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16 SOIL ENVIRONMENTAL CHEMISTRY

16.1. SOIL AND AGRICULTURE

Soil and agricultural practices are strongly tied with the environment. Some of these considerations are addressed later in this chapter along with a discussion of soil erosion and conservation. Cultivation of land and agricultural practices can influence both the atmosphere and the hydrosphere. Although this chapter deals primarily with soil, the topic of agriculture in general is introduced for perspective.

Agriculture

Agriculture, the production of food by growing crops and livestock, provides for the most basic of human needs. No other industry impacts as much as agriculture does on the environment. Agriculture is absolutely essential to the maintenance of the huge human populations now on earth. The displacement of native plants, destruction of wildlife habitat, erosion, pesticide pollution, and other environmental aspects of agriculture have enormous potential for environmental damage. Survival of humankind on earth demands that agricultural practice become as environmentally friendly as possible. On the other hand, growth of domestic crops removes (at least temporarily) greenhouse gas carbon dioxide from the atmosphere and provides potential sources of renewable resources of energy and fiber that can substitute for petroleum-derived fuels and materials.

Agriculture can be divided into the two main categories of **crop farming**, in which plant photosynthesis is used to produce grain, fruit, and fiber, and **livestock farming**, in which domesticated animals are grown for meat, milk, and other animal products. The major divisions of crop farming include production of cereals, such as wheat, corn or rice; animal fodder, such as hay; fruit; vegetables; and specialty crops, such as sugarcane, pineapple, sugar beets, tea, coffee, tobacco, cotton, and cacao. Livestock farming involves the raising of cattle, sheep, goats, swine, asses, mules, camels, buffalo, and various kinds of poultry. In addition to meat, livestock produce dairy products, eggs, wool, and hides. Freshwater fish and even crayfish are raised on “fish farms.” Beekeeping provides honey.

Agriculture is based on domestic plants engineered by early farmers from their wild plant ancestors. Without perhaps much of an awareness of what they were doing, early farmers selected plants with desired characteristics for the production of food. This selection of plants for domestic use brought about a very rapid evolutionary change, so profound that the products often barely resemble their wild ancestors. Plant breeding based on scientific principles of heredity is a very recent development dating from early in the present century. One of the major objectives of plant breeding has been to increase yield. An example of success in this area is the selection of dwarf varieties of rice, which yield much better and mature faster than the varieties that they replaced. Such rice was largely responsible for the “green revolution” dating from about the 1950s. Yields of crops can also be increased by selecting for resistance to insects, drought, and cold. In some cases the goal is to increase nutritional value, such as in the development of corn high in lysine, an amino acid essential for human nutrition, such that corn becomes a more complete food.

The development of hybrids has vastly increased yields and other desired characteristics of a number of important crops. Basically, **hybrids** are the offspring of crosses between two different **true-breeding** strains. Often quite different from either parent strain, hybrids tend to exhibit “hybrid vigor” and to have significantly higher yields. The most success with hybrid crops has been obtained with corn (maize). Corn is one of the easiest plants to hybridize because of the physical separation of the male flowers, which grow as tassels on top of the corn plant, from female flowers, which are attached to incipient ears on the side of the plant. Despite past successes by more conventional means and some early disappointments with “genetic engineering,” application of recombinant DNA technology (Section 16.10) will probably eventually overshadow all the advances ever made in plant breeding.

In addition to plant strains and varieties, numerous other factors are involved in crop production. Weather is an obvious factor, and shortages of water, chronic in many areas of the world, are mitigated by irrigation. Here, automated techniques and computer control are beginning to play an important, more environmentally friendly role by minimizing the quantities of water required. The application of chemical fertilizer has vastly increased crop yields. The judicious application of pesticides, especially herbicides, but including insecticides and fungicides as well, has increased crop yields and reduced losses greatly. Use of herbicides has had an environmental benefit in reducing the degree of mechanical cultivation of soil required. Indeed, “no-till” and “low-till” agriculture are now widely practiced on a large scale.

The crops that provide for most of human caloric food intake, as well as much food for animals, are **cereals**, which are harvested for their starch-rich seeds. In addition to corn, mentioned above, wheat used for making bread and related foods, and rice consumed directly, other major cereal crops include barley, oats, rye, sorghum, and millet. As applied to agriculture and food, **vegetables** are plants or their products that can be eaten directly by humans. A large variety of different parts of plants are consumed as vegetables. These include leaves (lettuce), stems (asparagus), roots (carrots), tubers (potato), bulb (onion), immature flower (broccoli), immature fruit (cucumber), mature fruit (tomato), and seeds (pea). Fruits, which are bodies of plant tissue containing the seed, may be viewed as a subclassification of vegetables. Common fruits include apple, peach, apricot, citrus (orange, lemon, lime, grapefruit), banana, cherry, and various kinds of berries.

The rearing of domestic animals may have significant environmental effects. The Netherlands' pork industry has been so productive that hog manure and its by-products have caused serious problems. Overflow from waste lagoons associated with hog production caused very damaging water pollution in Eastern North Carolina following the record rainfall from Hurricane Floyd in September 1999. Goats and sheep have destroyed pastureland in the Near East, Northern Africa, Portugal, and Spain. Of particular concern are the environmental effects of raising cattle. Significant amounts of forest land have been converted to marginal pasture land to raise beef. Production of one pound of beef requires about four times as much water and four times as much feed as does production of one pound of chicken. An interesting aspect of the problem is emission of greenhouse-gas methane by anaerobic bacteria in the digestive systems of cattle and other ruminant animals; cattle rank right behind wetlands and rice paddies as producers of atmospheric methane. However, because of the action of specialized bacteria in their stomachs, cattle and other ruminant animals are capable of converting otherwise unusable cellulose to food.

Pesticides and Agriculture

Pesticides, particularly insecticides and herbicides, are an integral part of modern agricultural production. In the United States, agricultural pesticides are regulated under the Federal Insecticide, Fungicide, and Rodenticide (FIFRA) act, first passed in 1947, revised in a major way in 1972, and subjected to several amendments since then.¹ Starting in 1989 under FIFRA, pre-1972 pesticides were required to undergo reregistration. Since this process began, manufacturers have withdrawn from the market several thousand products because of the expense of the safety review process. The problem has been especially severe for **minor-use pesticides** for which the market is not very large. In contrast to pesticides used on approximately 220 million acres of major crops in the U.S.—corn, soybeans, wheat, and cotton—minor-use pesticides are applied on only about 8 million acres of orchards, trees, ornamental plants, turf grass, fruits, nuts, and vegetables. Despite their limited use, about 40% of the monetary value of agricultural pesticides resides with minor-use pesticides. Complicating the reregistration process for many years was the well-intentioned but unrealistic 1958 Delaney Amendment to the Food, Drug, and Cosmetic Act which prohibited in food any chemical that had been shown to cause cancer in animals and humans. Many chemicals that are almost certainly safe as trace-level contaminants in food will, indeed, cause cancer when fed in massive doses to experimental animals. This effect has been attributed in part to the fact that huge doses of some chemicals destroy tissue, which the organism attempts to replace by growing new cells. Cells that are reproducing rapidly in an attempt to make up for tissue loss are more likely to become cancerous.

An interesting development regarding the use of herbicides in the late 1990s was the production of transgenic crops resistant to specific herbicides. The Monsanto company pioneered this approach with the development of "Roundup Ready" crops that resist the herbicidal effects of Monsanto's flagship Roundup® herbicide, a glyphosate compound with an annual market exceeding \$2 billion. The seedlings of crops resistant to the herbicide are not harmed by exposure to it, whereas competing

weeds are killed. In an interesting marketing strategy, Monsanto has licensed manufacturing and distribution rights for Roundup to other companies for application onto “Roundup Ready” crops sold by Monsanto.²

Soil

Soil, consisting of a finely divided layer of weathered minerals and organic matter upon which plants grow, is the most fundamental requirement for agriculture. To humans and most terrestrial organisms, soil is the most important part of the geosphere. Though only a tissue-thin layer compared to the earth's total diameter, soil is the medium that produces most of the food required by most living things. Good soil—and a climate conducive to its productivity—is the most valuable asset a nation can have.

In addition to being the site of most food production, soil is the receptor of large quantities of pollutants, such as particulate matter from power plant smokestacks. Fertilizers, pesticides, and some other materials applied to soil often contribute to water and air pollution. Therefore, soil is a key component of environmental chemical cycles.

Soils are formed by the weathering of parent rocks as the result of interactive geological, hydrological, and biological processes (see Chapter 15). Soils are porous and are vertically stratified into horizons as the result of downward-percolating water and biological processes, including the production and decay of biomass. Soils are open systems that undergo continual exchange of matter and energy with the atmosphere, hydrosphere, and biosphere.

16.2. NATURE AND COMPOSITION OF SOIL

Soil is a variable mixture of minerals, organic matter, and water capable of supporting plant life on the earth's surface.³ It is the final product of the weathering action of physical, chemical, and biological processes on rocks, which largely produces clay minerals. The organic portion of soil consists of plant biomass in various stages of decay. High populations of bacteria, fungi, and animals such as earthworms may be found in soil. Soil contains air spaces and generally has a loose texture (Figure 16.1).

The solid fraction of typical productive soil is approximately 5% organic matter and 95% inorganic matter. Some soils, such as peat soils, may contain as much as 95% organic material. Other soils contain as little as 1% organic matter.

Typical soils exhibit distinctive layers with increasing depth (Figure 16.2). These layers are called **horizons**. Horizons form as the result of complex interactions among processes that occur during weathering. Rainwater percolating through soil carries dissolved and colloidal solids to lower horizons where they are deposited. Biological processes, such as bacterial decay of residual plant biomass, produces slightly acidic CO₂, organic acids, and complexing compounds that are carried by rainwater to lower horizons where they interact with clays and other minerals, altering the properties of the minerals. The top layer of soil, typically several inches in thickness, is known as the A horizon, or **topsoil**. This is the layer of maximum biological activity in the soil and contains most of the soil organic matter. Metal ions

and clay particles in the A horizon are subject to considerable leaching. The next layer is the B horizon, or **subsoil**. It receives material such as organic matter, salts, and clay particles leached from the topsoil. The C horizon is composed of weathered parent rocks from which the soil originated.

