
SOIL ORGANIC MATTER

The organic fraction of soil is <5% living microbes, plant roots, and soil fauna and >95% dead plant and animal residues. Per unit mass, the organic fraction is the most chemically active portion of the soil. It is a reservoir for essential elements, particularly C, N, S, and P; promotes good soil structure; is a source of cation exchange capacity (CEC) and soil pH buffering; promotes good air–water relations in soils; and is a large and active reservoir and buffer of carbon in the environment. This chapter discusses the contributions of soil organic matter to the chemical properties of soils.

Soil organic matter (SOM) is mostly (>95%) an accumulation of dead plant matter and partially decayed and resynthesized plant and animal residues. Freshly fallen leaves and dying roots rapidly decompose and the residues become part of SOM, some portions of which remain in the soil for a very long time. Crop residues, weeds, grasses, tree leaves, worms, bacteria, fungi, and actinomycetes are also part of the complex mixture. Some definitions of SOM are restricted to soil humus, omitting any undecayed organic residues and soil organisms. *Humus* is generally defined as that organic material that has been transformed into relatively stable form by soil microorganisms. We use the term SOM in its broader sense, to include all carbon-containing compounds except carbonates. Stevenson (1982) and Schnitzer and Schulten (1998) give details on the details of SOM composition and structure. This chapter is concerned with nonliving substances (particularly humus) and its chemistry. Soil microbiology texts discuss the *live microbial tissue (microbial biomass)* in soils.

6.1 SOIL ORGANIC MATTER CONTENT

Soils vary greatly in their organic matter content. A prairie grassland soil (e.g., Mollisol) may contain 5 to 6% SOM by mass to a depth of 15 cm, whereas a sandy desert

soil (Aridisol) contains little more than 0.1%. Poorly drained soils (Aquepts) often have organic matter contents greater than 10%, and peat soils (Histosols) approach 100% organic matter. Although the organic matter content of most surface mineral soils is only 0.5 to 5% by mass, the active colloidal behavior of SOM strongly affects soil physical and chemical properties.

The factors of soil formation (Section 7.3) determine the SOM content of soils. The order of importance of the factors that determine the organic matter (and nitrogen) contents of well-drained soils in the United States is climate > vegetation > topography = parent material > age.

Climate affects (1) the array of plant species, (2) the quantity of plant material produced, and (3) the intensity of soil microbial activity. Vegetation and topographic effects are difficult to separate from climatic effects. Rather, all of the factors become integrated as a soil forms and account for the generalization that forest and grassland soils usually exceed other well-aerated soils in humus content, whereas desert and semidesert soils have very little SOM.

Tropical soils, both humid and arid, were once thought to have low organic matter contents because the soils lack the dark color that characterizes SOM in temperate regions, and because temperature is inversely correlated with SOM content in temperate soils. The high soil temperature should increase microbial oxidation of SOM. The organic matter contents of similar soil orders in tropical and temperate regions, however, are quite similar (Table 6.1). The high organic matter contents of the tropical soils may be due to strong interaction of organic matter with Fe and Al hydroxides and allophane. Strong interaction could stabilize the SOM against microbial decay. The high SOM content is also due to the high rate of year-round biomass production in the humid tropics.

Topography influences the amount of SOM in two ways. North-facing slopes (in the northern hemisphere) are cooler and moister, so the organic matter content is greater than in soils on south-facing slopes. A much greater effect is topography's control of water drainage. In poorly drained and swampy soils, plant matter can be covered with water, and oxygen excluded, as soon as the plant dies. In stagnant water, oxygen diffusion from the surface is the only means of oxygen supply to the

Table 6.1. Average organic carbon contents of several soil orders in temperate and tropical regions (to obtain approximate SOM values, multiply by 1.7)^a

Soil Order (0 to 15 cm depth)	Carbon Contents (%)			Mean Level
	United States	Brazil	Zaire	
Mollisols	2.44	—	—	2.44
Oxisols	—	2.01	2.13	2.07
Ultisols	1.58	1.61	0.8	1.39
Alfisols	1.55	1.06	1.30	1.30

^aFrom P. A. Sanchez. 1976. *Properties and Management of Soils in the Tropics*. Wiley-Interscience, New York.

organisms carrying out the decomposition. This slow rate of oxygen supply preserves much of the plant matter from decay. Fermentation can operate in the absence of oxygen, but its effect on decay is rather small. Running water can bring enough dissolved oxygen to oxidize organic matter in streams. The turnover of lake water in spring and fall supplies some oxygen to lake bottoms.

In stagnant water, dead and partially decayed plant matter can accumulate to the water surface. Such deposits were up to 30 m thick in the Sacramento–San Joaquin Delta of California, for example, before those areas were drained. Ireland has large areas of *peat* (a type of Histosol containing 50% or more by mass of organic matter) deposits more than 10 m thick. Low temperatures also enhance peat accumulation. Major areas of peat are found in central Canada, which is both cold and swampy, with lesser amounts in low-lying areas of northern Russia and northern Europe. Smaller, but substantial, areas of Histosols are found on every continent and even in the tropics. The largest area of contiguous peat or muck soils in the continental United States is in the Everglades area south of Lake Okeechobee in southern Florida.

