

18

SOILS AND CHEMICAL POLLUTION

*Black and portentous
this humor prove,
unless good counsel
may the cause remove . . .*

—W. SHAKESPEARE, ROMEO AND JULIET



Landfill soil silently accepts society's wastes. (R. Well)

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 products from a variety of sources—industrial, domestic, and agricultural—find their way into 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 how environmental quality suffers 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 13.10), 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 9.5). 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 13.9) 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 16.4).

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

Comprehensive information on cleaning contaminated soils at abandoned industrial sites:

www.epa.gov/brownfields/

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

These artificially synthesized compounds are termed **xenobiotics** because they are unfamiliar to the living world (Greek *xeno*, strange). Being nonnatural, many xenobiotics are both toxic to living organisms and resistant to biological decay. The chemical structures of xenobiotic compounds may be quite similar to those of naturally occurring compounds produced by microorganisms and plants. The difference is commonly the insertion of halogen atoms (Cl, F, Br) or multivalent nonmetal atoms (such as S and N) into the structure (see Figure 18.1).

Some xenobiotic 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, including people. 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, as military explosives, or as sprays applied to control pests in terrestrial ecosystems. 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 the Pesticide Problem

Pesticides are chemicals that are designed to kill pests (that is, any organism that the pesticide user perceives to be damaging). 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.

PROBLEMS WITH PESTICIDES. While the benefits to society from pesticides are great, so are the costs (Table 18.1). Widespread and heavy use of pesticides on agricultural soils and suburban landscapes has led to contamination of both surface and groundwater. Therefore, when pesticides are used, they should be chosen for low toxicity to humans and wildlife, low mobility on soils, and low persistence (see Section 18.3). Even then, the use of pesticides often has wide-ranging detrimental effects on the microbial and faunal communities. In fact, the harm done, though not always obvious, may outweigh the benefits. Examples include insecticides that kill natural enemies of pest species as well as the target pest (sometimes creating new major pests from species formerly controlled by natural enemies) and fungicides that kill both disease-causing and beneficial mycorrhizal fungi (see Section 11.9). Given these facts, it should not come as a surprise that despite the widespread use of pesticides, insects, diseases, and weeds still cause the loss of one-third of the crop production, about the same proportion of crops lost to these pests in the United States, before synthetic organic pesticides were in use.

ALTERNATIVES TO PESTICIDES. Pesticides should not be seen as a panacea, or even as indispensable. Some farmers, most notably the small but increasing number who practice **organic farming**,¹ produce profitable, high-quality yields without the use of pesticides. In managing the effects of pests in any type of plant community (agricultural, ornamental, or forest), chemical pesticides should be used as a *last* resort, rather than as a *first* resort. Before resorting to the use of an insecticide or herbicide, every effort should be made to minimize the detrimental effects of insects and weeds by means of crop diversification, establishment of habitat for beneficial insects, application of organic soil amendments, implementation of cultural practices to reduce weed competition, and selection of pest-resistant plant cultivars. Too often, because pesticides are available as a convenient crutch, these more sophisticated approaches to plant management are not explored.

NONTARGET DAMAGES. Although some pesticides are intentionally applied to soils, most reach the soil because they miss the insect or plant leaf that is the application target. 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.

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 chem-

¹The term *organic farming* has little to do with the chemical definition of organic, which simply indicates that a compound contains carbon. Rather, it refers to a system and philosophy of farming that eschews the use of synthetic chemicals while it emphasizes soil organic matter and biological interactions to manage agroecosystems.

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.

icals 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 American bald eagle) during the 1960s and 1970s called public attention to the sometimes-devastating environmental consequences of pesticide use. More recently, evidence is mounting to suggest 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 ORGANIC CONTAMINANTS

Industrial Organics

Industrial organics that often end up contaminating soils by accident or neglect include petroleum products used for fuel [gasoline components such as benzene, and more complex polycyclic aromatic hydrocarbons, (PAHs)], solvents used in manufacturing processes [such as trichloroethylene (TCE)], and military explosives such as trinitrotoluene (TNT). Several examples of their structures are shown in Figure 18.1. Polychlorinated biphenyls (PCBs) constitute a particularly troublesome class of widely dispersed compounds. These compounds can disrupt reproduction in birds and cause cancer and hormone effects in humans and other animals. Several hundred varieties of liquid or resinous PCBs were produced from 1930 to 1980 and used as specialized lubricants, hydraulic fluids, and electrical transformer insulators, as well as in certain epoxy paints and many other industrial and commercial applications. Because of their extreme resistance to natural decay and their ability to enter food chains, even today soil and water all over the globe contain at least traces of PCBs.

The sites most intensely contaminated with organic pollutants are usually located near chemical manufacturing plants or oil storage facilities, but railway, shipping, and highway accidents also produce hot spots of contamination. Thousands of neighborhood gas stations represent potential or actual sites of soil and groundwater contamination as gasoline leaks from old, rusting underground storage tanks (Figure 18.2). However, as already mentioned, by far the most widely dispersed xenobiotics are those designed to kill unwanted organisms (i.e., pests).