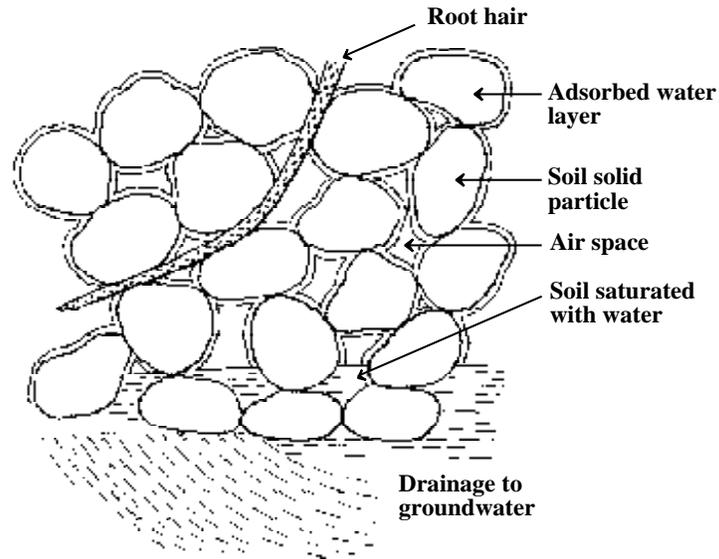


Figure 16.1. Fine structure of soil, showing solid, water, and air phases.

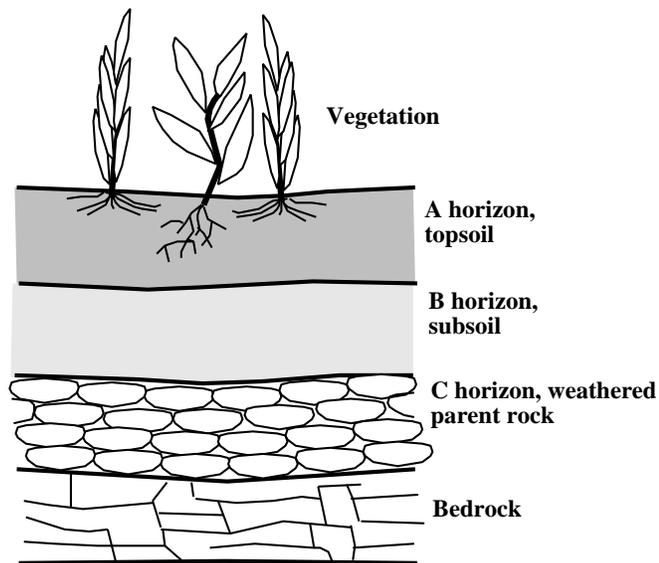


Figure 16.2. Soil profile showing soil horizons.

Soils exhibit a large variety of characteristics that are used for their classification for various purposes, including crop production, road construction, and waste disposal. Soil profiles are discussed above. The parent rocks from which soils are

formed obviously play a strong role in determining the composition of soils. Other soil characteristics include strength, workability, soil particle size, permeability, and degree of maturity. One of the more important classes of productive soils is the **podzol** type of soil formed under relatively high rainfall conditions in temperate zones of the world. These generally rich soils tend to be acidic (pH 3.5–4.5) such that alkali and alkaline earth metals and, to a lesser extent aluminum and iron, are leached from their A horizons, leaving kaolinite as the predominant clay mineral. At somewhat higher pH in the B horizons, hydrated iron oxides and clays are redeposited.

From the engineering standpoint, especially, the mechanical properties of soil are emphasized. These properties, which may have important environmental implications in areas such as waste disposal, are largely determined by particle size. According to the United Classification System (UCS), the four major categories of soil particle sizes are the following: Gravels (2–60 mm) > sands (0.06–2 mm) > silts (0.06–0.006 mm) > clays (less than 0.002 mm). In the UCS classification scheme clays represent a size fraction rather than a specific class of mineral matter.

Water and Air in Soil

Large quantities of water are required for the production of most plant materials. For example, several hundred kg of water are required to produce one kg of dry hay. Water is part of the three-phase, solid-liquid-gas system making up soil. It is the basic transport medium for carrying essential plant nutrients from solid soil particles into plant roots and to the farthest reaches of the plant's leaf structure (Figure 16.3). The water enters the atmosphere from the plant's leaves, a process called **transpiration**.

Normally, because of the small size of soil particles and the presence of small capillaries and pores in the soil, the water phase is not totally independent of soil solid matter. The availability of water to plants is governed by gradients arising from capillary and gravitational forces. The availability of nutrient solutes in water depends upon concentration gradients and electrical potential gradients. Water present in larger spaces in soil is relatively more available to plants and readily drains away. Water held in smaller pores or between the unit layers of clay particles is held much more strongly. Soils high in organic matter may hold appreciably more water than other soils, but it is relatively less available to plants because of physical and chemical sorption of the water by the organic matter.

There is a very strong interaction between clays and water in soil. Water is absorbed on the surfaces of clay particles. Because of the high surface/volume ratio of colloidal clay particles, a great deal of water may be bound in this manner. Water is also held between the unit layers of the expanding clays, such as the montmorillonite clays. As soil becomes waterlogged (water-saturated) it undergoes drastic changes in physical, chemical, and biological properties. Oxygen in such soil is rapidly used up by the respiration of microorganisms that degrade soil organic matter. In such soils, the bonds holding soil colloidal particles together are broken, which causes disruption of soil structure. Thus, the excess water in such soils is detrimental to plant growth, and the soil does not contain the air required by most plant roots. Most useful crops, with the notable exception of rice, cannot grow on waterlogged soils.

One of the most marked chemical effects of waterlogging is a reduction of pE by the action of organic reducing agents acting through bacterial catalysts. Thus, the redox condition of the soil becomes much more reducing, and the soil pE may drop

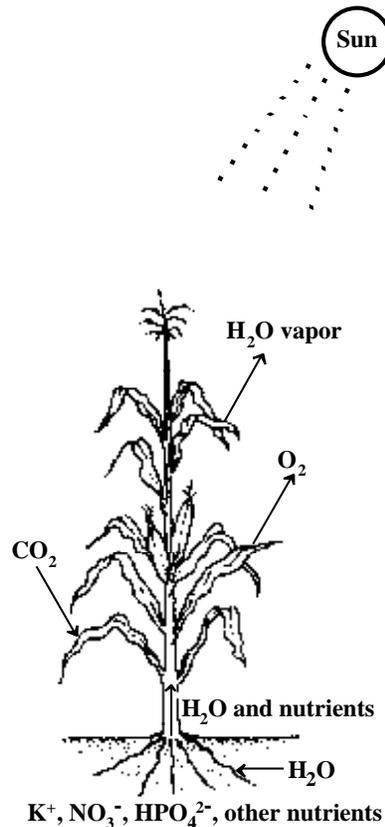
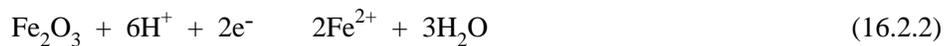
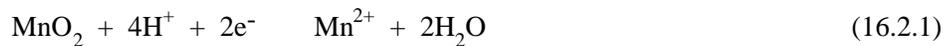


Figure 16.3. Plants transport water from the soil to the atmosphere by transpiration. Nutrients are also carried from the soil to the plant extremities by this process. Plants remove CO₂ from the atmosphere and add O₂ by photosynthesis. The reverse occurs during plant respiration.

from that of water in equilibrium with air (+13.6 at pH 7) to 1 or less. One of the more significant results of this change is the mobilization of iron and manganese as soluble iron(II) and manganese(II) through reduction of their insoluble higher oxides:



Although soluble manganese generally is found in soil as Mn²⁺ ion, soluble iron(II) frequently occurs as negatively charged iron-organic chelates. Strong chelation of iron(II) by soil fulvic acids (Chapter 3) apparently enables reduction of iron(III) oxides at more positive pE values than would otherwise be possible. This causes an upward shift in the Fe(II)-Fe(OH)₃ boundary shown in [Figure 4.4](#).

Some soluble metal ions such as Fe^{2+} and Mn^{2+} are toxic to plants at high levels. Their oxidation to insoluble oxides may cause formation of deposits of Fe_2O_3 and MnO_2 , which clog tile drains in fields.

Roughly 35% of the volume of typical soil is composed of air-filled pores. Whereas the normal dry atmosphere at sea level contains 21% O_2 and 0.03% CO_2 by volume, these percentages may be quite different in soil air because of the decay of organic matter:



This process consumes oxygen and produces CO_2 . As a result, the oxygen content of air in soil may be as low as 15%, and the carbon dioxide content may be several percent. Thus, the decay of organic matter in soil increases the equilibrium level of dissolved CO_2 in groundwater. This lowers the pH and contributes to weathering of carbonate minerals, particularly calcium carbonate (see Reaction 3.7.6). As discussed in Section 16.3, CO_2 also shifts the equilibrium of the process by which roots absorb metal ions from soil.

The Inorganic Components of Soil

The weathering of parent rocks and minerals to form the inorganic soil components results ultimately in the formation of inorganic colloids. These colloids are repositories of water and plant nutrients, which may be made available to plants as needed. Inorganic soil colloids often absorb toxic substances in soil, thus playing a role in detoxification of substances that otherwise would harm plants. The abundance and nature of inorganic colloidal material in soil are obviously important factors in determining soil productivity.

The uptake of plant nutrients by roots often involves complex interactions with the water and inorganic phases. For example, a nutrient held by inorganic colloidal material has to traverse the mineral/water interface and then the water/root interface. This process is often strongly influenced by the ionic structure of soil inorganic matter.

As noted in Section 15.2, the most common elements in the earth's crust are oxygen, silicon, aluminum, iron, calcium, sodium, potassium, and magnesium. Therefore, minerals composed of these elements — particularly silicon and oxygen — constitute most of the mineral fraction of the soil. Common soil mineral constituents are finely divided quartz (SiO_2), orthoclase (KAlSi_3O_8), albite ($\text{NaAlSi}_3\text{O}_8$), epidote ($4\text{CaO} \cdot 3(\text{AlFe})_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot \text{H}_2\text{O}$), goethite ($\text{FeO}(\text{OH})$), magnetite (Fe_3O_4), calcium and magnesium carbonates (CaCO_3 , $\text{CaCO}_3 \cdot \text{MgCO}_3$), and oxides of manganese and titanium.