Peat accumulation depends on the rate of organic addition versus the rate of oxidation. The oxidation rate is a function of the rate of oxygen supply and temperature. The oxygen supply in turn depends on soil water content. When drained for cultivation, peat oxidizes as it contacts oxygen and also shrinks as it dries. Shrinkage and oxidation lowered the level of cultivated peat land in California and Florida by as much as 25 to 50 mm yr⁻¹. This rate has slowed in recent years as we have learned to better manage these materials. The peat islands in California are encircled by dikes to keep out the water. The peat surface is now as much as 10 m below the river level. The dikes must be continually strengthened as the peat oxidizes and shrinks. In recent years the maintenance of these dikes has become so costly that some of the islands have been abandoned after winter floods broke through the dikes. Wind erosion of the dry surface and accidental burning of the peat also contributed to the loss of these extremely productive soils.

In the formerly glaciated areas of Canada, Europe, and Siberia, peat has been accumulating for 10 000 to 15 000 years, since the glaciers retreated. This accumulation rate varies from year to year, with a rough average of about 0.1 mm yr⁻¹ in northern Canada. Since these areas were scraped bare by the glaciers, they represent a great transfer and redistribution of SOM and biomass carbon from more southern regions, and of CO₂ from the atmosphere, to the peat lands. The coal and petroleum deposits of the Carboniferous Era formed from enormous accumulations of peat soils in many areas of the world. They represent beds of SOM that were laid down under conditions similar to those that produce the peat lands of today.

Parent material influences SOM contents mainly through its effect on soil texture. In an area of similar climate and topography, SOM content tends to increase with soil clay content. The intimate association of humic substances with inorganic solids as organomineral complexes preserves organic matter. Montmorillonitic clays because of their high surface areas have particularly high adsorptive capacities for organic molecules and are particularly effective in protecting nitrogenous constituents from attack by microorganisms. This strong interaction between clays and organic matter also gives rise to important effects of SOM on soil physical and chemical properties.

As conditions change so does the SOM content. If humanity or nature lays soil bare, the SOM content can recover rapidly by geologic time standards to its previous state, but not fast enough for the human inhabitants of the area. Several years after the volcanic eruptions of Mt. St. Helens in Washington and of Mt. Pinatubo in the Phillipines, plants are reestablishing themselves on fresh-deposited pumice. Mine spoils and their revegetation also show this behavior. Plant growth is sparse in the first years as sulfides in the ores oxidize to sulfuric acid and as the rock minerals begin to weather. After the acid is leached out and some weathering has occurred, the plant increase and the rate of SOM increase follow an S-shaped curve. They start slowly, then increase exponentially, and the rate eventually levels off to a steady-state SOM content determined by climate and topography. The steady state may require 50 years for fine-textured parent material in humid climates, or as much as 1500 years for sandy soils in arid regions. These "new" soils also include flood plain deposits, road cuts, and land no longer cultivated.

Farming more subtly affects SOM. SOM levels may decrease by as much as one-half when untilled lands are cleared and cultivated. The oxidation rate is relatively fast during the first years as the cultivating tools shear soil aggregates and expose SOM that had been relatively protected from microbial attack by a coating of more resistant organic matter. The "minimum tillage" form of cultivation has the goals of minimizing the energy costs of cultivation and of increasing the SOM and nitrogen content.

6.2 THE DECAY PROCESS

The decay of SOM is the oxidation of organic carbon by heterotrophic organisms that utilize the energy of oxidation for their metabolism. The initial breakup of tree trunks and large objects is carried out by animals foraging for grubs, by termites, and by earthworms. Saprophytic plants such as mushrooms and snowflowers also obtain their energy from this partially decomposed plant matter. As the organic matter becomes more finely divided, the size of the decomposing organisms also decreases. Decay proceeds as long as the oxygen, water, temperature, and nutrient levels are adequate for the decomposing organisms. In the desert, the absence of water greatly hinders the oxidation rate of organic material at the soil surface. Beneath the surface of arid soils, where the moisture content is more likely to be adequate, decomposition is rapid.

The annual input rate of dead plant matter to soils in temperate regions, the *net primary productivity* of plants, is about 1 kg m^{-2} of carbon or 20 Mg ha^{-1} of dry matter. The annual input rate is perhaps 2 kg C m^{-2} or 40 Mg ha^{-1} of dry matter in humid tropical forests, and decreases to virtually zero to 0.1 kg C m^{-2} in deserts and arctic tundra. This input is part of the nonhumus organic matter, which includes original plant and microbial tissue and partially decomposed material. These nonhumus substances contain carbohydrates and related compounds, proteins and their derivatives, fats, lignins, tannins, and various partially decomposed products in roots and plant tops. The portion contributed by dead animal matter is insignificant because the

amount of carbon as plant biomass is 10 000 times greater than the carbon in animal biomass.