Alternative cleanup technologies for leaking underground storage tanks: www.epa.gov/swerust1/pubs/index.htm#tums

Pesticides

Pesticides are commonly classified according to the group of pest organisms targeted: (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



FIGURE 18.2 Leaking underground storage tank (LUST) replacement at a gas station in California. The old rusting steel tanks have been removed and replaced by more corrosion-resistant fiberglass tanks, which are set in the ground and covered with pea gravel. The soil and groundwater aquifer beneath the tanks were cleaned up using special techniques to stimulate soil microorganisms and to pump out volatile organics such as benzene vapors. Remediation and replacement typically costs \$500,000 for a single gas station. (Photo courtesy of R. Weil)

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.

HERBICIDES. The quantity of herbicides used in the United States exceeds that of the other 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. One of the most widely used herbicides, *glyphosate* (Roundup), does not belong to any of the aforementioned chemical groups. Unlike most herbicides, it is nonselective, meaning that it will kill almost any plant, including crops. However, a gene that confers resistance to its effects has been discovered and engineered into several major crops. These genetically engineered crops can then be grown with a very simple, convenient method of weed control that usually consists of one or two sprayings of glyphosate that will kill all plants other than the resistant crop.

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, soil fauna, 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 as widely used as herbicides and insecticides, some of them are known to contaminate soils and the water draining from treated soils. For example, some carbamate nematocides dissolve readily in water, are not adsorbed onto soil surfaces, and consequently easily leach downward and into the groundwater. Other nematocidal chemicals are volatile soil fumigants that kill virtually all life in the soil, both the helpful and the harmful (Section 18.4). Methyl bromide, once the most commonly used of these fumigants, has been banned because of its adverse effects on the atmosphere and parts of the environment. Happily, the search for substitutes has led to the development of many nonchemical means to manage the pests once controlled by this highly toxic chemical (e.g., see Figure 11.14).

18.3 BEHAVIOR OF ORGANIC CHEMICALS IN SOIL²

Once they reach the soil, organic chemicals, such as pesticides or hydrocarbons, move in one or more of seven directions (Figure 18.3): (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

²For reviews on organic chemicals in the soil environment, see Sawhney and Brown (eds.) (1989) and Pierzynski, et al. (2000); for pesticides, see Cheng (ed.) (1990).