Organic Matter in Soil

Though typically comprising less than 5% of a productive soil, organic matter largely determines soil productivity. It serves as a source of food for microorganisms, undergoes chemical reactions such as ion exchange, and influences the physical properties of soil. Some organic compounds even contribute to the weathering of mineral matter, the process by which soil is formed. For example, $\text{C}_2\text{O}_4^{2-}$, oxalate ion, produced as a soil fungi metabolite, occurs in soil as the calcium

salts whewellite and weddellite. Oxalate in soil water dissolves minerals, thus speeding the weathering process and increasing the availability of nutrient ion species. This weathering process involves oxalate complexation of iron or aluminum in minerals, represented by the reaction



in which M is Al or Fe. Some soil fungi produce citric acid and other chelating organic acids which react with silicate minerals and release potassium and other nutrient metal ions held by these minerals.

The strong chelating agent 2-ketogluconic acid is produced by some soil bacteria. By solubilizing metal ions, it may contribute to the weathering of minerals. It may also be involved in the release of phosphate from insoluble phosphate compounds.

Biologically active components of the organic soil fraction include polysaccharides, amino sugars, nucleotides, and organic sulfur and phosphorus compounds. Humus, a water-insoluble material that biodegrades very slowly, makes up the bulk of soil organic matter. The organic compounds in soil are summarized in [Table 16.1](#).

Table 16.1. Major Classes of Organic Compounds in Soil

Compound type	Composition	Significance
Humus	Degradation-resistant residue from plant decay, largely C, H, and O	Most abundant organic component, improves soil physical properties, exchanges nutrients, reservoir of fixed N
Fats, resins, and waxes	Lipids extractable by organic solvents	Generally, only several percent of soil organic matter, may adversely affect soil physical properties by repelling water, perhaps phytotoxic
Saccharides	Cellulose, starches, hemicellulose, gums	Major food source for soil microorganisms, help stabilize soil aggregates
N-containing organics	Nitrogen bound to humus, amino acids, amino sugars, other compounds	Provide nitrogen for soil fertility
Phosphorus compounds	Phosphate esters, inositol phosphates (phytic acid), phospholipids	Sources of plant phosphate

The accumulation of organic matter in soil is strongly influenced by temperature and by the availability of oxygen. Since the rate of biodegradation decreases with decreasing temperature, organic matter does not degrade rapidly in colder climates and tends to build up in soil. In water and in waterlogged soils, decaying vegetation

does not have easy access to oxygen, and organic matter accumulates. The organic content may reach 90% in areas where plants grow and decay in soil saturated with water.

The presence of naturally occurring polynuclear aromatic (PAH) compounds is an interesting feature of soil organic matter. These compounds, some of which are carcinogenic, are discussed as air pollutants in Sections 10.8 and 12.4. PAH compounds found in soil include fluoranthene, pyrene, and chrysene. PAH compounds in soil result in part from combustion from both natural sources (grass fires) or pollutant sources. Terpenes also occur in soil organic matter. Extraction of soil with ether and alcohol yields the pigments β -carotene, chlorophyll, and xanthophyll.

Soil Humus

Of the organic components listed in Table 16.1, **soil humus** is by far the most significant.⁴ Humus, composed of a base-soluble fraction called humic and fulvic acids (described in Section 3.17), and an insoluble fraction called humin, is the residue left when bacteria and fungi biodegrade plant material. The bulk of plant biomass consists of relatively degradable cellulose and degradation-resistant lignin, which is a polymeric substance with a higher carbon content than cellulose. Among lignin's prominent chemical components are aromatic rings connected by alkyl chains, methoxyl groups, and hydroxyl groups. These structural artifacts occur in soil humus and give it many of its characteristic properties.

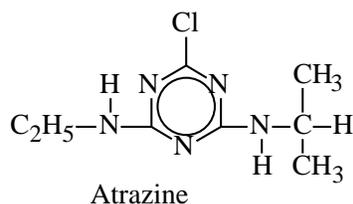
The process by which humus is formed is called **humification**. Soil humus is similar to its lignin precursors, but has more carboxylic acid groups. Part of each molecule of humic substance is nonpolar and hydrophobic, and part is polar and hydrophilic. Such molecules are called **amphiphiles**, and they form micelles (see Section 5.4 and Figure 5.4) in which the nonpolar parts compose the inside of small colloidal particles and the polar functional groups are on the outside. Amphiphilic humic substances probably also form bilayer surface coatings on mineral grains in soil.

An increase in nitrogen/carbon ratio is a significant feature of the transformation of plant biomass to humus through the humification process. This ratio starts at approximately 1/100 in fresh plant biomass. During humification, microorganisms convert organic carbon to CO₂ to obtain energy. Simultaneously, the bacterial action incorporates bound nitrogen with the compounds produced by the decay processes. The result is a nitrogen/carbon ratio of about 1/10 upon completion of humification. As a general rule, therefore, humus is relatively rich in organically bound nitrogen.

Humic substances influence soil properties to a degree out of proportion to their small percentage in soil. They strongly bind metals, and serve to hold micronutrient metal ions in soil. Because of their acid-base character, humic substances serve as buffers in soil. The water-holding capacity of soil is significantly increased by humic substances. These materials also stabilize aggregates of soil particles, and increase the sorption of organic compounds by soil.

Humic materials in soil strongly sorb many solutes in soil water and have a particular affinity for heavy polyvalent cations. Soil humic substances may contain levels of uranium more than 10⁴ times that of the water with which they are in equilibrium. Thus, water becomes depleted of its cations (or purified) in passing through humic-rich soils. Humic substances in soils also have a strong affinity for organic

compounds with low water-solubility such as DDT or Atrazine, a herbicide widely used to kill weeds in corn fields.



In some cases, there is a strong interaction between the organic and inorganic portions of soil. This is especially true of the strong complexes formed between clays and humic (fulvic) acid compounds. In many soils, 50-100% of soil carbon is complexed with clay. These complexes play a role in determining the physical properties of soil, soil fertility, and stabilization of soil organic matter. One of the mechanisms for the chemical binding between clay colloidal particles and humic organic particles is probably of the flocculation type (see Chapter 5) in which anionic organic molecules with carboxylic acid functional groups serve as bridges in combination with cations to bind clay colloidal particles together as a floc. Support is given to this hypothesis by the known ability of NH_4^+ , Al^{3+} , Ca^{2+} , and Fe^{3+} cations to stimulate clay-organic complex formation. The synthesis, chemical reactions, and biodegradation of humic materials are affected by interaction with clays. The lower-molecular-weight fulvic acids may be bound to clay, occupying spaces in layers in the clay.

The Soil Solution

The **soil solution** is the aqueous portion of soil that contains dissolved matter from soil chemical and biochemical processes in soil and from exchange with the hydrosphere and biosphere.⁵ This medium transports chemical species to and from soil particles and provides intimate contact between the solutes and the soil particles. In addition to providing water for plant growth, it is an essential pathway for the exchange of plant nutrients between roots and solid soil.

Obtaining a sample of soil solution is often very difficult because the most significant part of it is bound in capillaries and as surface films. The most straightforward means is collection of drainage water. Soil solution can be isolated from moist solid soil by displacement with a water-immiscible fluid, mechanical separation by centrifugation, or pressure or vacuum treatment.

Dissolved mineral matter in soil is largely present as ions. Prominent among the cations are H^+ , Ca^{2+} , Mg^{2+} , K^+ , Na^+ , and usually very low levels of Fe^{2+} , Mn^{2+} , and Al^{3+} . The last three cations may be present in partially hydrolyzed form, such as FeOH^+ , or complexed by organic humic substance ligands. Anions that may be present are HCO_3^- , CO_3^{2-} , HSO_4^- , SO_4^{2-} , Cl^- , and F^- . In addition to being bound to H^+ in species such as bicarbonate, anions may be complexed with metal ions, such as in AlF^{2+} . Multivalent cations and anions form ion pairs with each other in soil solutions. Examples of these are CaSO_4 and FeSO_4 .

16.3. ACID-BASE AND ION EXCHANGE REACTIONS IN SOILS

One of the more important chemical functions of soils is the exchange of cations. As discussed in Chapter 5, the ability of a sediment or soil to exchange cations is expressed as the cation-exchange capacity (CEC), the number of milliequivalents (meq) of monovalent cations that can be exchanged per 100 g of soil (on a dry-weight basis). The CEC should be looked upon as a conditional constant since it may vary with soil conditions such as pE and pH. Both the mineral and organic portions of soils exchange cations. Clay minerals exchange cations because of the presence of negatively charged sites on the mineral, resulting from the substitution of an atom of lower oxidation number for one of higher number, for example, magnesium for aluminum. Organic materials exchange cations because of the presence of the carboxylate group and other basic functional groups. Humus typically has a very high cation-exchange capacity. The cation-exchange capacity of peat may range from 300-400 meq/100 g. Values of cation-exchange capacity for soils with more typical levels of organic matter are around 10-30 meq/100 g.

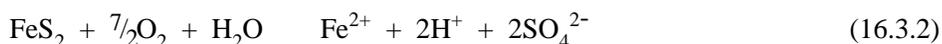
Cation exchange in soil is the mechanism by which potassium, calcium, magnesium, and essential trace-level metals are made available to plants. When nutrient metal ions are taken up by plant roots, hydrogen ion is exchanged for the metal ions. This process, plus the leaching of calcium, magnesium, and other metal ions from the soil by water containing carbonic acid, tends to make the soil acidic:



Soil acts as a buffer and resists changes in pH. The buffering capacity depends upon the type of soil.

Production of Mineral Acid in Soil

The oxidation of pyrite in soil causes formation of acid-sulfate soils sometimes called "cat clays":



Cat clay soils may have pH values as low as 3.0. These soils, which are commonly found in Delaware, Florida, New Jersey, and North Carolina, are formed when neutral or basic marine sediments containing FeS₂ become acidic upon oxidation of pyrite when exposed to air. For example, soil reclaimed from marshlands and used for citrus groves has developed high acidity detrimental to plant growth. In addition, H₂S released by reaction of FeS₂ with acid is very toxic to citrus roots.

Soils are tested for potential acid-sulfate formation using a peroxide test. This test consists of oxidizing FeS₂ in the soil with 30% H₂O₂,



then testing for acidity and sulfate. Appreciable levels of sulfate and a pH below 3.0 indicate potential to form acid-sulfate soils. If the pH is above 3.0, either little FeS₂ is present or sufficient CaCO₃ is in the soil to neutralize the H₂SO₄ and acidic Fe³⁺.

