycling in the soil–water–air–organism ecosystem. It should be noted that the content of metals in tissue generally builds up from left to right, indicating the vulnerability of humans to heavy metal toxicity.

18.8 POTENTIAL HAZARDS OF CHEMICALS IN SEWAGE SLUDGE

The domestic and industrial sewage sludges considered in Chapter 16 can be important sources of potentially toxic chemicals. Nearly half of the municipal sewage sludge produced in the United States is being applied to the soil, either on agricultural land or to remediate land disturbed by mining and industrial activities. Industrial sludges commonly carry significant quantities of inorganic as well as organic chemicals that can have harmful environmental effects.

Source Reduction Programs. A great deal was learned during the 1970s and 1980s about the contents, behavior, and toxicity of metals in municipal sewage sludges. As a result of the research, source-reduction programs were implemented, which required industries to clean pollutants out of their wastewater *before* sending it to municipal wastewater treatment plants. In many cases, the recovery of valuable metal pollutants was actually profitable for industries. Because of these programs, municipal sewage sludges are much cleaner than in the past (Table 18.9). Note that the median levels of the most toxic industrial pollutants (Cd, Cr, Pb, and PCB) declined dramatically between the 1976 survey and the 1990 survey. Since much of the copper comes from the plumbing in homes (metallic copper is slightly solubilized in areas with acidic water supplies), that metal has been less affected by the source reduction regulations.

TABLE 18.9 Median Pollutant Concentrations Reported in Sewage Sludges Surveyed Across the United States in 1976 and 1990 and in Uncontaminated Agricultural Soils and Cow Manure

	Concentration, mg/kg dry weight			
Pollutant	*Sludges surveyed in 1990*[a]	*Sludges surveyed in 1976*[b]	*Agricultural soils*[d]	*Typical values for cow manure*
As	6	10	—	4
Cd	7	260	0.20	1
Cr	40	890	—	56
Cu	463	850	18.5	62
Hg	4	5	—	0.2
Mo	11	—	—	14
Ni	29	82	18.2	29
Pb	106	500	11.0	16
Zn	725	1740	53.0	71
PCB	0.21	9[c]	—	0

[a] Data from Chaney (1990).
[b] Data from Sommers (1977).
[c] 1976 PCB value is median of cities in New York; from Furr, et al. (1976).
[d] Median of 3045 surface soils reported by Holmgren, et al. (1993).

TABLE 18.10 Regulatory Limits on Inorganic Pollutants (Heavy Metals) in Sewage Sludge Applied to Agricultural Land

Element	*Maximum concentration in sludge, USEP,*[a] *mg/kg*	*Annual pollutant loading rates, USEPA, kg/ha/yr*	*Cumulative pollutant loading rates, kg/ha*		
			USEPA	*Germany*	*Ontario*
As	75	2.0	41		14
Cd	85	1.9	39	6	1.6
Cr	3000	150.0	3000	200	210
Cu	4300	75.0	1500	200	150
Hg	840	15.0	300	4	0.8
Mo	57	0.85	17	—	4
Ni	75	0.90	18	100	32
Pb	420	21.0	420	200	90
Se	100	5.0	100	—	2.4
Zn	7500	140	2800	600	330

[a] U.S. Environmental Protection Agency (1993).

REGULATION OF SLUDGE APPLICATION TO LAND. The lower levels of metals (and of organic pollutants) make municipal sewage sludges much more suitable for application to soils than in the past. Today, the amount of sludge that can be applied to agricultural land is more often limited by the potential for nitrate pollution from the nitrogen it contains, rather than by the metal content of the sludge. Nonetheless, application of sewage sludge to farmland is closely regulated to ensure that the metal concentrations in the sludge do not exceed the standards and that the total amount of metal applied to the soil over the years does not exceed the maximum accumulative loading limit listed in Table 18.10. The fact that metal-loading standards differ considerably between the United States and Europe (see Table 18.10) is an indication that the nature of the metal contamination threat is still somewhat controversial.

TOXIC EFFECTS FROM SLUDGE. The uncertainties as to the nature of many of the organic chemicals found in the sludge, as well as the cumulative nature of the metals problem, dictate continued caution in the regulations governing application of sludge to croplands. The effect of application of a high-metal sludge on heavy metal content of soils and of earthworms living in the soil is illustrated in Table 18.11. The sludge-treated soil areas, as well as the bodies of earthworms living in these soils, were higher in some of these elements than was the case in areas where sludge had not been applied. One would expect further concentration to take place in the tissue of birds and fish, many of which consume the earthworms.

Farmers must be assured that the levels of inorganic chemicals in sludge are not sufficiently high to be toxic to plants (a possibility mainly for zinc and copper) or to humans and other animals who consume the plants (a serious consideration for Cd, Cr, and Pb). For relatively low-metal municipal sludges, application at rates just high enough to supply needed nitrogen seems to be quite safe (Table 18.12).

TABLE 18.11 The Effect of Sewage Sludge Treatment on the Content of Heavy Metals in Soil and in Earthworms Living in the Soil

Note the high concentration of cadmium and zinc in the earthworms.

	Concentration of metal, mg/kg			
	Soil		*Earthworms*	
Metal	*Control*	*Sludge-treated*	*Control*	*Sludge-treated*
Cd	0.1	2.7	4.8	57
Zn	56	132	228	452
Cu	12	39	13	31
Ni	14	19	14	14
Pb	22	31	17	20

From Beyer, et al. (1982).

TABLE 18.12 Uptake of Metals by Corn After 19 Years of Fertilizing a Minnesota Soil (Typic Hapludoll) with Lime-Stabilized Municipal Sewage Sludge

Note that the metals show the typical pattern of less accumulation in the grain than in the leaves and stalks (stover). The annual sludge rate of about 10.5 Mg was designed to supply the nitrogen needs of the corn. The sludge had little effect on the metal content of the plants, except in the case of zinc (which increased, but not beyond the normal range for corn).

	Uptake, mg/kg					
Treatment	*Zn*	*Cu*	*Cd*	*Pb*	*Ni*	*Cr*
	Stover					
Fertilizer	18	8.4	0.16	0.9	0.7	0.9
Sludge	46.5	7.0	0.18	0.8	0.6	1.4
	Grain					
Fertilizer	20	3.2	0.29	0.4	0.4	0.2
Sludge	26	3.2	0.31	0.5	0.3	0.2
Cumulative metal applied in sludge, kg/ha	175	135	1.2	49	4.9	1045

Data abstracted from Dowdy, et al. (1994).