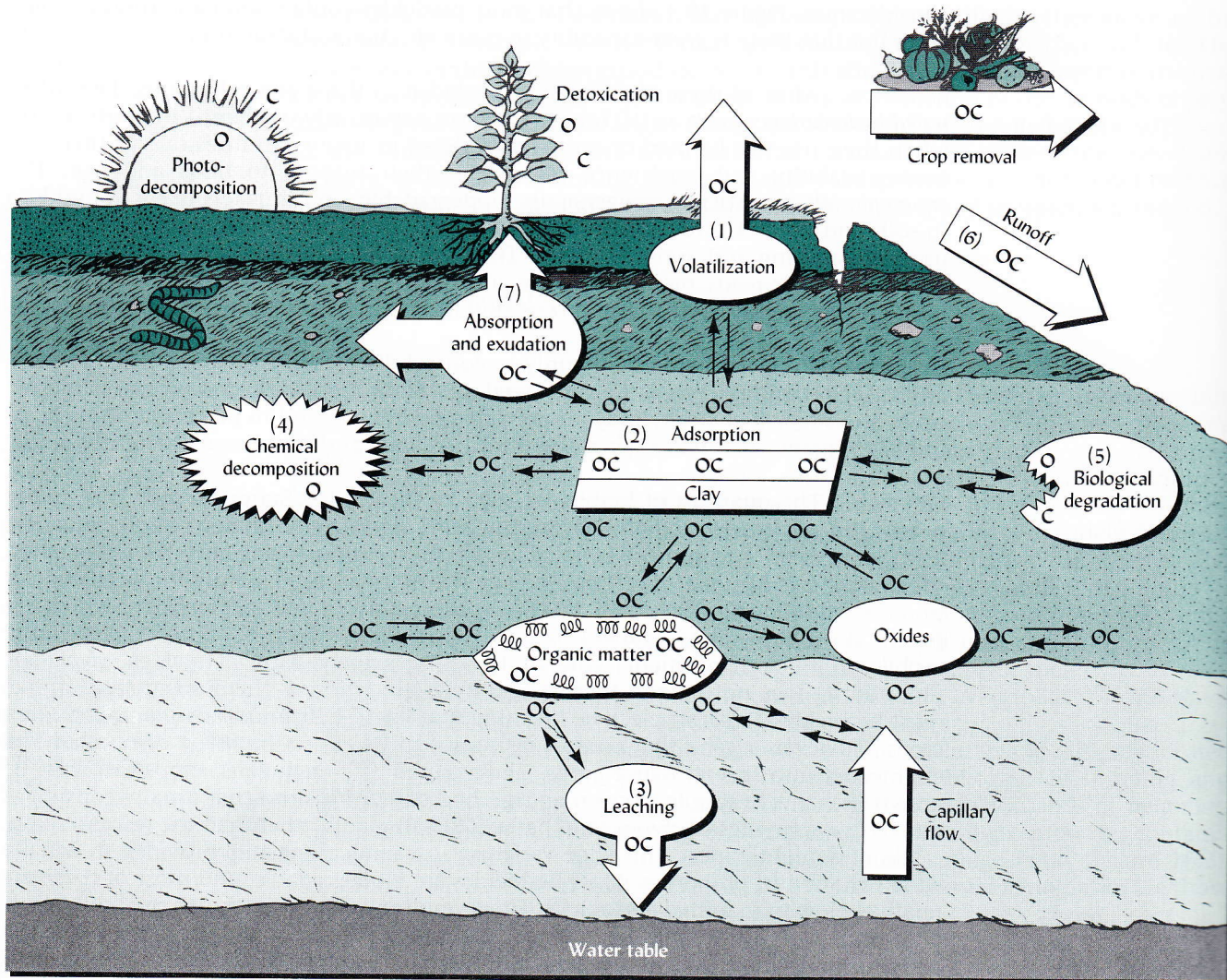


FIGURE 18.3 Processes affecting the dissipation of organic chemicals (OC) in soils. Note that the OC symbol is split up by decomposition (both by light and chemical reaction) and degradation by microorganisms, indicating that these processes alter or destroy the organic chemical. In transfer processes, the OC remains intact. [From Weber and Miller (1989)]

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 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 18.4),

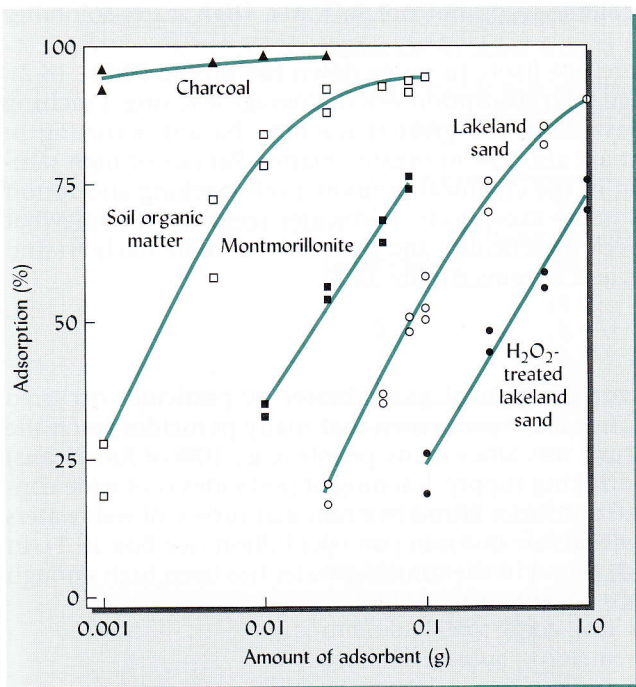


FIGURE 18.4 Adsorption of polychlorinated biphenyl (PCB) by different soil materials. The Lakeland sand (Typic Quartzipsamments) lost much of its adsorption capacity when treated with hydrogen peroxide to remove its organic matter. The amount of soil material required to adsorb 50% of the PCB was approximately 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 Streck and Weber (1982)]

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 8.3) 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 18.5), 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

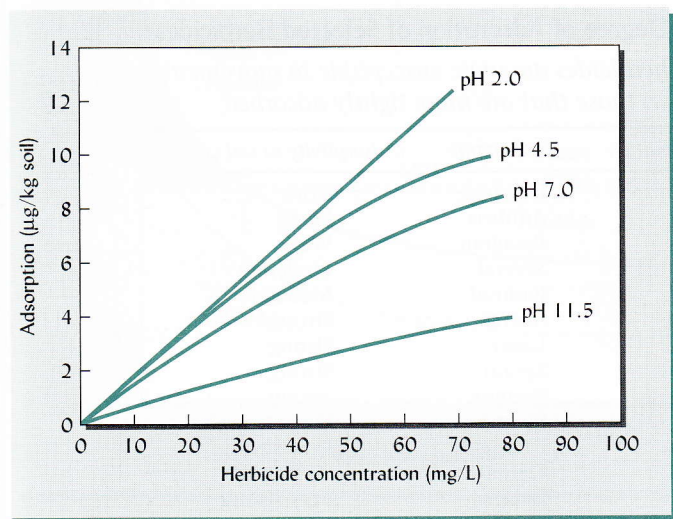


FIGURE 18.5 The effect of pH of kaolinite on the adsorption of glyphosate, a widely used herbicide (Brand name Roundup®). [Reprinted with permission from J. S. McConnell and L. R. Hossner, *J. Agric. Food Chem.* 33:1075-78 (1985); copyright 1985 American Chemical Society]

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 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 18.6).

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.

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.

<i>Common name or designation</i>	<i>Trade name</i>	<i>Adsorptivity to soil colloids</i>
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
Glyphosate	Roundup	Very strong
Paraquat	Paraquat	Very strong
Trifluralin	Treflan	Very strong
DCPA	Dacthal	Very strong

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.

Year of study	Atrazine loss, g/ha				Rainfall, May-June, mm
	Surface runoff loss	Drainage water loss	Total dissolved loss	Percent of total applied, %	
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).

apparently by a variety of organisms (Figure 18.7). 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.

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.