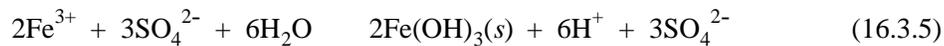
Pyrite-containing mine spoils (residue left over from mining) also form soils similar to acid-sulfate soils of marine origin. In addition to high acidity and toxic H_2S , a major chemical species limiting plant growth on such soils is Al(III) . Aluminum ion liberated in acidic soils is very toxic to plants.

Adjustment of Soil Acidity

Most common plants grow best in soil with a pH near neutrality. If the soil becomes too acidic for optimum plant growth, it may be restored to productivity by liming, ordinarily through the addition of calcium carbonate:



In areas of low rainfall, soils may become too basic (alkaline) due to the presence of basic salts such as Na_2CO_3 . Alkaline soils may be treated with aluminum or iron sulfate, which release acid on hydrolysis:



Sulfur added to soils is oxidized by bacterially mediated reactions to sulfuric acid:



and sulfur is used, therefore, to acidify alkaline soils. The huge quantities of sulfur now being removed from fossil fuels to prevent air pollution by sulfur dioxide may make the treatment of alkaline soils by sulfur much more attractive economically.

Ion Exchange Equilibria in Soil

Competition of different cations for cation exchange sites on soil cation exchangers may be described semiquantitatively by exchange constants. For example, soil reclaimed from an area flooded with seawater will have most of its cation exchange sites occupied by Na^+ , and restoration of fertility requires binding of nutrient cations such as K^+ :



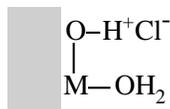
The exchange constant is K_c ,

$$K_c = \frac{N_K[\text{Na}^+]}{N_{\text{Na}}[\text{K}^+]} \quad (16.3.8)$$

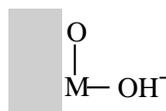
which expresses the relative tendency of soil to retain K^+ and Na^+ . In this equation, N_K and N_{Na} are the equivalent ionic fractions of potassium and sodium, respectively, bound to soil, and $[\text{Na}^+]$ and $[\text{K}^+]$ are the concentrations of these ions in the surrounding soil water. For example, a soil with all cation exchange sites

occupied by Na^+ would have a value of 1.00 for N_{Na} ; with one-half of the cation exchange sites occupied by Na^+ , N_{Na} is 0.5; etc. The exchange of anions by soil is not nearly so clearly defined as is the exchange of cations. In many cases, the exchange of anions does not involve a simple ion-exchange process. This is true of the strong retention of orthophosphate species by soil. At the other end of the scale, nitrate ion is very weakly retained by the soil.

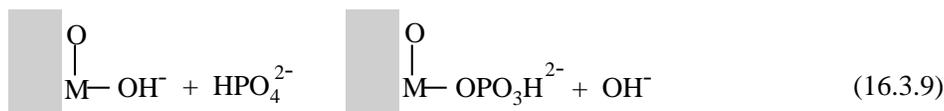
Anion exchange may be visualized as occurring at the surfaces of oxides in the mineral portion of soil. A mechanism for the acquisition of surface charge by metal oxides is shown in Chapter 5, Figure 5.5, using MnO_2 as an example. At low pH, a metal oxide surface may have a net positive charge enabling it to hold anions, such as chloride, by electrostatic attraction as shown below where M represents a metal:



At higher pH values, the metal oxide surface has a net negative charge due to the formation of OH^- ion on the surface caused by loss of H^+ from the water molecules bound to the surface:



In such cases, it is possible for anions such as HPO_4^{2-} to displace hydroxide ion and bond directly to the oxide surface:



16.4. MACRONUTRIENTS IN SOIL

One of the most important functions of soil in supporting plant growth is to provide essential plant nutrients—macronutrients and micronutrients. Macronutrients are those elements that occur in substantial levels in plant materials or in fluids in the plant. Micronutrients (Section 16.6) are elements that are essential only at very low levels and generally are required for the functioning of essential enzymes.

The elements generally recognized as essential macronutrients for plants are carbon, hydrogen, oxygen, nitrogen, phosphorus, potassium, calcium, magnesium, and sulfur. Carbon, hydrogen, and oxygen are obtained from the atmosphere. The other essential macronutrients must be obtained from soil. Of these, nitrogen, phosphorus, and potassium are the most likely to be lacking and are commonly added to soil as fertilizers. Because of their importance, these elements are discussed separately in Section 16.5.

Calcium-deficient soils are relatively uncommon. Application of lime, a process used to treat acid soils (see Section 16.3), provides a more than adequate calcium supply for plants. However, calcium uptake by plants and leaching by carbonic acid

(Reaction 16.3.1) may produce a calcium deficiency in soil. Acid soils may still contain an appreciable level of calcium which, because of competition by hydrogen ion, is not available to plants. Treatment of acid soil to restore the pH to near-neutrality generally remedies the calcium deficiency. In alkaline soils, the presence of high levels of sodium, magnesium, and potassium sometimes produces calcium deficiency because these ions compete with calcium for availability to plants.

Most of the 2.1% of magnesium in earth's crust is rather strongly bound in minerals. Exchangeable magnesium held by ion-exchanging organic matter or clays is considered available to plants. The availability of magnesium to plants depends upon the calcium/magnesium ratio. If this ratio is too high, magnesium may not be available to plants and magnesium deficiency results. Similarly, excessive levels of potassium or sodium may cause magnesium deficiency.

Sulfur is assimilated by plants as the sulfate ion, SO_4^{2-} . In addition, in areas where the atmosphere is contaminated with SO_2 , sulfur may be absorbed as sulfur dioxide by plant leaves. Atmospheric sulfur dioxide levels have been high enough to kill vegetation in some areas (see Chapter 11). However, some experiments designed to show SO_2 toxicity to plants have resulted in increased plant growth where there was an unexpected sulfur deficiency in the soil used for the experiment.

Soils deficient in sulfur do not support plant growth well, largely because sulfur is a component of some essential amino acids and of thiamin and biotin. Sulfate ion is generally present in the soil as immobilized insoluble sulfate minerals, or as soluble salts which are readily leached from the soil and lost as soil water runoff. Unlike the case of nutrient cations such as K^+ , little sulfate is adsorbed to the soil (that is, bound by ion exchange binding) where it is resistant to leaching while still available for assimilation by plant roots.

Soil sulfur deficiencies have been found in a number of regions of the world. Whereas most fertilizers used to contain sulfur, its use in commercial fertilizers has declined. With continued use of sulfur-deficient fertilizers, it is possible that sulfur will become a limiting nutrient in more cases.

As noted in Section 16.3, the reaction of FeS_2 with acid in acid-sulfate soils may release H_2S , which is very toxic to plants and which also kills many beneficial microorganisms. Toxic hydrogen sulfide can also be produced by reduction of sulfate ion through microorganism-mediated reactions with organic matter. Production of hydrogen sulfide in flooded soils may be inhibited by treatment with oxidizing compounds, one of the most effective of which is KNO_3 .

16.5. NITROGEN, PHOSPHORUS, AND POTASSIUM IN SOIL

Nitrogen, phosphorus, and potassium are plant nutrients that are obtained from soil. They are so important for crop productivity that they are commonly added to soil as fertilizers. The environmental chemistry of these elements is discussed here and their production as fertilizers in Section 16.7.

Nitrogen

Figure 16.4 summarizes the primary sinks and pathways of nitrogen in soil. In most soils, over 90% of the nitrogen content is organic. This organic nitrogen is

primarily the product of the biodegradation of dead plants and animals. It is eventually hydrolyzed to NH_4^+ , which can be oxidized to NO_3^- by the action of bacteria in the soil.

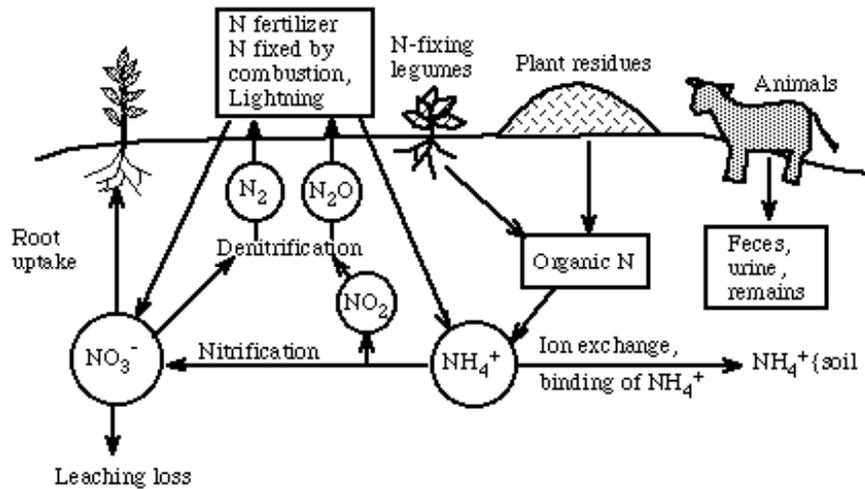


Figure 16.4. Nitrogen sinks and pathways in soil.

Nitrogen bound to soil humus is especially important in maintaining soil fertility. Unlike potassium or phosphate, nitrogen is not a significant product of mineral weathering. Nitrogen-fixing organisms ordinarily cannot supply sufficient nitrogen to meet peak demand. Inorganic nitrogen from fertilizers and rainwater is often largely lost by leaching. Soil humus, however, serves as a reservoir of nitrogen required by plants. It has the additional advantage that its rate of decay, hence its rate of nitrogen release to plants, roughly parallels plant growth—rapid during the warm growing season, slow during the winter months.

Nitrogen is an essential component of proteins and other constituents of living matter. Plants and cereals grown on nitrogen-rich soils not only provide higher yields, but are often substantially richer in protein and, therefore, more nutritious. Nitrogen is most generally available to plants as nitrate ion, NO_3^- . Some plants such as rice may utilize ammonium nitrogen; however, other plants are poisoned by this form of nitrogen. When nitrogen is applied to soils in the ammonium form, nitrifying bacteria perform an essential function in converting it to available nitrate ion.