Direct ingestion of soils and sludge is also an important pathway for human and animal exposure. Animals should not be allowed to graze on sludge-treated pastures until rain or irrigation has washed the sludge from the forage. Children may eat soil while they play, and a considerable amount of soil eventually becomes dust in many households. Direct ingestion of soil and dust is particularly harmful in lead toxicity.

18.9 REACTIONS OF INORGANIC CONTAMINANTS IN SOILS

Heavy Metals in Sewage Sludge

Concern over the possible buildup of heavy metals in soils resulting from large land applications of sewage sludges has prompted research on the fate of these chemicals in soils. Most attention has been given to zinc, copper, nickel, cadmium, and lead, which are commonly present in significant levels in these sludges. Studies have shown that if the soil is not very acid, these elements are generally bound by soil constituents; they do not then easily leach from the soil, and they are not then readily available to plants. Only in moderately to strongly acid soils is there significant movement down the profile from the layer of application of the sludge. Monitoring soil acidity and using judicious applications of lime can prevent leaching into groundwaters and can minimize uptake by plants.

FORMS FOUND IN SOILS TREATED WITH SLUDGE. By using chemical extractants, researchers have found that heavy metals are associated with soil solids in four major ways (Table 18.13). First, a very small proportion is held in *adsorbed* or *exchangeable forms,* which are available for plant uptake. Second, the elements are bound by the *soil organic matter* and by the *organic materials* in the sludge. A high proportion of the copper is commonly found in this form, while lead is not so highly attracted. Organically bound elements are not readily available to plants, but can be released over a period of time.

The third association of heavy metals in soils is with *carbonates* and with *oxides of iron and manganese.* These forms are less available to plants than either the exchangeable or organically bound forms, especially if the soils are not allowed to become too acid. The fourth association is commonly known as the *residual form,* which consists of sulfides and other very insoluble compounds that are less available to plants than any of the other forms.

TABLE 18.13 **Forms of Six Heavy Metals Found in a Greenfield Sandy Loam (Coarse Loamy, Mixed, Thermic Typic Haploxeralf) That Had Received 45 Mg/ha Sewage Sludge Annually for 5 Years**

	Percentage of elements in each form					
Forms	*Cd*	*Cr*	*Cu*	*Ni*	*Pb*	*Zn*
Exchangeable/adsorbed	1	1	2	5	1	2
Organically bound	20	5	34	24	3	28
Carbonate/iron oxides	64	19	36	33	85	39
Residual[a]	16	77	29	40	12	31

[a] Sulfides and other very insoluble forms.
From Chang, et al. (1984).

It is fortunate that soil-applied heavy metals are not readily absorbed by plants and that they are not easily leached from the soil. However, the immobility of the metals means that they will accumulate in soils if repeated sludge applications are made. Care must be taken not to add such large quantities that the capacity of the soil to react with a given element is exceeded. It is for this reason that regulations set maximum cumulative loading limits for each metal (see Table 18.10).

Chemicals from Other Sources

Arsenic has accumulated in orchard soils following years of application of arsenic-containing pesticides. Being present in an anionic form (e.g., $H_2AsO_4^-$), this element is absorbed (as are phosphates) by hydrous iron and aluminum oxides, especially in acid soils. In spite of the capacity of most soils to tie up arsenates, long-term additions of arsenical sprays can lead to toxicities for sensitive plants and earthworms. The arsenic toxicity can be reduced by applications of sulfates of zinc, iron, and aluminum, which tie up the arsenic in insoluble forms.

Contamination of soils with *lead* comes primarily from airborne lead from automobile exhaust and from paint chips and dust from woodwork coated with old lead-pigmented paints. It is most concentrated within 100 m of major roadways, near urban centers, and in the soil near older homes. Some lead is deposited on the vegetation and some reaches the soil directly. In any case, most of the lead is tied up in the soil as insoluble carbonates, sulfides, and in combination with iron, aluminum, and manganese oxides (see Table 18.13). Consequently, the lead is largely unavailable to plants, but may injure children who put contaminated soil in their mouths.

Soil contamination by *boron* can occur from irrigation water high in this element, by excessive fertilizer application, or by the use of power plant fly ash as a soil amendment. The boron can be adsorbed by organic matter and clays but is still available to plants, except at high soil pH. Boron is relatively soluble in soils, toxic quantities being leachable, especially from acid sandy soils. Boron toxicity is usually considered a localized problem and is probably much less important than the deficiency of the element.

Fluorine toxicity is also generally localized. Drinking water for animals and fluoride fumes from industrial processes often contain toxic amounts of fluorine. The fumes can be ingested directly by animals or deposited on nearby plants. If the fluorides are adsorbed by the soil, their uptake by plants is restricted. The fluorides formed in soils are highly insoluble, the solubility being least if the soil is well supplied with lime.

Mercury contamination of lake beds and of swampy areas has resulted in toxic levels of mercury among certain species of fish. Insoluble forms of mercury in soils, not normally available to plants or, in turn, to animals, are converted by microorganisms to an organic form, methylmercury, in which it is more soluble and available for plant and animal absorption. The methylmercury is concentrated in fatty tissue as it moves up the food chain, until it accumulates in some fish to levels that may be toxic to humans. This series of transformations illustrates how reactions in soil can influence human toxicities.

18.10 PREVENTION AND ELIMINATION OF INORGANIC CHEMICAL CONTAMINATION

Three primary methods of alleviating soil contamination by toxic inorganic compounds are (1) to eliminate or drastically reduce the soil application of the toxins; (2) to immobilize the toxin by means of soil management, to prevent it from moving into food or water supplies; and (3) in the case of severe contamination, to remove the toxin by chemical, physical, or biological remediation.

Reducing Soil Application

The first method requires action to reduce unintentional aerial contamination from industrial operations and from automobile, truck, and bus exhausts. Decision makers must recognize the soil as an important natural resource that can be seriously damaged if its contamination by accidental addition of inorganic toxins is not curtailed. Also, there must be judicious reductions in intended applications to soil of the toxins through pesticides, fertilizers, irrigation water, and solid wastes.

Immobilizing the Toxins

Soil and crop management can help reduce the continued cycling of these inorganic chemicals. This is done primarily by keeping the chemicals in the soil rather than encouraging their uptake by plants. The soil becomes a sink for the toxins, and thereby breaks the soil–plant–animal (humans) cycle through which the toxin exerts its effect. The soil breaks the cycle by immobilizing the toxins. For example, most of these elements are rendered less mobile and less available if the pH is kept near neutral or above (Figure 18.13). Liming of acid soils reduces metal mobility; hence, regulations require that the pH of sludge-treated land be maintained at 6.5 or higher.