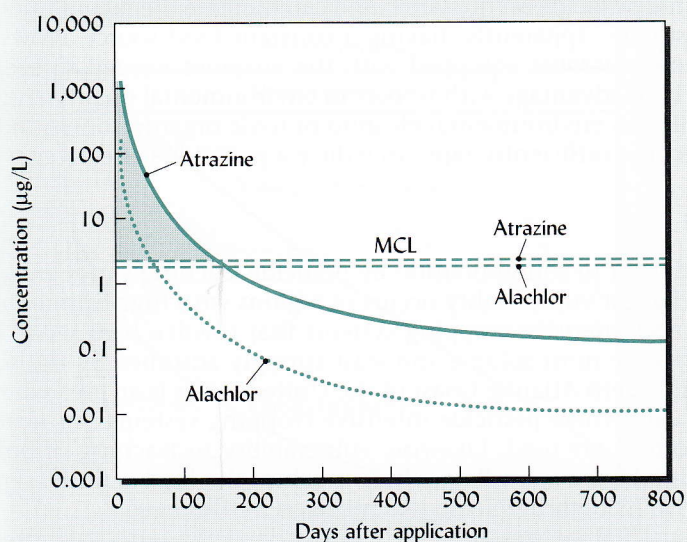


FIGURE 18.6 Concentration of two widely used herbicides, atrazine and alachlor, in the runoff from watersheds in Ohio planted to corn, along with the allowed Maximum Contaminant Level (MCL) for drinking water. Note that the concentration far exceeds the MCL, especially for atrazine, during the first 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)]

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.

Pesticide	Level found, parts per billion			
	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.

Persistence in Soils

The persistence of chemicals in the soil is the net result of all their reactions, movements, and degradations. Marked differences in persistence are the rule (see Figure 18.7). 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 a principle sometimes applied in environmental cleanup of toxic organic compounds, but the breakdown may become sufficiently rapid to reduce a pesticide's effectiveness.

Regional Vulnerability to Pesticide Leaching

The vulnerability of groundwater to contamination by pesticide leaching 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 most soluble and least strongly adsorbed by the soil colloids. For example, the southern Atlantic Coast of the United States is an area where sandy soils are prominent, and where pesticide-intensive cropping systems (for fruits, vegetables, peanuts, and cotton) are used. Likewise, vulnerability to leaching of both pesticides and nitrates is high in the Corn Belt, where much of the land is under continuous corn production with its high herbicide and nitrogen fertilizer use.

It should be pointed out that pesticide hazards are site-specific, and that these regional generalizations might mask localized areas of vulnerability. For example, in arid regions irrigated areas of intensive vegetable crop production may experience con-

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 $\mu\text{g}/\text{kg}$. In water this would be $\mu\text{g}/\text{L}$. 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 potassium cyanide, a very toxic substance consisting of a carbon, a potassium, and a nitrogen atom linked together (KCN). If you drank just *one drop* of this water, you would be ingesting almost 1 *trillion* molecules of potassium cyanide:

$$\frac{6.023 \times 10^{23} \text{ molecules}}{1 \text{ mol}} \times \frac{1 \text{ mol}}{65 \text{ g KCN}} \times \frac{1 \text{ g KCN}}{10^6 / \mu\text{g KCN}} \times \frac{1 \mu\text{g KCN}}{\text{L}} \times \frac{\text{L}}{10^3 \text{ cm}^3} \times \frac{\text{cm}^3}{10 \text{ drops}} = \frac{9.3 \times 10^{11} \text{ molecules}}{\text{drop}}$$

In the case of potassium 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.

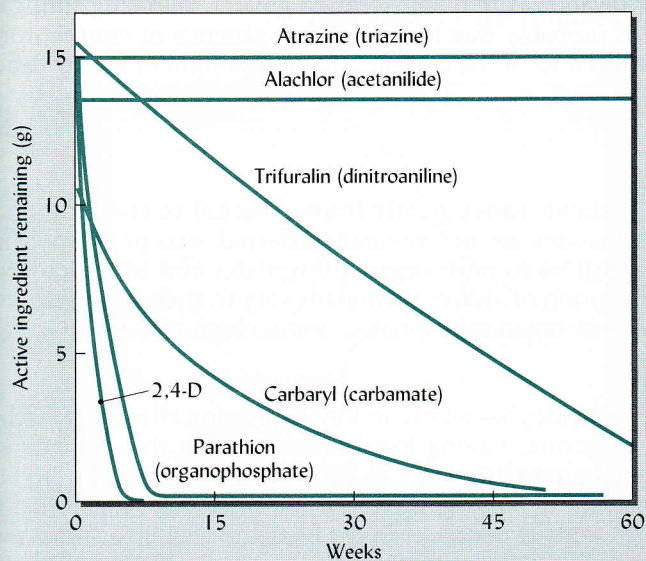


FIGURE 18.7 Degradation of four herbicides (alachlor, atrazine, 2,4-D, and trifluralin) and two insecticides (parathion and carbaryl), all of which are used extensively in the Midwest of the United States. Note that atrazine and alachlor are quite slowly degraded, whereas parathion and 2,4-D are quickly 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]

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.