Plants may absorb excessive amounts of nitrate nitrogen from soil. This phenomenon occurs particularly in heavily fertilized soils under drought conditions. Forage crops containing excessive amounts of nitrate can poison ruminant animals such as cattle or sheep. Plants having excessive levels of nitrate can endanger people when used for ensilage, an animal food consisting of finely chopped plant material such as partially matured whole corn plants, fermented in a structure called a silo. Under the reducing conditions of fermentation, nitrate in ensilage may be reduced to toxic NO_2 gas, which can accumulate to high levels in enclosed silos. There have been many cases reported of persons being killed by accumulated NO_2 in silos.

Nitrogen fixation is the process by which atmospheric N_2 is converted to nitrogen compounds available to plants. Human activities are resulting in the fixation

of a great deal more nitrogen than would otherwise be the case. Artificial sources now account for 30-40% of all nitrogen fixed. These include chemical fertilizer manufacture, nitrogen fixed during fuel combustion, combustion of nitrogen-containing fuels, and the increased cultivation of nitrogen-fixing legumes (see the following paragraph). A major concern with this increased fixation of nitrogen is the possible effect upon the atmospheric ozone layer by N_2O released during denitrification of fixed nitrogen.

Before the widespread introduction of nitrogen fertilizers, soil nitrogen was provided primarily by legumes. These are plants such as soybeans, alfalfa, and clover, which contain on their root structures bacteria capable of fixing atmospheric nitrogen. Leguminous plants have a symbiotic (mutually advantageous) relationship with the bacteria that provide their nitrogen. Legumes may add significant quantities of nitrogen to soil, up to 10 pounds per acre per year, which is comparable to amounts commonly added as synthetic fertilizers. Soil fertility with respect to nitrogen may be maintained by rotating plantings of nitrogen-consuming plants with plantings of legumes, a fact recognized by agriculturists as far back as the Roman era.

The nitrogen-fixing bacteria in legumes exist in special structures on the roots called root nodules (see Fig. 16.5). The rod-shaped bacteria that fix nitrogen are members of a special genus, *Rhizobium*. These bacteria may exist independently, but cannot fix nitrogen except in symbiotic combination with plants. Although all species of *Rhizobium* appear to be very similar, they exhibit a great deal of specificity in their choice of host plants. Curiously, legume root nodules also contain a form of hemoglobin, which must somehow be involved in the nitrogen-fixation process.

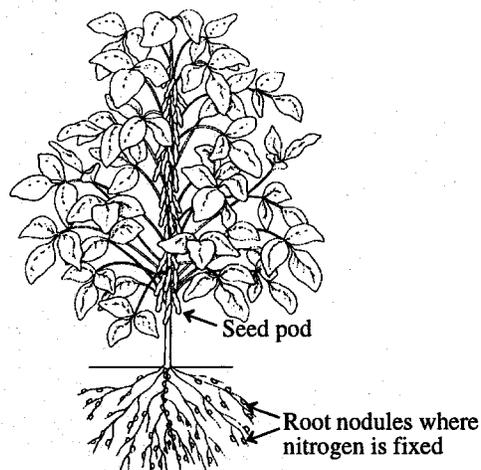


Figure 16.5. A soybean plant, showing root nodules where nitrogen is fixed.

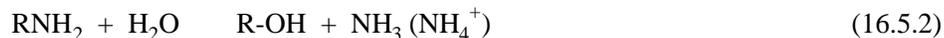
Nitrate pollution of some surface waters and groundwater has become a major problem in some agricultural areas (see Chapter 7). Although fertilizers have been implicated in such pollution, there is evidence that feedlots are a major source of nitrate pollution. The growth of livestock populations and the concentration of livestock in feedlots have aggravated the problem. Such concentrations of cattle, coupled with the fact that a steer produces approximately 18 times as much waste

material as a human, have resulted in high levels of water pollution in rural areas with small human populations. Streams and reservoirs in such areas frequently are just as polluted as those in densely populated and highly industrialized areas.

Nitrate in farm wells is a common and especially damaging manifestation of nitrogen pollution from feedlots because of the susceptibility of ruminant animals to nitrate poisoning. The stomach contents of ruminant animals such as cattle and sheep constitute a reducing medium (low pE) and contain bacteria capable of reducing nitrate ion to toxic nitrite ion:



The origin of most nitrate produced from feedlot wastes is amino nitrogen present in nitrogen-containing waste products. Approximately one-half of the nitrogen excreted by cattle is contained in the urine. Part of this nitrogen is proteinaceous and the other part is in the form of urea, NH_2CONH_2 . As a first step in the degradation process, the amino nitrogen is probably hydrolyzed to ammonia, or ammonium ion:



This product is then oxidized through microorganism-catalyzed reactions to nitrate ion:

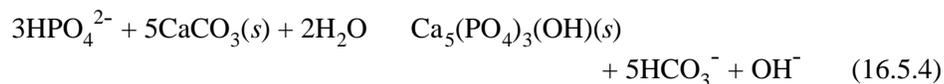


Under some conditions, an appreciable amount of the nitrogen originating from the degradation of feedlot wastes is present as ammonium ion. Ammonium ion is rather strongly bound to soil (recall that soil is a generally good cation exchanger), and a small fraction is fixed as nonexchangeable ammonium ion in the crystal lattice of clay minerals. Because nitrate ion is not strongly bound to soil, it is readily carried through soil formations by water. Many factors, including soil type, moisture, and level of organic matter, affect the production of ammonia and nitrate ion originating from feedlot wastes, and a marked variation is found in the levels and distributions of these materials in feedlot areas.

Phosphorus

Although the percentage of phosphorus in plant material is relatively low, it is an essential component of plants. Phosphorus, like nitrogen, must be present in a simple inorganic form before it can be taken up by plants. In the case of phosphorus, the utilizable species is some form of orthophosphate ion. In the pH range that is present in most soils, H_2PO_4^- and HPO_4^{2-} are the predominant orthophosphate species.

Orthophosphate is most available to plants at pH values near neutrality. It is believed that in relatively acidic soils, orthophosphate ions are precipitated or sorbed by species of Al(III) and Fe(III). In alkaline soils, orthophosphate may react with calcium carbonate to form relatively insoluble hydroxyapatite:



In general, because of these reactions, little phosphorus applied as fertilizer leaches from the soil. This is important from the standpoint of both water pollution and utilization of phosphate fertilizers.

Potassium

Relatively high levels of potassium are utilized by growing plants. Potassium activates some enzymes and plays a role in the water balance in plants. It is also essential for some carbohydrate transformations. Crop yields are generally greatly reduced in potassium-deficient soils. The higher the productivity of the crop, the more potassium is removed from soil. When nitrogen fertilizers are added to soils to increase productivity, removal of potassium is enhanced. Therefore, potassium may become a limiting nutrient in soils heavily fertilized with other nutrients.

Potassium is one of the most abundant elements in the earth's crust, of which it makes up 2.6%; however, much of this potassium is not easily available to plants. For example, some silicate minerals such as leucite, $K_2O \cdot Al_2O_3 \cdot 4SiO_2$, contain strongly bound potassium. Exchangeable potassium held by clay minerals is relatively more available to plants.

16.6. MICRONUTRIENTS IN SOIL

Boron, chlorine, copper, iron, manganese, molybdenum (for N-fixation), and zinc are considered essential plant **micronutrients**. These elements are needed by plants only at very low levels and frequently are toxic at higher levels. There is some chance that other elements will be added to this list as techniques for growing plants in environments free of specific elements improve. Most of these elements function as components of essential enzymes. Manganese, iron, chlorine, and zinc may be involved in photosynthesis. Though not established for all plants, it is possible that sodium, silicon, and cobalt may also be essential plant nutrients.

Iron and manganese occur in a number of soil minerals. Sodium and chlorine (as chloride) occur naturally in soil and are transported as atmospheric particulate matter from marine sprays (see Chapter 10). Some of the other micronutrients and trace elements are found in primary (unweathered) minerals that occur in soil. Boron is substituted isomorphically for Si in some micas and is present in tourmaline, a mineral with the formula $NaMg_3Al_6B_3Si_6O_{27}(OH,F)_4$. Copper is isomorphically substituted for other elements in feldspars, amphiboles, olivines, pyroxenes, and micas; it also occurs as trace levels of copper sulfides in silicate minerals. Molybdenum occurs as molybdenite (MoS_2). Vanadium is isomorphically substituted for Fe or Al in oxides, pyroxenes, amphiboles, and micas. Zinc is present as the result of isomorphous substitution for Mg, Fe, and Mn in oxides, amphiboles, olivines, and pyroxenes and as trace zinc sulfide in silicates. Other trace elements that occur as specific minerals, sulfide inclusions, or by isomorphous substitution for other elements in minerals are chromium, cobalt, arsenic, selenium, nickel, lead, and cadmium.

The trace elements listed above may be coprecipitated with secondary minerals (see Section 15.2) that are involved in soil formation. Such secondary minerals include oxides of aluminum, iron, and manganese (precipitation of hydrated oxides of iron and manganese very efficiently removes many trace metal ions from solution); calcium and magnesium carbonates; smectites; vermiculites; and illites.

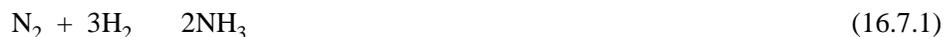
Some plants accumulate extremely high levels of specific trace metals. Those accumulating more than 1.00 mg/g of dry weight are called **hyperaccumulators**. Nickel and copper both undergo hyperaccumulation in some plant species. As an example of a metal hyperaccumulator, *Aeolanthus biformifolius DeWild* growing in copper-rich regions of Shaba Province, Zaire, contains up to 1.3% copper (dry weight) and is known as a “copper flower”.

The hyperaccumulation of metals by some plants has led to the idea of **phytoremediation** in which plants growing on contaminated ground accumulate metals, which are then removed with the plant biomass. *Brassica juncea* and *Brassica chinensis* (Chinese cabbage) have been shown to hyperaccumulate as much as 5 grams of uranium per kg plant dry weight when grown on uranium-contaminated soil.⁶ Uranium accumulation in the plants was enhanced by the addition of citrate, which complexes uranium and makes it more soluble.