Draining wet soils should be beneficial, since the oxidized forms of the several toxic elements are generally less soluble and less available for plant uptake than are the reduced forms. However, the opposite is true for chromium, which occurs principally in two forms, Cr^{3+} and Cr^{6+}. Hexavalent Cr forms compounds that are mobile under a wide

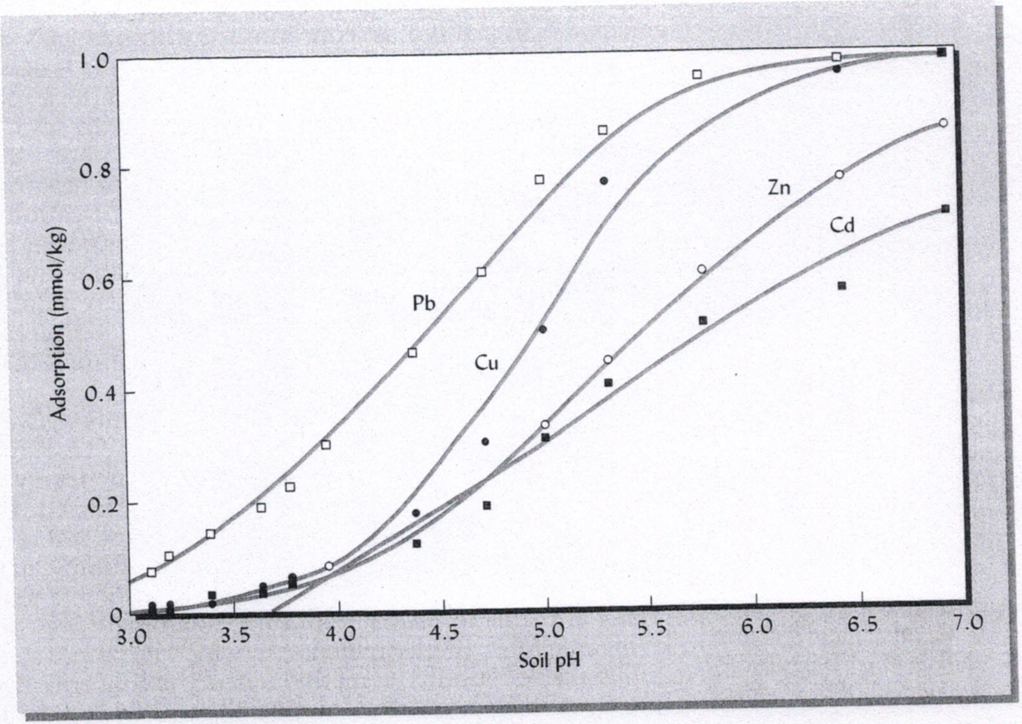


FIGURE 18.13 The effect of soil pH on the adsorption of four heavy metals. Maintaining the soil near neutral provides the highest adsorption of each of these metals and especially of lead and copper. The soil was a Typic Paleudult (Christiana silty clay loam). [From Elliot, et al. (1986)]

range of pH conditions and are highly toxic to humans. Trivalent Cr, on the other hand, forms oxides and hydroxides that are quite immobile except in very acid soils. Therefore, it is desirable to reduce Cr^{6+} to Cr^{3+} in chromium-contaminated soils. Fortunately, active soil organic matter is quite effective at reducing chromium, and the Cr^{3+}, once formed, does not tend to reoxidize (Figure 18.14).

Heavy phosphate applications reduce the availability of some metal cations but may have the opposite effect on arsenic, which is found in the anionic form. Leaching may be effective in removing excess boron, although moving the toxin from the soil to water may not be of any real benefit.

Care should be taken in selecting plants to be grown on metal-contaminated soil. Generally, plants translocate much larger quantities of metals to their leaves than to their fruits or seeds (see Table 18.12). The greatest risk for food-chain contamination with metals is therefore through leafy vegetables, such as lettuce and spinach, or through forage crops eaten by livestock.

Bioremediation by Metal Hyperaccumulating Plants

Certain plants that have evolved in soils naturally very high in metals are able to take up and accumulate extremely high concentrations of metals without suffering from toxicity. Plants have been found that accumulate more than 20,000 mg/kg nickel, 40,000 mg/kg zinc, and 1000 mg/kg cadmium. While such *hyperaccumulating* plants would pose a serious health hazard if eaten by animals or people, they may facilitate a new kind of bioremediation for metal-contaminated soils.

If sufficiently vigorously growing genotypes of such plants can be found, it may be possible to use them to remove metals from contaminated soils. For example, several plants in the genus *Thlaspi* have been grown in soils contaminated by smelter fumes (Figure 18.15). These soils are so contaminated that they are virtually barren. Accumulating more than 30,000 mg/kg (about 3%) zinc in their tissues, the *Thlaspi* plants grown on this site could be harvested to remove large quantities of the metals from the soil. The plant tissue is so concentrated that it could be used as an "ore" for smelting new metal. This and other bioremediation technologies for metals (e.g., the bioreduc-