<i>Organic chemical</i>	<i>Persistence in soils</i>
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
Glyphosate herbicide	6–20 mo
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

siderable leaching of both pesticides and nitrates. Likewise, application of certain water-soluble pesticides may result in groundwater contamination even where the soil may not be coarse in texture.

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 such fumigants as 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.

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 herbicides, 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 18.8). Thus, earthworms can magnify the pesticide exposure of birds, rodents, and other creatures that prey upon them.

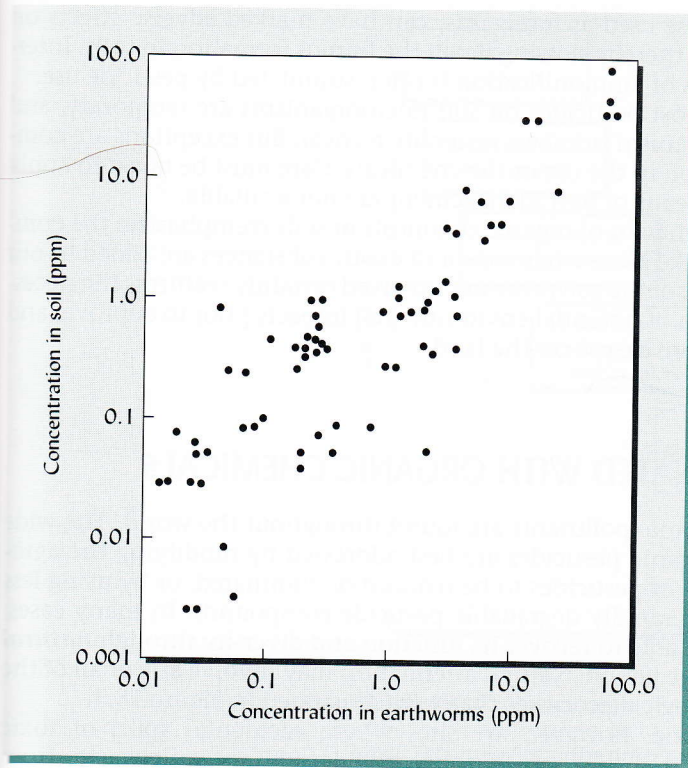


FIGURE 18.8 Effect of concentration of pesticides in soil on their concentration in earthworms. Birds or rodents eating the earthworms at any level of concentration would further concentrate the pesticides. [Data from several sources gathered by Thompson and Edwards (1974); used with permission of Soil Science Society of America]

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 18.9). 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.

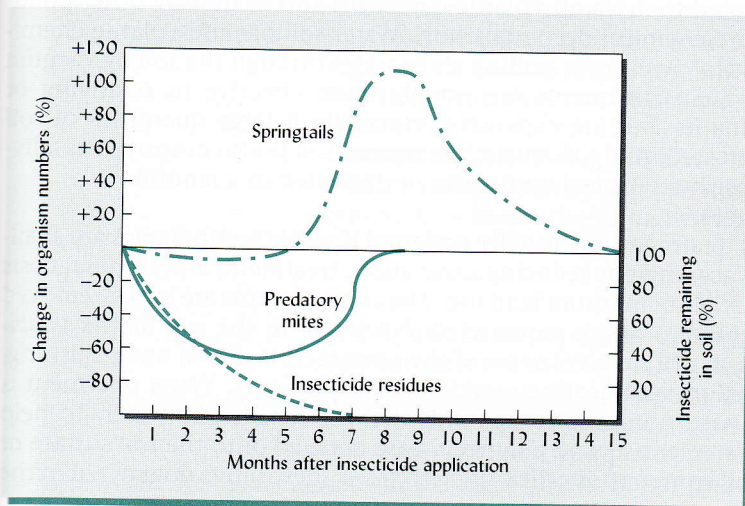


FIGURE 18.9 The direct effect of insecticide on predatory mites in a soil and the indirect effect of reducing mite numbers on the population of springtails (tiny insects) that serve as prey for the mites. [Replotted from Edwards (1978); used with permission of Academic Press, Inc., London]

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.

18.6 CONTAMINATION WITH TOXIC INORGANIC SUBSTANCES⁴

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, copper, manganese, and zinc are relatively lower in mammalian toxicity. Table 18.7 provides background information on the uses, sources, and effects of some of these elements. Although the metallic elements (see periodic table, Appendix B) are not all, strictly speaking, "heavy" metals, for the sake of simplicity this term is often used in referring to them.

⁴For a review of this subject, see Kabata-Pendias and Pendias (1992).

TABLE 18.7 Sources of Selected Inorganic Soil Pollutants

<i>Chemical</i>	<i>Major uses and sources of soil contamination</i>	<i>Organisms principally harmed^a</i>	<i>Human health effects</i>
Arsenic	Pesticides, plant desiccants, animal feed additives, coal and petroleum, mine tailings, detergents, and irrigation water	H, A, F, B	Cumulative poison, cancer, skin lesions
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; solder in water-pipes; paint pigment	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.