16.7. FERTILIZERS

Crop fertilizers contain nitrogen, phosphorus, and potassium as major components. Magnesium, sulfate, and micronutrients may also be added. Fertilizers are designated by numbers, such as 6-12-8, showing the respective percentages of nitrogen expressed as N (in this case 6%), phosphorus as P₂O₅ (12%), and potassium as K₂O (8%). Farm manure corresponds to an approximately 0.5-0.24-0.5 fertilizer. The organic fertilizers such as manure must undergo biodegradation to release the simple inorganic species (NO₃⁻, H_xPO₄^{X-3}, K⁺) assimilable by plants.

Most modern nitrogen fertilizers are made by the Haber process, in which N₂ and H₂ are combined over a catalyst at temperatures of approximately 500°C and pressures up to 1000 atm:



The anhydrous ammonia product has a very high nitrogen content of 82%. It may be added directly to the soil, for which it has a strong affinity because of its water solubility and formation of ammonium ion:

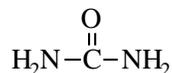


Special equipment is required, however, because of the toxicity of ammonia gas. Aqua ammonia, a 30% solution of NH₃ in water, may be used with much greater safety. It is sometimes added directly to irrigation water. It should be pointed out that ammonia vapor is toxic and NH₃ is reactive with some substances. Improperly discarded or stored ammonia can be a hazardous waste.

Ammonium nitrate, NH₄NO₃, is a common solid nitrogen fertilizer. It is made by oxidizing ammonia over a platinum catalyst, converting the nitric oxide product to nitric acid, and reacting the nitric acid with ammonia. The molten ammonium nitrate product is forced through nozzles at the top of a *prilling tower* and solidifies to form small pellets while falling through the tower. The particles are coated with a water repellent. Ammonium nitrate contains 33.5% nitrogen. Although convenient to apply

to soil, it requires considerable care during manufacture and storage because it is explosive. Ammonium nitrate also poses some hazards. It is mixed with fuel oil to form an explosive that serves as a substitute for dynamite in quarry blasting and construction. This mixture was used to devastating effect in the dastardly bombing of the Oklahoma City Federal Building in 1995.

Urea,



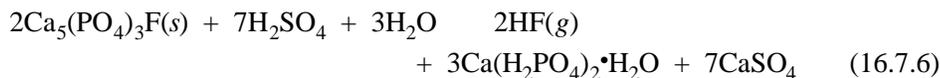
is easier to manufacture and handle than ammonium nitrate. It is now the favored solid nitrogen-containing fertilizer. The overall reaction for urea synthesis is



involving a rather complicated process in which ammonium carbamate, chemical formula $\text{NH}_2\text{CO}_2\text{NH}_4$, is an intermediate.

Other compounds used as nitrogen fertilizers include sodium nitrate (obtained largely from Chilean deposits, see Section 15.2), calcium nitrate, potassium nitrate, and ammonium phosphates. Ammonium sulfate, a by-product of coke ovens, used to be widely applied as fertilizer. The alkali metal nitrates tend to make soil alkaline, whereas ammonium sulfate leaves an acidic residue.

Phosphate minerals are found in several states, including Idaho, Montana, Utah, Wyoming, North Carolina, South Carolina, Tennessee, and Florida. The principal mineral is fluorapatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$. The phosphate from fluorapatite is relatively unavailable to plants, and fluorapatite is frequently treated with phosphoric or sulfuric acids to produce superphosphates:



The superphosphate products are much more soluble than the parent phosphate minerals. The HF produced as a byproduct of superphosphate production can create air pollution problems.

Phosphate minerals are rich in trace elements required for plant growth, such as boron, copper, manganese, molybdenum, and zinc. Ironically, these elements are lost to a large extent when the phosphate minerals are processed to make fertilizer. Ammonium phosphates are excellent, highly soluble phosphate fertilizers. Liquid ammonium polyphosphate fertilizers consisting of ammonium salts of pyrophosphate, triphosphate, and small quantities of higher polymeric phosphate anions in aqueous solution work very well as phosphate fertilizers. The polyphosphates are believed to have the additional advantage of chelating iron and other micronutrient metal ions, thus making the metals more available to plants.

Potassium fertilizer components consist of potassium salts, generally KCl. Such salts are found as deposits in the ground or may be obtained from some brines. Very

large deposits are found in Saskatchewan, Canada. These salts are all quite soluble in water. One problem encountered with potassium fertilizers is the luxury uptake of potassium by some crops, which absorb more potassium than is really needed for their maximum growth. In a crop where only the grain is harvested, leaving the rest of the plant in the field, luxury uptake does not create much of a problem because most of the potassium is returned to the soil with the dead plant. However, when hay or forage is harvested, potassium contained in the plant as a consequence of luxury uptake is lost from the soil.

16.8. WASTES AND POLLUTANTS IN SOIL

Soil receives large quantities of waste products. Much of the sulfur dioxide emitted in the burning of sulfur-containing fuels ends up as soil sulfate. Atmospheric nitrogen oxides are converted to nitrates in the atmosphere, and the nitrates eventually are deposited on soil. Soil sorbs NO and NO₂, and these gases are oxidized to nitrate in the soil. Carbon monoxide is converted to CO₂ and possibly to biomass by soil bacteria and fungi. Particulate lead from automobile exhausts is found at elevated levels in soil along heavily traveled highways. Elevated levels of lead from lead mines and smelters are found on soil near such facilities.

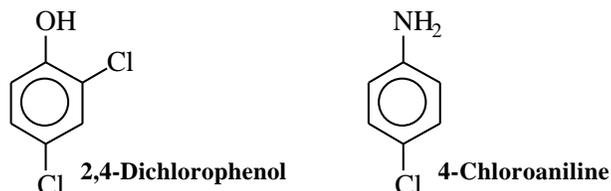
Soil is the receptor of many hazardous wastes from landfill leachate, lagoons, and other sources (see Section 19.13). In some cases, land farming of degradable hazardous organic wastes is practiced as a means of disposal and degradation. The degradable material is worked into the soil, and soil microbial processes bring about its degradation. As discussed in Chapter 8, sewage and fertilizer-rich sewage sludge may be applied to soil.

Volatile organic compounds (VOC) such as benzene, toluene, xylenes, dichloromethane, trichloroethane, and trichloroethylene, may contaminate soil in industrialized and commercialized areas, particularly in countries in which enforcement of regulations is not very stringent. One of the more common sources of these contaminants is leaking underground storage tanks. Landfills built before current stringent regulations were enforced and improperly discarded solvents are also significant sources of soil VOCs.

Measurements of levels of polychlorinated biphenyls (PCBs) in soils that have been archived for several decades provide interesting insight into the contamination of soil by pollutant chemicals and subsequent loss of these substances from soil.⁷ Analyses of soils from the United Kingdom dating from the early 1940s to 1992 showed that the PCB levels increased sharply from the 1940s, reaching peak levels around 1970. Subsequently, levels fell sharply and now are back to early 1940s concentrations. This fall was accompanied by a shift in distribution to the more highly chlorinated PCBs, which was attributed by those doing the study to volatilization and long range transport of the lighter PCBs away from the soil. These trends parallel levels of PCB manufacture and use in the United Kingdom from the early 1940s to the present. This is consistent with the observation that relatively high concentrations of PCBs have been observed in remote Arctic and sub-Arctic regions, attributed to condensation in colder climates of PCBs volatilized in warmer regions.

Some pollutant organic compounds are believed to become bound with humus during the humification process that occurs in soil. This largely immobilizes and

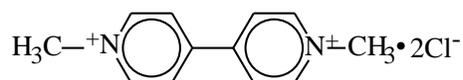
detoxifies the compounds. Binding of pollutant compounds by humus is particularly likely to occur with compounds that have structural similarities to humic substances, such as phenolic and anilinic compounds illustrated by the following two examples:



Such compounds can become covalently bonded to humic substance molecules, largely through the action of microbial enzymes. After binding they are known as **bound residues** and are highly resistant to extraction with solvents by procedures that would remove unbound parent compounds.⁸ Compounds in the bound residues are resistant to biological and chemical attack.

Soil receives enormous quantities of pesticides as an inevitable result of their application to crops. The degradation and eventual fate of these pesticides on soil largely determines their ultimate environmental effects. Detailed knowledge of these effects are now required for licensing of a new pesticide (in the U.S. under the Federal Insecticide, Fungicide, and Rodenticide act, FIFRA). Among the factors to be considered are the sorption of the pesticide by soil; leaching of the pesticide into water, as related to its potential for water pollution; effects of the pesticide on microorganisms and animal life in the soil; and possible production of relatively more toxic degradation products.

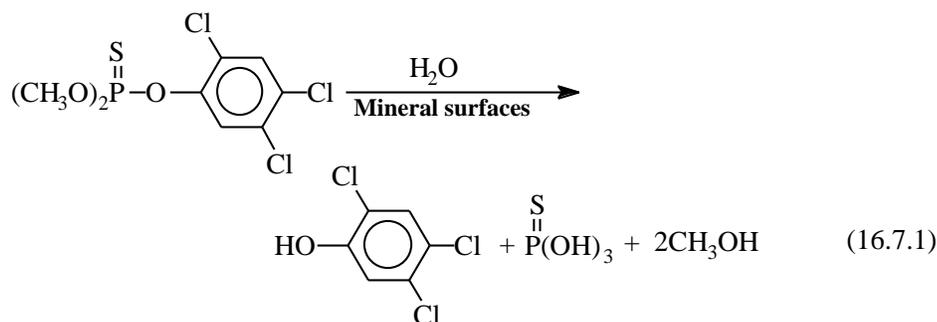
Adsorption by soil is a key aspect of pesticide degradation and plays a strong role in the speed and degree of degradation. The degree of adsorption and the speed and extent of ultimate degradation are influenced by a number of other factors. Some of these, including solubility, volatility, charge, polarity, and molecular structure and size, are properties of the medium. Adsorption of a pesticide by soil components may have several effects. Under some circumstances, it retards degradation by separating the pesticide from the microbial enzymes that degrade it, whereas under other circumstances the reverse is true. Purely chemical degradation reactions may be catalyzed by adsorption. Loss of the pesticide by volatilization or leaching is diminished. The toxicity of a herbicide to plants may be reduced by sorption on soil. The forces holding a pesticide to soil particles may be of several types. Physical adsorption involves van der Waals forces arising from dipole-dipole interactions between the pesticide molecule and charged soil particles. Ion exchange is especially effective in holding cationic organic compounds, such as the herbicide paraquat,



to anionic soil particles. Some neutral pesticides become cationic by protonation and are bound as the protonated positive form. Hydrogen bonding is another mechanism by which some pesticides are held to soil. In some cases a pesticide may act as a ligand coordinating to metals in soil mineral matter.