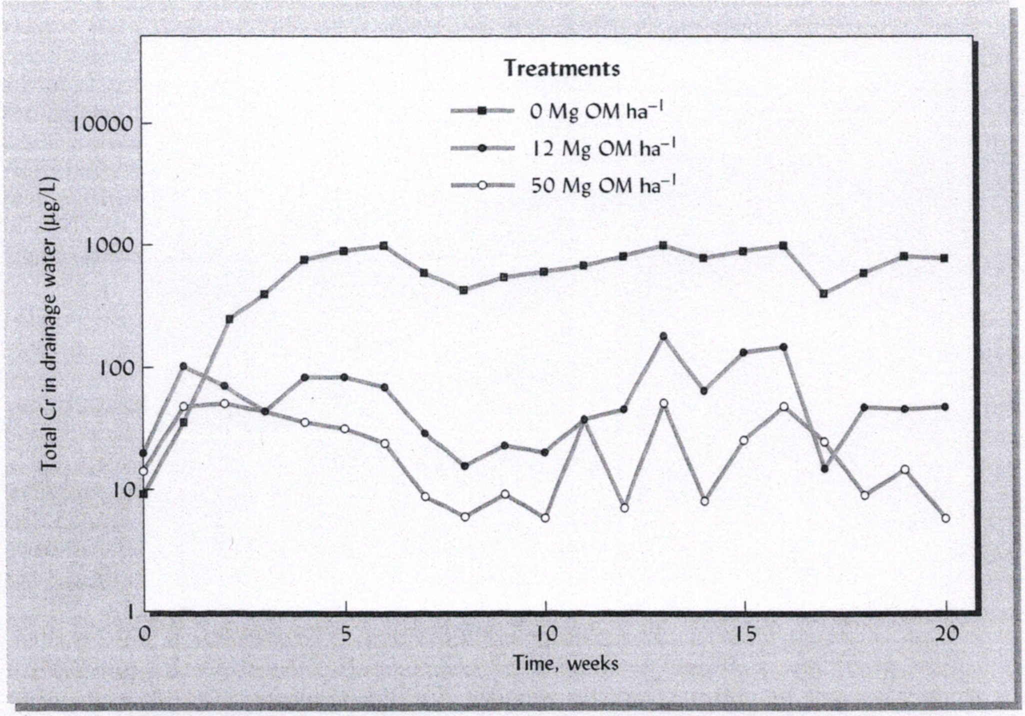


FIGURE 18.14 Effect of adding dried cattle manure (OM) on the concentration of chromium in drainage water from a chromium-contaminated soil. Oxidation of the manure caused the reduction of toxic, mobile Cr^{6+} to relatively immobile Cr^{3+}. Note the log scale for Cr in the water. The coarse-textured soil was a Typic Torripsamment in California. [Adapted from Losi, et al. (1994)]

FIGURE 18.15 *Thlaspi caerulescens,* a zinc and cadmium hyperaccumulator plant growing in smelter-contaminated soil near Palmerton, Pa. This plant has been reported to accumulate up to 4% zinc in its tissue (dry weight basis). Research with such plants aims at developing technology to biologically remove and recover metals from heavily contaminated soils. (Photo by H. Witham; courtesy of R. Chaney, USDA)

tion of chromium and selenium discussed earlier) hold promise for cleaning up badly contaminated soils without resorting to expensive and destructive excavation and soil-washing methods.

Genetic and bioengineering techniques are being utilized to develop high-yielding hyperaccumulating plants that can remove larger quantities of heavy metal contaminants from soils. For example, wide genetic variation in heavy metal accumulation by different strains of Alpine pennycress suggests the potential for breeding improved accumulating plants. Also, research to insert genes responsible for contaminant accumulation into other higher-yielding plants, such as canola and Indian mustard, is underway.

A combination of chelates and phytoremediation has been used to remove lead from contaminated soil. This element is sparingly available to plants, being strongly bound by both mineral and organic matter. The chelates solubilize the lead, and plants such as Indian mustard are used to remove it.

18.11 LANDFILLS

A visit to the local landfill would convince anyone of the wastefulness of modern societies. Roughly 250 million Mg of municipal wastes are generated each year by people in the United States. Most (about 70%) of this waste material is organic in nature, largely paper, cardboard, and yard wastes (e.g., grass clippings, leaves, and tree prunings). The other 30% consists mainly of such nonbiodegradeables as glass, metals, and plastic. Currently, despite an upsurge in recycling efforts, the great majority of these materials are buried in the earth (Figure 18.16).

The Solid Waste Problem

We know that the entire waste disposal problem could be greatly reduced by creating less waste in the first place. Second, it is possible to eliminate most problems associated with waste disposal by two simple measures: (1) keeping the metals, glass, plastics, and paper separate in the household for easy recycling, and (2) composting the yard wastes, food wastes, and some of the paper products. The composted product from a number of municipalities is successfully used as a beneficial soil amendment (see Section 16.7). The small fraction of more hazardous wastes remaining can then be detoxified or concentrated and immobilized.

The present reality is that most municipal solid wastes are buried in the earth and will probably continue to be disposed of in this manner for some time to come. In the past, wastes were merely placed in open dumps and, often, set afire. The term *landfill* came into use because wastes were often dumped in swampy lowland areas where, eventually, their accumulation filled up the lowland, creating upland areas for such uses as city parks and other facilities. Locating landfills on wetlands is no longer an acceptable practice.

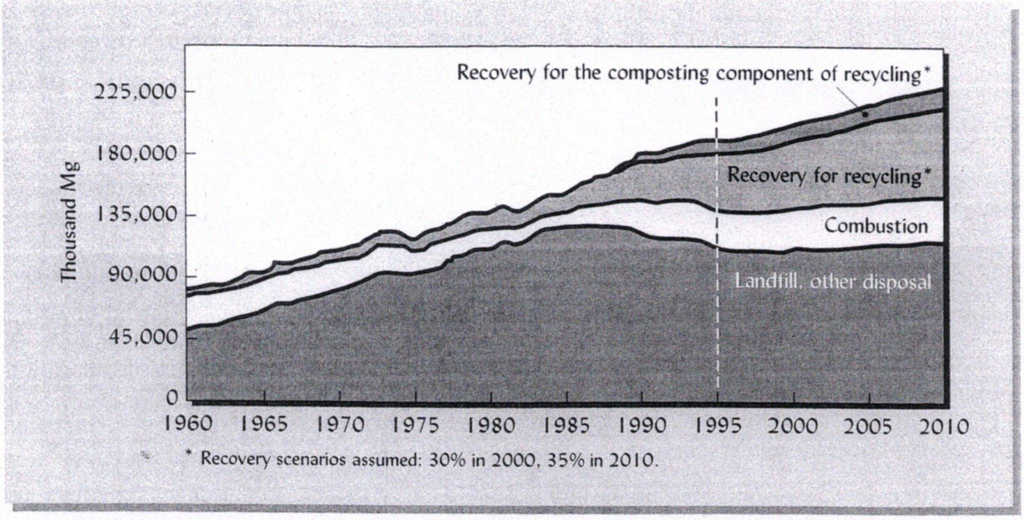


FIGURE 18.16 Historical and predicted trends in municipal solid-waste management in the United States. Soils play a central role in the composting and landfilling options (shown in dark green). Data from U.S. EPA (1997).

Two Basic Types of Landfill Design

Although landfill designs vary with the characteristics of both the site and the wastes, two basic types of landfills (Figure 18.17) can be distinguished: (1) the natural attenuation or unsecured landfill, and (2) the containment or secured landfill. We will briefly discuss the main features of each.

Natural Attenuation Landfills

The purpose of a natural attenuation landfill is to contain nonhazardous municipal wastes in a sanitary manner, protect them from animals and wind dispersal, and, finally, to cover them sufficiently to allow revegetation and possible reuse of the site. Some rainwater is allowed to percolate through the waste and down to the groundwater. Natural processes are relied upon to attenuate the leachate contaminants before the leachate reaches the groundwater. Soils play a major role in these natural attenuation processes through physical filtering, adsorption, biodegradation, and chemical precipitation (Table 18.14).