Sources and Accumulation

There are many sources of the inorganic chemical contaminants that can accumulate in soils. The burning of fossil fuels, smelting (Figure 18.19), 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 soil 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



FIGURE 18.19 A partially denuded hillside just downwind from a copper smelter in Anaconda, Montana. The heavy metal-laden fumes have contaminated this area with copper, zinc, nickel, and other metals to levels that are highly toxic to most plants and many other organisms, decimating the ecosystems of the area. Note the serious erosion that has resulted from the devegetation, despite the recent invasion of the area by a few metal-tolerant plant species. (Photo courtesy of R. Weil)

BOX 18.2 LEAD CONTAMINATION AND POISONING.

Lead contamination is one of the most serious and widespread problems of inorganic soil pollution. Long-term exposure to low levels of lead can have profoundly deleterious effects on child development and neurological functioning, including intelligence. Lead poisoning has been shown to contribute to mental retardation, poor academic performance, and juvenile delinquency. The U.S. EPA reports that nearly 1 million children in America today have dangerously elevated levels of lead in their blood. In the past (and, unfortunately, in the present in many developing countries that still use leaded gasoline), much of the lead came from burning leaded fuels. The content of lead in soils commonly increases with proximity to major highways. The lead content of soils also usually increases as the distance from the center of a major city decreases. Residents of inner cities generally live surrounded by lead-contaminated soils. The soil on the windward side of apartment buildings often shows the highest accumulations of lead, as it is there that the wind-carried particulates tend to settle out of the air.

A second reason for high lead concentrations in urban soils is related to the lead-based pigments in paint from pre-1970 buildings. Paint chips, flakes, and dust from sanding painted surfaces spread the lead around, and eventually much of it ends up in the soil. During dry weather, soil particles blow about, spreading the lead and contributing to the dust that settles on floors and windowsills. Although plants do not readily take up lead through their roots, lead-contaminated dust may stick to foliage and fruits. Eating these garden products and breathing in lead-contaminated dust are two pathways for human lead exposure (see Figure 18.20).

However, the most serious pathway, at least for young children, is thought to be hand-to-mouth activity—basically, eating dirt. Anyone who has observed a toddler knows that the child's hands are continually in its mouth. Lead-contaminated dust on surfaces in the home can therefore be an important source of lead exposure for young children; so, too, can lead-contaminated soil in outdoor play areas. Having children wash their hands frequently can significantly cut down their exposure to this insidious toxin.

In 2001, the U.S. EPA set new standards for the cleanup of lead in soil around homes: 400 parts per million (ppm) of lead in bare soil in children's play areas or 1200 ppm average for bare soil in the rest of the yard. Soils with lead levels higher than these standards require some remediation.

Until suitable phytoremediation techniques are found, protecting children from lead in soil around the home will continue to be largely a matter of stabilizing the lead away from the reach of children and dust-creating winds. Excavation of soil around homes is extremely expensive and, given the low mobility of lead in soils, probably not necessary. Instead, some areas may be covered with a thick layer of uncontaminated topsoil; others may be paved over, or a wooden deck may be built over them. A well-maintained cover of turfgrass will prevent most dust formation and soil ingestion. Removal of lead-based paints is likewise very expensive and difficult, so isolating the lead-based paint under several coats of fresh paint may be a better way to avoid exposure.

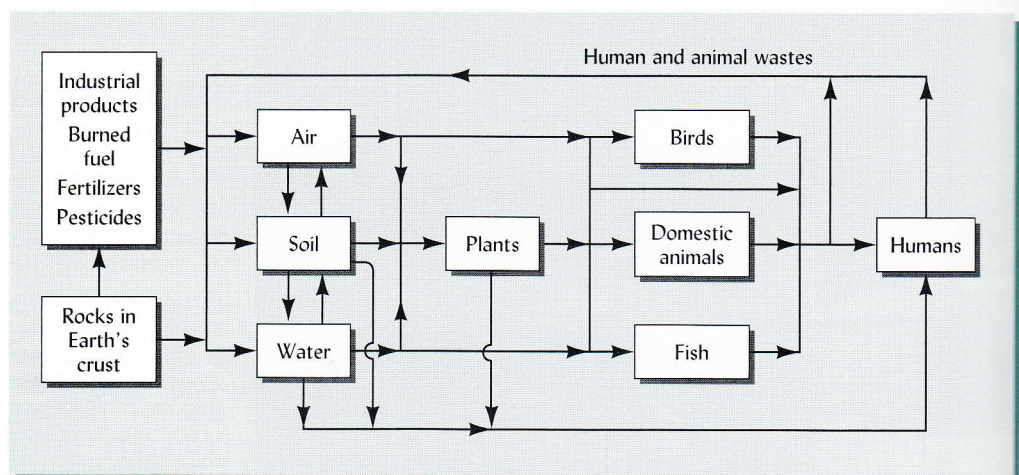


FIGURE 18.20 Sources of heavy metals and their cycling in the soil–water–air–organism ecosystem. It should be noted that the content of metals in tissue generally builds up from left to right, indicating the vulnerability of humans to heavy metal toxicity.

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 (see Box 18.2).

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 18.20). 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.

18.7 POTENTIAL HAZARDS OF CHEMICALS IN ENVIRONMENT

18.8 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. Many studies have suggested that if only moderate amounts of sludge are added, and the soil is not very acid ($\text{pH} > 6.5$), 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 have most studies shown significant movement down the profile from the layer of application of the sludge. Monitoring soil acidity and using judicious applications of lime have been widely recommended to prevent leaching into groundwaters and minimize uptake by plants.