The three primary ways in which pesticides are degraded in or on soil are *chemical degradation*, *photochemical reactions*, and, most important, *biodegradation*. Various combinations of these processes may operate in the degradation of a pesticide.

Chemical degradation of pesticides has been observed experimentally in soils and clays sterilized to remove all microbial activity. For example, clays have been shown to catalyze the hydrolysis of *o,o*-dimethyl-*o*-2,4,5-trichlorophenyl thiophosphate (also called Trolene, Ronnel, Etrolene, or trichlorometafos), an effect attributed to -OH groups on the mineral surface:



Many other purely chemical hydrolytic reactions of pesticides occur in soil.

A number of pesticides have been shown to undergo **photochemical reactions**, that is, chemical reactions brought about by the absorption of light (see Chapter 9). Frequently, isomers of the pesticides are formed as products. Many of the studies reported apply to pesticides in water or on thin films, and the photochemical reactions of pesticides on soil and plant surfaces remain largely a matter of speculation.

Biodegradation and the Rhizosphere

Although insects, earthworms, and plants may play roles in the **biodegradation** of pesticides and other pollutant organic chemicals, microorganisms have the most important role. Several examples of microorganism-mediated degradation of organic chemical species are given in Chapter 6.

The **rhizosphere**, the layer of soil in which plant roots are especially active, is a particularly important part of soil with respect to biodegradation of wastes. It is a zone of increased biomass and is strongly influenced by the plant root system and the microorganisms associated with plant roots. The rhizosphere may have more than ten times the microbial biomass per unit volume compared to nonrhizospheric zones of soil. This population varies with soil characteristics, plant and root characteristics, moisture content, and exposure to oxygen. If this zone is exposed to pollutant compounds, microorganisms adapted to their biodegradation may also be present.

Plants and microorganisms exhibit a strong synergistic relationship in the rhizosphere, which benefits the plant and enables highly elevated populations of rhizospheric microorganisms to exist. Epidermal cells sloughed from the root as it grows and carbohydrates, amino acids, and root-growth-lubricant mucigel secreted from the roots all provide nutrients for microorganism growth. Root hairs provide a hospitable biological surface for colonization by microorganisms.

The biodegradation of a number of synthetic organic compounds has been demonstrated in the rhizosphere. Understandably, studies in this area have focused on herbicides and insecticides that are widely used on crops. Among the organic species for which enhanced biodegradation in the rhizosphere has been demonstrated are the following (associated plant or crop shown in parentheses): 2,4-D herbicide (wheat, African clover, sugarcane, flax), parathion (rice, bush bean), carbofuran (rice), atrazine (corn), diazinon (wheat, corn, peas), volatile aromatic alkyl and aryl hydrocarbons and chlorocarbons (reeds), and surfactants (corn, soybean, cattails). It is interesting to note that enhanced biodegradation of polycyclic aromatic hydrocarbons (PAH) was observed in the rhizospheric zones of prairie grasses. This observation is consistent with the fact that in nature such grasses burn regularly and significant quantities of PAH compounds are deposited on soil as a result.

16.9. SOIL LOSS AND DEGRADATION

Soil is a fragile resource that can be lost by erosion or become so degraded that it is no longer useful to support crops. The physical properties of soil and, hence, its susceptibility to erosion, are strongly affected by the cultivation practices to which the soil is subjected.⁹ **Desertification** refers to the process associated with drought and loss of fertility by which soil becomes unable to grow significant amounts of plant life. Desertification caused by human activities is a common problem globally, occurring in diverse locations such as Argentina, the Sahara, Uzbekistan, the U.S. Southwest, Syria, and Mali. It is a very old problem dating back many centuries to the introduction of domesticated grazing animals to areas where rainfall and groundcover were marginal. The most notable example is desertification aggravated by domesticated goats in the Sahara region. Desertification involves a number of interrelated factors, including erosion, climate variations, water availability, loss of fertility, loss of soil humus, and deterioration of soil chemical properties.

A related problem is **deforestation**, loss of forests. The problem is particularly acute in tropical regions, where the forests contain most of the existing plant and animal species. In addition to extinction of these species, deforestation can cause devastating deterioration of soil through erosion and loss of nutrients.

Soil erosion can occur by the action of both water and wind, although water is the primary source of erosion. Millions of tons of topsoil are carried by the Mississippi River and swept from its mouth each year. About one-third of U.S. topsoil has been lost since cultivation began on the continent. At the present time, approximately one-third of U.S. cultivated land is eroding at a rate sufficient to reduce soil productivity. It is estimated that 48 million acres of land, somewhat more than 10 percent of that under cultivation, is eroding at unacceptable levels, taken to mean a loss of more than 14 tons of topsoil per acre each year. Specific areas in which the greatest erosion is occurring include northern Missouri, southern Iowa, west Texas, western Tennessee, and the Mississippi Basin. [Figure 16.6](#) shows the pattern of soil erosion in the continental U.S. in 1977.

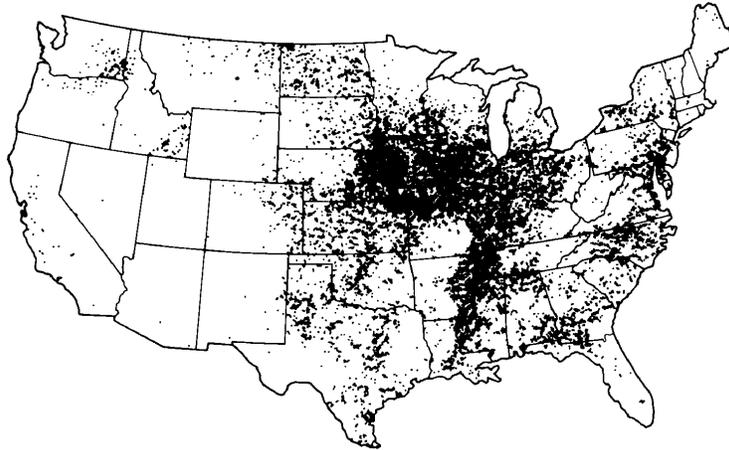


Figure 16.6. Pattern of soil erosion in the continental U.S. as of 1977. The dark areas indicate locations where the greatest erosion is occurring.

Problems involving soil erosion were aggravated in the 1970s and early 1980s when high prices for farmland resulted in the intensive cultivation of high-income crops, particularly corn and soybeans. These crops grow in rows with bare soil in between, which tends to wash away with each rainfall. Furthermore, the practice of planting corn and soybeans year after year without intervening plantings of soil-restoring clover or grass became widespread. The problem of decreased productivity due to soil erosion has been masked somewhat by increased use of chemical fertilizers.

Wind erosion, such as occurs on the generally dry, high plains soils of eastern Colorado, poses another threat. After the Dust Bowl days of the 1930s, much of this land was allowed to revert to grassland, and the topsoil was held in place by the strong root systems of the grass cover. However, in an effort to grow more wheat and improve the sale value of the land, much of it was later returned to cultivation. For example, from 1979 through 1982, more than 450,000 acres of Colorado grasslands were plowed. Much of this was done by speculators who purchased grassland at a low price of \$100-\$200 per acre, broke it up, and sold it as cultivated land at more than double the original purchase price. Although freshly cultivated grassland may yield well for one or two years, the nutrients and soil moisture are rapidly exhausted and the land becomes very susceptible to wind erosion.

The preservation of soil from erosion is commonly termed **soil conservation**. There are a number of solutions to the soil erosion problem. Some are old, well-known agricultural practices such as terracing, contour plowing, and periodically planting fields with cover crops such as clover. For some crops **no-till agriculture**, now commonly called **conservation tillage**,^{10,11} greatly reduces erosion. This practice consists of planting a crop among the residue of the previous year's crop without plowing.¹² Weeds are killed in the newly planted crop row by application of a herbicide prior to planting. The surface residue of plant material left on top of the soil prevents erosion.

Another, more experimental, solution to the soil erosion problem is the cultivation of perennial plants which develop large root systems and come up each spring after being harvested the previous fall. For example, a perennial corn plant has been developed by crossing corn with a distant, wild relative, teosinte, which grows in Central America. Unfortunately, the resulting plant does not give outstanding grain yields. It should be noted that an annual plant's ability to propagate depends upon producing large quantities of seeds, whereas a perennial plant must develop a strong root system with bulbous growths called rhizomes which store food for the coming year. However, it is possible that the application of genetic engineering (see Section 16.9) may result in the development of perennial crops with good seed yields. The cultivation of such a crop would cut down on a great deal of soil erosion.

The best known perennial plants are trees, which are very effective in stopping soil erosion. Wood from trees can be used as biomass fuel, as a source of raw materials, and as food (see below). There is a tremendous unrealized potential for an increase in the production of biomass from trees. For example, the production of biomass from natural forests of loblolly pine trees in South Carolina has been about three dry tons per hectare per year. This has now been increased at least four-fold through selection of superior trees, and 30 tons may eventually be possible. In Brazil, experiments were conducted with a species of Eucalyptus, which has a seven-year growth cycle. With improved selection of trees, the annual yields for three successive cycles of these trees in dry tons per hectare per year were 23, 33, and 40.

The most important use for wood is, of course, as lumber for construction. This use will remain important as higher energy prices increase the costs of other construction materials such as steel, aluminum, and cement. Wood is about 50 percent cellulose, which can be hydrolyzed by rapidly improving enzyme processes to yield glucose sugar. The glucose can be used directly as food, fermented to ethyl alcohol for fuel (gasohol), or employed as a carbon and energy source for protein-producing yeasts. Given these and other potential uses, the future of trees as an environmentally desirable and profitable crop is very bright.

Soil and Water Resources

The conservation of soil and the protection of water resources are strongly inter-related. Most fresh water falls initially on soil, and the condition of the soil largely determines the fate of the water and how much is retained in a usable condition. The land area upon which rainwater falls is called a **watershed**. In addition to collecting the water, the watershed determines the direction and rate of flow and the degree of water infiltration into groundwater aquifers (see the hydrologic cycle in [Figure 2.1](#)). Excessive rates of water flow prevent infiltration, lead to flash floods, and cause soil erosion. Measures taken to enhance the utility of land as a watershed also fortunately help prevent erosion. Some of these measures involve modification of the contour of the soil, particularly terracing, construction of waterways, and construction of water-retaining ponds. Waterways are planted with grass to prevent erosion, and water-retaining crops and bands of trees can be planted on the contour to achieve much the same goal. Reforestation and control of damaging grazing practices conserve both soil and water.