Soil Requirements. Finding a site with suitable soil characteristics is critical for this type of landfill. There must be at least 1.5 m of soil material between the bottom of the landfill and the highest groundwater level. This layer of soil should be only moderately permeable. If too permeable (sandy, gravelly, or highly structured), it will allow the leachate to pass through so quickly that little attenuation of contaminants will take place. The soil must have sufficient cation exchange capacity to adsorb the cations (NH_4^+, K^+, Na^+, Cd^{2+}, Ni^{2+}, and other metallic cations) that the wastes are expected to release. If too slowly permeable, the leachate will build up, flood the landfill, and seep out laterally.

The site for a natural attenuation landfill should also provide soils suitable for daily and final cover materials (Figure 18.18*a*). At the end of every workday, the waste must be covered by a layer of relatively impermeable soil material. The final cover for the landfill is much thicker than the daily covers, and includes a thick layer of low-permeability, fine-textured material underneath a thinner layer of loamy "topsoil." The impermeable cover is meant to minimize percolation of water into the landfill, and the topsoil is meant to support a vigorous plant cover that will prevent erosion and use up water by evapotranspiration. The whole system is designed to limit the amount of water percolating through the waste, so that the amounts of contaminated leachate generated will not overwhelm the attenuating capacity of the soil between the landfill bottom and the groundwater.

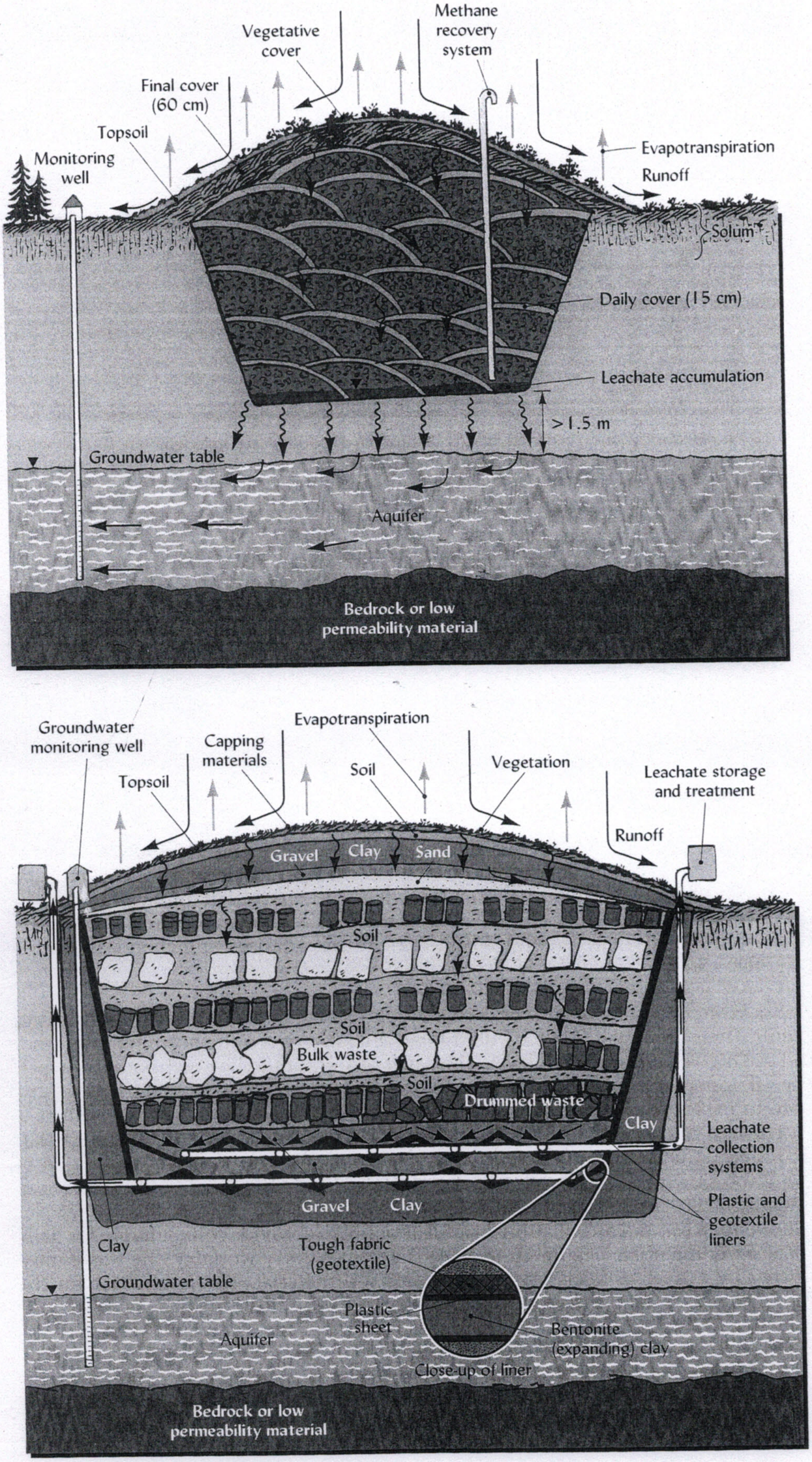


FIGURE 18.17 Two types of landfills. The natural attenuation landfill (top) depends largely on soil processes to attenuate the contaminants in the leachate before they reach the groundwater. The containment-type landfill (bottom) is used for more hazardous wastes or when soil conditions on the site are unsuitable for natural attenuation. it is designed to collect all the leachate and pump it out for storage and treatment.

TABLE 18.14 **Partial List of Organic and Inorganic Contaminants in Untreated Leachate from the City of Guelph (Ontario, Canada) Municipal Solid Waste Landfill**

Typical sources of these contaminants in landfills and mechanisms by which soils can attenuate the contaminants are also given. Although leachates vary greatly among landfills, the contaminants in this list are fairly typical.