More recently, studies using large amounts of sludge (up to and exceeding what is permitted by U.S. EPA regulations) have suggested that metals from sludge may initially be more mobile in soils than was previously thought. In fact, several studies have reported that from 20 to 80 percent of the metals applied with sludge at high rates have been leached from the root zone and, in all likelihood, lost to the groundwater. The metals in these studies probably moved as soluble organic complexes while the sludge-soil mixture was still fresh. Over time, the metals remaining in the soil appear to be stabilized in various low-solubility soil fractions (Table 18.12).

FORMS FOUND IN SOILS TREATED WITH SLUDGE. By using a sequence of chemical extractants, researchers have found that heavy metals are associated with soil solids in four major ways (Table 18.12). First, a very small proportion is held in *soluble* 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. High proportions of the copper and chromium are commonly found in this form, while lead is not so highly attracted. Organically bound elements are not readily available to plants, but may be released over a period of time.

TABLE 18.12 Forms of Six Heavy Metals Found in the Ap Horizon of a Metea Sandy Loam (Typic Hapludalfs) in Michigan That Received 870 Mg/ha (Dry Weight) of a "Dirty" Sewage Sludge Over 10 Years

The sludge application rate far exceeded that required to supply nitrogen to the crops grown, suggesting that the purpose was disposal rather than utilization. The sludge was incorporated into the soil between 1977 and 1986, prior to the implementation of source reduction programs to reduce the metal contents of most sewage sludges. The data are for soil samples taken 4 years after the last sludge application. The soil CEC was 7 cmol_c/kg, the organic matter content was 7%, and the pH was 6.9.

Forms in Soil	Solubility	Metal Content, mg/kg					
		Cd	Cr	Cu	Pb	Ni	Zn
Exchangeable and dissolved	Most	—	<1	4	<4	62	520
Acid soluble (carbonates, some organic)		3	38	140	19	170	1940
Organic matter	↓	<1 ^a	200	56	35	31	89
Fe and Mn oxides	↓	<1	331	96	28	180	370
Residual (very insoluble sulfides, etc.)	Least	<1	48	11	99	24	56
Total of all forms		≈4.5	617	307	≈181	467	2975

Totals	Metal Content, kg/ha ^b					
	Cd	Cr	Cu	Pb	Ni	Zn
Total measured in Ap horizon	≈12	1728	859	≈507	1308	8330
Total content in sludge applied	21	3000	1800	480	2100	11300
Apparent recovery, %	≈60	58	48	≈106	62	74

^aNumbers preceded by < indicate that the level present was less than the lowest concentration detectable by the analytical method used.

^bThe conversion from mg/kg to kg/ha assumes a bulk density of 1.4 Mg/m³ and a sampling depth of 20 cm. Metal concentration data from Berti and Jacobs (1996). See also McBride, et al. (1999) for further evidence of sludge-borne metal mobility in soils.

The third and fourth associations of heavy metals in soils are with *carbonates* and with *oxides of iron and manganese*. These forms are less available to plants than either the exchangeable or the organically bound forms, especially if the soils are not allowed to become too acid. The fifth 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.

It is fortunate that most 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 18.9).

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., H₂AsO₄⁻), 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* is primarily from airborne deposition and comes from automobile exhaust and from paint chips and dust from woodwork coated with old lead-pigmented paints. 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 18.12). Consequently, the lead is largely unavailable to plants and is unlikely to contaminate groundwater, but may injure children who put contaminated soil in their mouths (Box 18.2).

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.

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18.11 RADIONUCLIDES IN SOIL

U.S. EPA division of
radiation:
www.epa.gov/radiation/

Soils contain small quantities of ^{238}U , ^{40}K , ^{87}Rb , ^{14}C , and a number of other naturally occurring radioactive isotopes (radionuclides) that are characterized by long half-lives and give off minute amounts of radiation in the form of alpha particles (bundles of two neutrons and two protons) and beta particles (positive or negatively charged particles). As a radionuclide decays, its nucleus discharges these particles, transforming the atom into a different isotope or element with a lighter nucleus. The time it takes for one-half of the atoms of a particular radioactive isotope to undergo such decay is termed the *half-life* of the isotope. After 10 half-lives, 99.1% of the original atoms will have decayed. The intensity of radioactivity present—or, more precisely, the rate of radioactive decay—is expressed using the SI unit *becquerel* (Bq), which represents one decay per second. An older metric unit, still in wide use, is the *curie* (Ci), which equals 3.7×10^{10} Bq.⁶

Radioactivity from Nuclear Fission

The process of nuclear fission, in connection with atomic weapons testing and nuclear power generation, has contaminated soils with a number of additional radionuclides. 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 level of ^{90}Sr in soil in the United States is about 14.4 kilobecquerels per square meter (kBq/m²) or 388 millicuries per square kilometer (mCi)/km². The average level for ^{137}Cs is about 22.9 kBq/m² (620 mCi/km²). The levels of radioactivity caused by fallout are quite small compared to that for naturally occurring radionuclides. For example, for naturally occurring ^{40}K the average level is about 1900 kBq/m² (51,800 mCi/km²).