16.10. GENETIC ENGINEERING AND AGRICULTURE

The nuclei of living cells contain the genetic instruction for cell reproduction. These instructions are in the form of a special material called deoxyribonucleic acid, DNA. In combination with proteins, DNA makes up the cell chromosomes. During the 1970s the ability to manipulate DNA through genetic engineering became a reality, and during the 1980s it became the basis of a major industry. Such manipulation falls into the category of recombinant DNA technology. Recombinant DNA gets its name from the fact that it contains DNA from two different organisms, recombined together. This technology promises some exciting developments in agriculture and, indeed, is expected to lead to a “second green revolution.”¹³

The first “green revolution” of the mid-1960s used conventional plant-breeding techniques of selective breeding, hybridization, cross-pollination, and back-crossing to develop new strains of rice, wheat, and corn which, when combined with chemical fertilizers, yielded spectacularly increased crop yields. For example, India’s output of grain increased 50 percent. By working at the cellular level, however, it is now possible to greatly accelerate the process of plant breeding. Thus, plants may be developed that resist particular diseases, grow in seawater, or have much higher productivity. The possibility exists for developing entirely new kinds of plants.

One exciting possibility with genetic engineering is the development of plants other than legumes that fix their own nitrogen. For example, if nitrogen-fixing corn could be developed, the savings in fertilizer would be enormous. Furthermore, since the nitrogen is fixed in an organic form in plant root structures, there would be no pollutant runoff of chemical fertilizers.

Another promising possibility with genetic engineering is increased efficiency of photosynthesis. Plants utilize only about one percent of the sunlight striking their leaves, so there is appreciable room for improvement in that area.

Cell-culture techniques can be applied in which billions of cells are allowed to grow in a medium and develop mutants which, for example, might be resistant to particular viruses or herbicides or have other desirable qualities. If the cells with the desired qualities can be regenerated into whole plants, results can be obtained that might have taken decades using conventional plant-breeding techniques.

Despite the enormous potential of the “green revolution,” genetic engineering, and more intensive cultivation of land to produce food and fiber, these technologies cannot be relied upon to support an uncontrolled increase in world population, and may even simply postpone an inevitable day of reckoning with the consequences of population growth. Changes in climate resulting from global warming (greenhouse effect, Section 14.2), ozone depletion (by chlorofluorocarbons, Section 14.4), or natural disasters such as massive volcanic eruptions or collisions with large meteorites can, and almost certainly will, result in worldwide famine conditions in the future that no agricultural technology will be able to alleviate.

There has been strong resistance to transgenic crops and livestock in some quarters. This is especially true in Europe. Reports that pollen from transgenic corn producing an insecticide of bacterial origin has killed monarch butterfly caterpillars led the European Commission, the executive body of the the European Union, to suspend action on seven transgenic crops that it was considering for approval.¹⁴ The Commission had already approved 16 varieties of transgenic corn, potatoes, rape, sugar beets, turnips, and other crops. As of 1999 it appeared that major agricultural

product processors in the U.S. would have to certify products as “GM free” (free of genetically modified products) for export to Europe.

16.11. AGRICULTURE AND HEALTH

Some authorities hold that soil has an appreciable effect upon health. An obvious way in which such an effect might be manifested is the incorporation into food of micronutrient elements essential for human health. One such nutrient (which is toxic at overdose levels) is selenium. It is definitely known that the health of animals is adversely affected in selenium-deficient areas as it is in areas of selenium excess. Human health might be similarly affected.

There are some striking geographic correlations with the occurrence of cancer, some of which may be due to soil type. A high incidence of stomach cancer occurs in areas with certain types of soil in the Netherlands, the United States, France, Wales, and Scandinavia. These soils are high in organic matter content, are acidic, and are frequently waterlogged. A “stomach cancer-prone lifestyle” has been described,¹⁵ which includes consumption of home-grown food, consumption of water from one’s own well, and reliance on native and uncommon foodstuffs.

One possible reason for the existence of “stomach cancer-producing soils” is the production of cancer-causing secondary metabolites by plants and microorganisms. Secondary metabolites are biochemical compounds that are of no apparent use to the organism producing them. It is believed that they are formed from the precursors of primary metabolites when the primary metabolites accumulate to excessive levels.

The role of soil in environmental health is not well known, nor has it been extensively studied. The amount of research on the influence of soil in producing foods that are more nutritious and lower in content of naturally occurring toxic substances is quite small compared to research on higher soil productivity. It is to be hoped that the environmental health aspects of soil and its products will receive much greater emphasis in the future.

Chemical Contamination

Human activities, most commonly pesticide application, may contaminate food grown on soil. An interesting example of such contamination occurred in Hawaii in early 1982.¹⁶ It was found that milk from several sources on Oahu contained very high levels of heptachlor (see [Table 7.5](#)). This pesticide causes cancer and liver disorders in mice; therefore, it is a suspected human carcinogen. Remarkably, in this case it was not until 57 days after the initial discovery that the public was informed of the contamination by the Department of Health. The source of heptachlor was traced to contaminated “green chop,” chopped-up pineapple leaves fed to cattle. Although heptachlor was banned for most applications, Hawaiian pineapple growers had obtained special federal permission to use it to control mealybug wilt. Although it was specified that green chop could not be collected within one year of the last application of the pesticide, this regulation was apparently violated, and the result was distribution of contaminated milk to consumers.

In the late 1980s, Alar residues on food caused considerable controversy in the marketplace. **Alar**, daminozide, is a growth regulator that was widely used on apples to bring about uniform ripening of the fruit, and to improve the firmness and color of

the apples. It was discontinued for this purpose after 1988 because of concerns that it might cause cancer, particularly in those children who consume relatively large amounts of apples, apple juice, and other apple products. Dire predictions were made in the industry of crop losses and financial devastation. However, the 1989 apple crop, which was the first without Alar in the U.S., had a value of \$1.0 billion, only \$0.1 billion less than that of the 1988 crop. Production of apples has continued since then without serious problems from the unavailability of Alar.

A possible source of soil contamination results from recycling industrial wastes for fertilizer.¹⁷ According to data compiled by the Environmental Working Group (EWG) during the 1990s, approximately 25 million kg per year of potentially toxic wastes were used to prepare fertilizers that contained elevated levels of arsenic, cadmium, lead, radioactive materials, and dioxins. A potential source of heavy metal pollution in fertilizers is ash from furnaces used to recycle steel, commonly processed to provide zinc in zinc-deficient soils.

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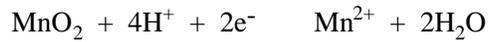
QUESTIONS AND PROBLEMS

1. Give two examples of reactions involving manganese and iron compounds that may occur in waterlogged soil.
2. What temperature and moisture conditions favor the buildup of organic matter in soil?
3. "Cat clays" are soils containing a high level of iron pyrite, FeS_2 . Hydrogen peroxide, H_2O_2 , is added to such a soil, producing sulfate as a test for cat clays. Suggest the chemical reaction involved in this test.
4. What effect upon soil acidity would result from heavy fertilization with ammonium nitrate accompanied by exposure of the soil to air and the action of aerobic bacteria?

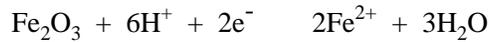
5. How many moles of H^+ ion are consumed when 200 kilograms of NaNO_3 undergo denitrification in soil?
6. What is the primary mechanism by which organic material in soil exchanges cations?
7. Prolonged waterlogging of soil does **not** (a) increase NO_3^- production, (b) increase Mn^{2+} concentration, (c) increase Fe^{2+} concentration, (d) have harmful effects upon most plants, (e) increase production of NH_4^+ from NO_3^- .
8. Of the following phenomena, the one that eventually makes soil more basic is (a) removal of metal cations by roots, (b) leaching of soil with CO_2 -saturated water, (c) oxidation of soil pyrite, (d) fertilization with $(\text{NH}_4)_2\text{SO}_4$, (e) fertilization with KNO_3 .
9. How many metric tons of farm manure are equivalent to 100 kg of 10-5-10 fertilizer?
10. How are the chelating agents that are produced from soil microorganisms involved in soil formation?
11. What specific compound is both a particular animal waste product and a major fertilizer?
12. What happens to the nitrogen/carbon ratio as organic matter degrades in soil?
13. To prepare a rich potting soil, a greenhouse operator mixed 75% “normal” soil with 25% peat. Estimate the cation-exchange capacity in milliequivalents/100 g of the product.
14. Explain why plants grown on either excessively acidic or excessively basic soils may suffer from calcium deficiency.
15. What are two mechanisms by which anions may be held by soil mineral matter?
16. What are the three major ways in which pesticides are degraded in or on soil?
17. Lime from lead mine tailings containing 0.5% lead was applied at a rate of 10 metric tons per acre of soil and worked in to a depth of 20 cm. The soil density was 2.0 g/cm. To what extent did this add to the burden of lead in the soil? There are 640 acres per square mile and 1,609 meters per mile.
18. Match the soil or soil-solution constituent in the left column with the soil condition described on the right, below:

(1) High Mn^{2+} content in soil solution	(a) “Cat clays” containing initially high levels of pyrite, FeS_2
(2) Excess H^+	(b) Soil in which biodegradation has not occurred to a great extent
(3) High H^+ and SO_4^{2-} content	(c) Waterlogged soil
(4) High organic content	(d) Soil, the fertility of which can be improved by adding limestone.
19. What are the processes occurring in soil that operate to reduce the harmful effects of pollutants?

20. Under what conditions do the reactions,



and



occur in soil? Name two detrimental effects that can result from these reactions.

21. What are four important effects of organic matter in soil?

22. How might irrigation water treated with fertilizer containing potassium and ammonia become depleted of these nutrients in passing through humus-rich soil?

10. Match the following:

- | | |
|--------------|--|
| 1. Subsoil | (a) Weathered parent rocks from which the soil originated |
| 2. Gravels | (b) Largest particle size fraction (2–60 mm) according to the United Classification System |
| 3. Topsoil | (c) B horizon of soil |
| 4. C horizon | (d) Layer of maximum biological activity in soil that contains most of the soil organic matter |