Chemical	*Concentration, μg/L*	*Common sources*	*Mechanisms of attenuation*
		Organics	
Chemical oxygen demand (COD) for general organics	14,300	Rotting yard wastes, paper, and garbage	Biological degradation
Benzene	20	Adhesives, deodorants, oven cleaner, solvents, paint thinner, and medicines	Filtration, biodegradation, and methanogenesis
Dichloroethane	406	Adhesives and degreasers	Biodegradation and dilution
Toluene	165	Glues, paint cleaners and strippers, adhesives, paints, dandruff shampoo, and carburetor cleaners	Biodegradation and dilution
Xylene	212	Oil and fuel additives, paints, and carburetor cleaners	Biodegradation and dilution
		Metals	
Nickel	0.38	Batteries, electrodes, and spark plugs	Adsorption and precipitation
Chromium	0.14	Cleaners, paint, linoleum, and batteries	Precipitation, adsorption, and exchange
Cadmium	0.03	Paint, batteries, and plastics	Precipitation and adsorption

Leachate data from Cureton, et al. (1991).

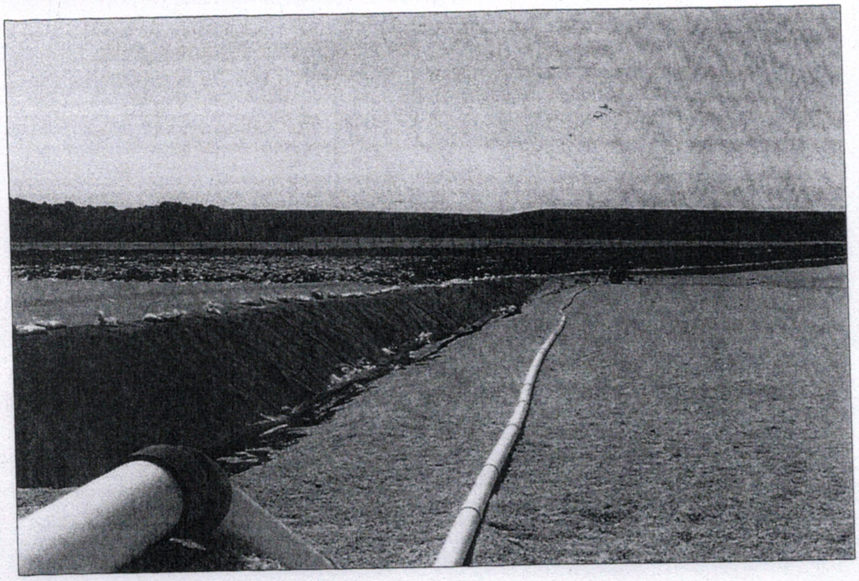
Containment or Secured Landfills

The second main type of landfill is much more complex and expensive to construct, but its construction is much less dependent on finding a site with suitable soils. The design is intended to contain all leachate from the landfill, rather than depending on the soil for cleansing before the leachate enters the groundwater. To accomplish the containment, one or more impermeable liners are set in place around the sides and bottom of the landfill. These are often made of expanding clays (e.g., bentonite) that swell to a very low permeability when wet. Plastic, watertight geomembranes, and tough, nonwoven, synthetic fabric (geotextiles) are also used in making the liners. A layer of gravel or sand is used to protect the liner from accidental punctures, and a system of slotted pipes and pumps is installed to collect all the leachate from the bottom of the landfill. The collected leachate is then treated on or off the site. The principal soil-related concern is the requirement for suitable sources of sand and gravel, for clayey material to form the final cover, and for topsoil to support protective vegetation (see Figure 18.18*b*).

Environmental Impacts of Landfills

Today, regulations require that wastes be buried in carefully located and designed sanitary landfills. As a result, the number of landfill sites in the United States was reduced from about 16,000 in 1967 to less than 2500 in 1998. A major concern with regard to landfills is the potential water pollution from the rainwater that percolates through the wastes, dissolving and carrying away all manner of organic and inorganic contaminants (see Table 18.14). In addition to the oxygen-demanding general dissolved organics, many of the contaminants in landfill leachate are highly toxic and would create a serious pollution problem if they reached the groundwater under the landfill.

In addition to efficiency of resource use, avoidance of particular landfill management problems is another reason that the organic components of refuse (mainly paper, yard trimmings and food waste) should be composted to produce a soil amendment rather than landfilled. First, as these materials decompose in a finished landfill, they lose volume and cause the landfill to settle and the landfill surface to subside. This physical instability severely limits the use that can be made of the land once a landfill is completed.



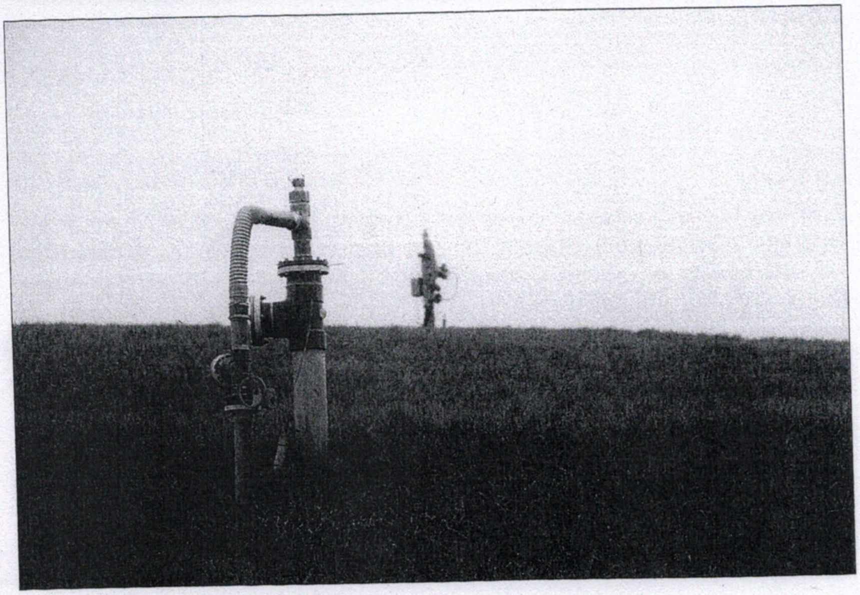


FIGURE 18.18 Modern landfill technology and soil processes. (*Top*) A bulldozer compacts and covers refuse in a natural attenuation landfill in deep, well-drained soils. Soil material for daily cover is excavated in the background. (*Center*) A black geomembrane liner covered with white pea gravel and a leachate collection pipe in a new cell being prepared in a containment-type landfill. The low hills in the background are completed cells blanketed with a vegetated final cover. (*Bottom*) Gas wells collecting methane gas from anaerobic decomposition in a completed landfill cell. The methane is used to fuel turbines that generate electricity for the waste-disposal operation and to sell to the local electric utility company. (Photos courtesy of R. Weil)

Second, decomposition of the organic refuse produces undesirable liquid and gaseous products. Within a few weeks, decomposition uses up the oxygen in the landfill, and the processes of anaerobic metabolism take over, changing the cellulose in paper wastes into butyric, propionic, and other volatile organic acids, as well as hydrogen and carbon dioxide. After a month or so methane-producing bacteria become dominant, and for several years (or even decades) a gaseous mixture of about one-third carbon dioxide and two-thirds methane (known as *landfill gas*) is generated in quantity.