Partly because of the cation-exchange properties of soils, the levels of these fission radionuclides found in most soils are not high enough to be hazardous. Most of the ^{90}Sr and ^{137}Cs reaching the soil is adsorbed by the soil colloids in exchange for other cations previously adsorbed, with the result that plants take up mainly the replaced cations rather than the added radionuclides (see Section 8.8). Even during the peak periods of weapons testing in the early 1960s, soils did not contribute significantly to the level of these nuclides in plants. Atmospheric fallout directly onto foliage 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. Such high levels of ^{90}Sr and ^{137}Cs , as well as ^{131}I , did contaminate soils in Ukraine, Scandinavia, and Eastern Europe in the wake of the 1986 reactor meltdown at Chernobyl in Ukraine (then part of the Soviet Union). The accident deposited more than 200 kBq/m² of radioactivity on soils as far away as the United Kingdom. Fortunately, considerable research has been accomplished on the behavior of these nuclides in the soil-plant system.

STRONTIUM 90. In the soil-plant-animal system, ^{90}Sr behaves very much like calcium, to which it is closely related chemically (see periodic table, Appendix B). It enters the soil from the atmosphere in soluble forms and is quickly adsorbed by the colloidal fraction, both organic and inorganic. It is taken up by plants and assimilated much like 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. Fortunately, when it exchanges with aluminum or hydrogen ions adsorbed on the colloids in an acid soil, it comprises such a minute fraction of the exchangeable cations that its availability is quite low. However, should these soils be limed, the large quantities of added calcium are likely to cause the desorption of the strontium from the exchange sites, making it more available for leaching. However, the preponderance of calcium in the limed soil solution would compete with strontium for uptake by plant roots, and so reduce the amount of strontium entering the food chain.

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

⁶The curie was named after Marie and Pierre Curie, Polish scientists who discovered radium, an element that decays at the rate of 3.7×10^{10} Bq/g. The becquerel was named after Antoine Henry Becquerel, a French scientist who discovered radioactivity in uranium.

some interlayers of clay (see Box 8.3 and Section 14.16). Plant uptake of ^{137}Cs from vermiculitic 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.

IODINE 131. When it partially melted down, the nuclear reactor at Chernobyl emitted significant quantities of ^{131}I , which accumulates in the human thyroid. People in the area around the reactor have since suffered an increased incidence of thyroid cancer. Because of its short half-life (8.1 days), reactions in the soil and movement through the soil-plant-animal food chain are less significant than contamination of drinking water, inhalation of contaminated dust particles, and contamination of edible plant foliage.

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

Radioactive Wastes⁷

In addition to radionuclides added to soils because of weapons testing and nuclear power plant accidents, soils may interact with radioactive waste materials that have leaked from their holding tanks or have been intentionally buried for disposal. Plutonium, uranium, americium, neptunium, curium, and cesium are among the elements whose nuclides occur in radioactive wastes. These wastes are generated by research and medical facilities (where the radionuclides are used in cancer therapy and the like), and at power plants and weapons manufacturing sites.

Because of the secrecy and lack of regulation associated with the latter, they constitute some of the most polluted locations on Earth. For example, the U.S. Defense Department's now-abandoned plutonium-production complex at Hanford, Idaho, represents one of the biggest environmental cleanup challenges in the world. Among the hazards plaguing that site are hundreds of huge, in many cases leaking, underground tanks, in which high-level radioactive wastes have been stored for decades. Billions of cubic meters of soil and water have been contaminated with radioactive wastes at U.S. weapons manufacturing sites and at similar, equally polluted sites in the former Soviet Union.

PLUTONIUM TOXICITY. Plutonium-239, a major pollutant at these sites, is dangerous both because of its intense radioactivity and because of its high level of toxicity to humans. The ^{239}Pu itself is quite immobile in soils, having a K_d estimated at about 1000. Nor is it taken up readily by plants, so it does not accumulate along terrestrial food chains. It does, however, accumulate in algae. Furthermore, oily liquid wastes carrying ^{239}Pu seep into the groundwater and nearby rivers, and contaminated surface soil blows in the desert wind, spreading the radionuclides for many kilometers. Cleanup may be impossible at some of these former weapons sites; the agencies responsible are struggling merely to stabilize and contain the contamination. With a half-life of 24,400 years, ^{239}Pu contamination is a problem that will not go away.

LOW-LEVEL WASTES. Low-level radioactive wastes also present some environmental challenges. Even though the waste materials may be solidified before being placed in shallow land burial pits, some dissolution and subsequent movement in the soil are possible. Nuclides in wastes vary greatly in water solubility, uranium compounds being quite soluble, compounds of plutonium and americium being relatively insoluble, and cesium compounds being 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 interme-

⁷The July 1981 issue of *Soil Science* (vol. 132) provides extensive technical information on radioactive waste interaction with soils. For a description of the environmental challenges at the Hanford site, see Zorpette (1996).

TABLE 18.14 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.

Soil suborder	No. of samples	²³⁸ U breakdown products, Bq/kg			²³² Th breakdown products, Bq/kg		
		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).

diate 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 18.14 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.