The production of methane gas by the anaerobic decomposition of organic wastes in a landfill can present a very serious explosion hazard if this gas is not collected (and possibly burned as an energy source; see Figure 18.18*c*). Where the soil is rather permeable, the gas may diffuse into basements up to several hundred meters away from the landfill. A number of fatal explosions have occurred by this process. Anaerobic decomposition in landfills also emits other harmful gases, the effects of which are less well known.

18.12 SOILS AS ORGANIC WASTE DISPOSAL SITES

In the United States, nearly 250 million Mg of domestic wastes are generated each year. To this must be added the nearly 2 billion Mg of farm animal wastes, as well as millions of megagrams of organic wastes from food- and fiber-processing plants and industrial operations.

It is no longer environmentally acceptable to dispose of these wastes by dumping them into waterways or the oceans or by burning, thus releasing reaction products into the atmosphere. The soil offers an alternative disposal sink which is being more and more widely used. These organic wastes can improve soil physical and chemical properties and can provide nutrients for increased plant growth. Such positive effects will likely encourage continued land application of these wastes. At the same time, when wastes are applied in excess quantities, soil productivity may be depressed by salts, or soil and water pollution may occur.

18.13 RADIONUCLIDES IN SOIL

Nuclear fission in connection with atomic weapons testing and nuclear power generation provides another source of soil contamination. To the naturally occurring radionuclides in soil (e.g., ^{40}K, ^{87}Rb, and ^{14}C), a number of fission products have been added. However, only two of these are sufficiently long-lived to be of significance in soils: strontium 90 (half-life = 28 yr) and cesium 137 (half-life = 30 yr). The average levels of these nuclides in soil in the United States are about 388 millicuries (mC)/km^2 for ^{90}Sr and 620 mC/km^2 for ^{137}Cs. A comparable figure for the naturally occurring ^{40}K is 51,800 mC/km^2. These normal soil levels of the fission radionuclides are not high enough to be hazardous. Even during the peak periods of weapons testing, soils did not contribute significantly to the level of these nuclides in plants. Atmospheric fallout on the vegetation was the primary source of radionuclides in the food chain. Consequently, only in the event of a catastrophic supply of fission products could toxic soil levels of ^{90}Sr and ^{137}Cs be expected. Fortunately, considerable research has been accomplished on the behavior of these two nuclides in the soil–plant system.

Strontium 90

Strontium 90 behaves in soil in much the same manner as does calcium, to which it is closely related chemically. It enters soil from the atmosphere in soluble forms and is quickly adsorbed by the colloidal fraction, both organic and inorganic. It undergoes cation exchange and is available to plants much as is calcium. Contamination of forages and, ultimately, of milk by this radionuclide is of concern, as the ^{90}Sr could potentially be assimilated into the bones of the human body. The possibility that strontium is involved in the same plant reactions as calcium probably accounts for the fact that high soil calcium tends to decrease the uptake of ^{90}Sr.

Research is underway to take advantage of plant uptake of radionuclides in phytoremediation exercises. Plants, such as sunflowers, are being used to remove ^{137}Cs and ^{90}Sr from a pond area near the Chernobyl, Ukraine nuclear disaster. Indian mustard is also being used in nearby sites to remove such nucleotide contaminants.

Cesium 137

Although chemically related to potassium, cesium tends to be less readily available in many soils. Apparently, ^{137}Cs is firmly fixed by vermiculite and related interstratified minerals. The fixed nuclide is nonexchangeable, much as is fixed potassium in some interlayers of clay (see Section 14.15). Plant uptake of ^{137}Cs from such soils is very limited. Where vermiculite and related clays are absent, as in some tropical soils, ^{137}Cs uptake is more rapid. In any case, the soil tends to dampen the movement of ^{137}Cs into the food chain of animals, including humans.

Radioactive Wastes[6]

In addition to radionuclides added to soils as a result of weapons testing and accidents (such as that which occurred at Chernobyl, Ukraine), soils may interact with low-level radioactive waste materials that have been buried for disposal. Even though the materials may be in solid form when placed in shallow land burial pits, some dissolution and subsequent movement in the soil are possible. Plutonium, uranium, americium, neptunium, curium, and cesium are among the elements whose nuclides occur in radioactive wastes.

Nuclides in wastes vary greatly in water-solubility, uranium compounds being quite soluble, compounds of plutonium and americium being relatively insoluble, and cesium compounds intermediate in solubility. Cesium, a positively charged ion, is adsorbed by soil colloids. Uranium is thought to occur as a UO_2^{2+} ion that is also adsorbed by soil. The charge on plutonium and americium appears to vary, depending on the nature of the complexes these elements form in the soil.

There is considerable variability in the actual uptake by plants of these nuclides from soils, depending on such properties as pH and organic matter content. The uptake from soils by plants is generally lowest for plutonium, highest for neptunium, and intermediate for americium and curium. Fruits and seeds are generally much lower in these nuclides than are leaves, suggesting that grains may be less contaminated by nuclides than forage crops and leafy vegetables.

Since soils are being used as burial sites for low-level radioactive wastes, care should be taken that soils are chosen whose properties discourage leaching or significant plant uptake of the chemicals. Data in Table 18.15 illustrate differences in the ability of different soils to hold breakdown products of two radionuclides. It is evident that monitoring of nuclear waste sites will likely be needed to assure minimum transfer of the nuclides to other parts of the environment.

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[6] This summary is based largely on papers on this subject in *Soil Science,* 132 (July 1981).

TABLE 18.15 **Concentrations of Several Breakdown Products of Uranium 238 and Thorium 232 (Nucleotides) in Six Different Soil Suborders in Louisiana**

Note marked differences among levels in the different soils.

		^{238}U breakdown products			*^{232}Th breakdown products*		
Soil suborder	*No. of samples*	*^{226}Ra*	*^{214}Pb*	*^{214}Bi*	*^{212}Pb*	*^{137}Cs*	*^{40}K*
Udults	22	37.3	27.7	28.9	27.4	16.7	136
Aquults	24	30.4	36.7	38.1	50.0	10.9	100
Aqualfs	37	51.1	38.3	36.6	59.7	13.5	263
Aquepts	93	92.2	47.6	45.2	63.8	16.1	636
Aquolls	57	90.4	45.8	44.7	59.5	8.7	608
Hemists	18	136.3	49.4	49.0	74.9	19.4	783

From Meriwether, et al. (1988).

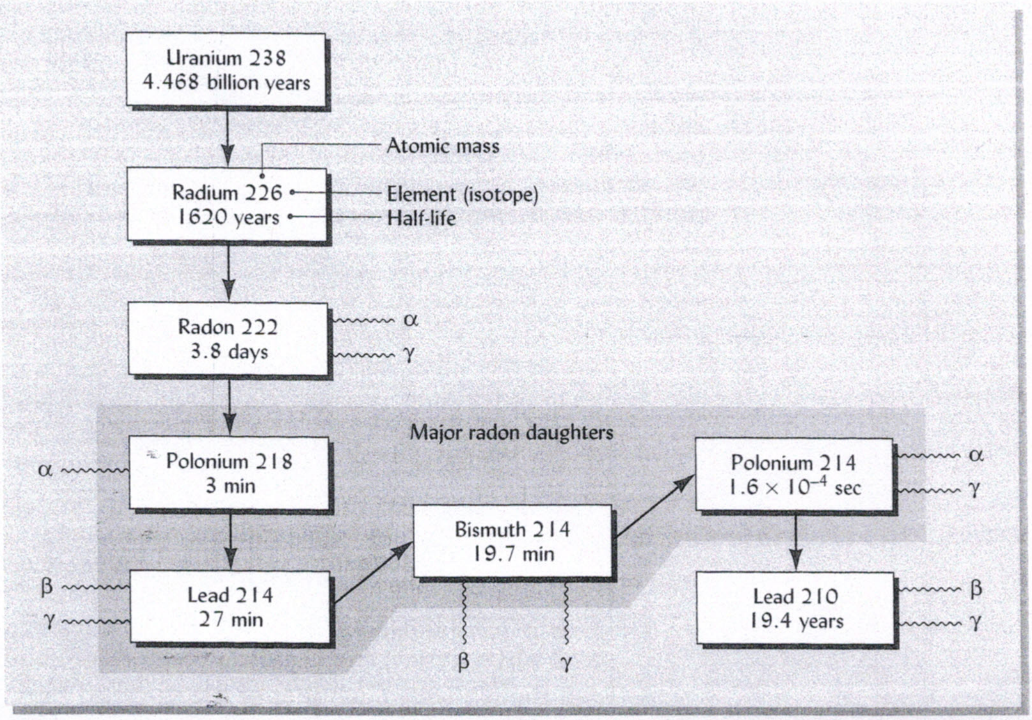

FIGURE 18.19 Radioactive decay of uranium 238 in soils that results in the formation of inert but radioactive radon. This gas emits alpha (α) particles and gamma (γ) rays and forms *radon daughters* that are capable of emitting alpha (α) and beta (β) particles and gamma (γ) rays. The alpha particles damage lung tissue and cause cancer. Radon gas may account for about 10,000 deaths annually in the United States. [Modified from Boyle (1988)]

18.14 RADON GAS FROM SOILS

The soil is the primary source of the colorless and odorless radioactive gas ***radon,*** which has been shown to cause lung cancer. Radon is formed from the radioactive decay of radium, a breakdown product of uranium found in minute quantities in most soils (Figure 18.19). Hazardous levels of radon occur in certain soils formed from uranium-rich igneous rocks and marine sediments. The health hazard from this gas stems from the transformation of its radioactive decay products into alpha rays, which can penetrate the lung tissue and cause cancer. Radon enters homes and other buildings from the surrounding soil. Since modern airtight buildings permit little exchange of air with the outside, radon can accumulate to harmful levels.

Radon usually moves into buildings through cracks in the basement walls and floors, and around openings where utility pipes enter the basement. If radon tests show that undesirable levels are present, the simplest remedial action is to seal all cracks and points of entry. Additional steps include constructing more elaborate systems to better ventilate the basement with outside air, in order to prevent a buildup of unhealthful levels of radon gas.

Since radon is an inert gas, it does not react with the soil, which merely serves as a channel through which the gas moves. Coarse, gravelly soils are more likely to transfer radon rapidly to basements than would finer-textured soils.

18.15 CONCLUSION

Three major conclusions may be drawn about soils in relation to environmental quality. First, since soils are valuable resources, they should be protected from environmental contamination, especially that which does permanent damage. Second, because of their vastness and remarkable capacities to absorb, bind, and break down added materials, soils offer promising mechanisms for the disposal and utilization of many wastes that otherwise may contaminate the environment. Third, soil contaminants and the products of their breakdown in soil reactions can be toxic to humans and other animals if they move from the soil into plants, the air, and—particularly—into water supplies.

To gain a better understanding of how soils might be used and yet protected in waste-management efforts, soil scientists devote a considerable share of their research efforts to environmental-quality problems. Furthermore, soil scientists have much to contribute to the research teams that search for better ways to clean up environmental contamination. Finding appropriate sites where soils can be safely used to clean up or store hazardous wastes involves geographic information about soils, the topic of the next chapter.

STUDY QUESTIONS

1. What agricultural practices contribute to soil and water pollution, and what steps must be taken to reduce or eliminate such pollution?
2. Discuss the types of reactions pesticides undergo in soils, and indicate what we can do to encourage or prevent such reactions.
3. Discuss the environmental problems associated with the disposal of large quantities of sewage sludge on agricultural lands, and indicate how the problems could be alleviated.
4. What is *bioremediation,* and what are its advantages and disadvantages compared with physical and chemical methods of handling organic wastes?
5. Even though large quantities of the so-called heavy metals are applied to soils each year, relatively small quantities find their way into human food. Why?
6. Compare the design, operation, and management of today's landfills with those in use 30 years ago, and indicate how the changes affect soil and water pollution.
7. What are *organoclays,* and how can they be used to help remediate soils polluted with nonpolar organic compounds?
8. Soil organic matter and some silicate clays chemically sorb some organic pollutants and protect them from microbial attack and leaching from the soil. What are the implications (positive and negative) of such protection for efforts to reduce soil and water pollution?
9. What radionuclides are of greatest concern in soil and water pollution, and why are they not more readily taken up by plants?
10. What are the comparative advantages and disadvantages of *in situ* and *ex situ* means of remediating soils polluted with organic compounds?
11. What is *phytoremediation,* and for what kinds of pollutants is it useful? Explain.

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