New plant material is an excellent source of food for soil microorganisms. Microbes are selective: Simple monomers of sugars, amino acids, and fats are oxidized first. The polymers—starch and proteins—follow close behind. Cellulose, the most prevalent plant component, decomposes more slowly. Lignin and hydrocarbons decompose even more slowly. Some plant materials (e.g., pine needles and oak leaves) and some synthetic organic chemicals contain inhibitory compounds and decompose slowly and by only a few microbial species. Shortly after fresh material contacts the soil, microbes begin decomposing it as a source of nutrients and energy (Fig. 6.1). The initial phase of microbial attack is a rapid loss of easily decomposable organic substances. Molds and spore-forming bacteria are especially active in consuming proteins, starches, and cellulose. Their major products are CO_2 and H_2O plus a small amount of new microbial tissue. By-products, especially in partially anaerobic conditions, include small amounts of NH_3 , H_2S , organic acids, plus other incompletely oxidized substances. In subsequent phases of decomposition, when aerobic conditions are present, these intermediate compounds and newly formed microbial tissues are attacked by other microorganisms, with production of some new biomass while a larger fraction of the organic carbon is converted to CO_2 .

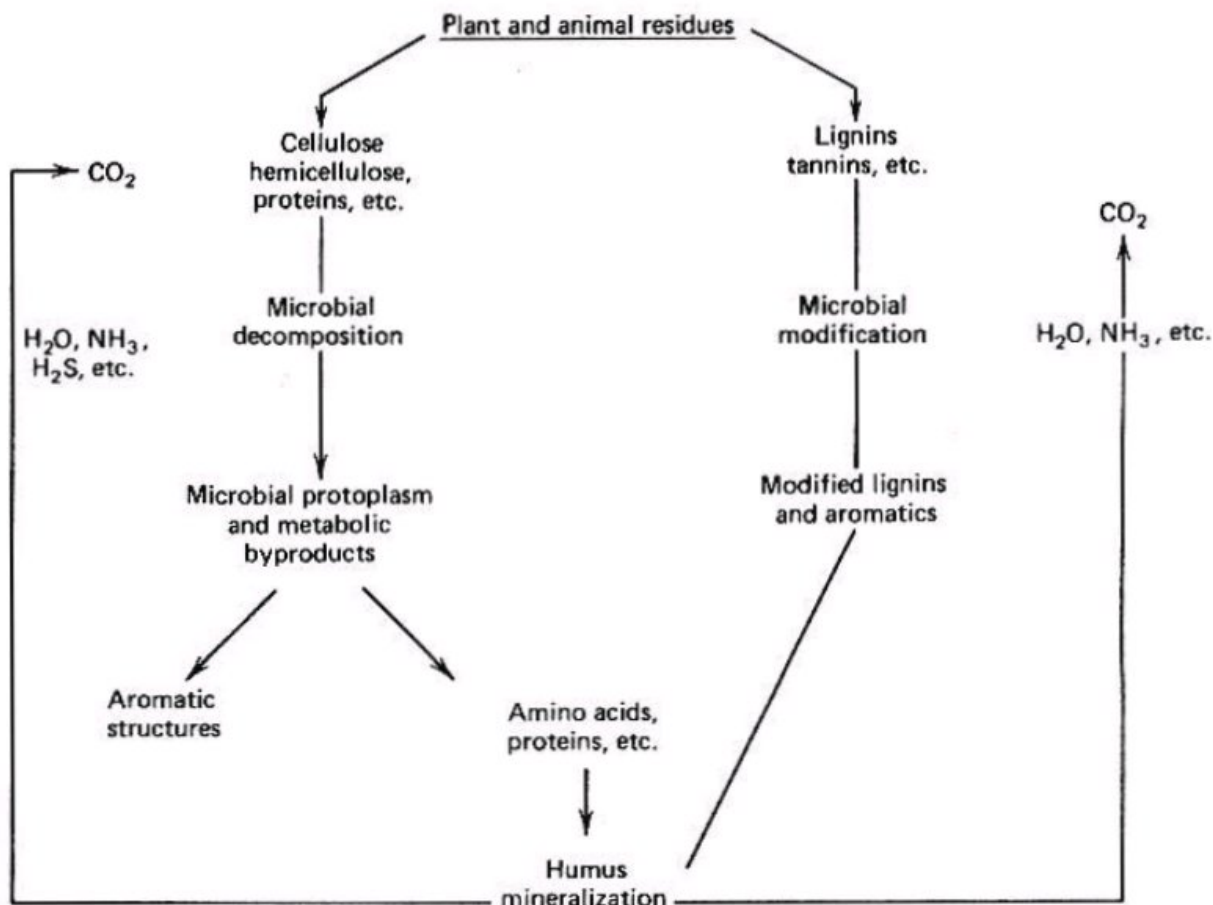


FIGURE 6.1. Organic matter decomposition and formation of humic substances. (From F. E. Bear, ed. 1964. *Chemistry of the Soil*, ACS Monograph Series No. 160, p. 258.)

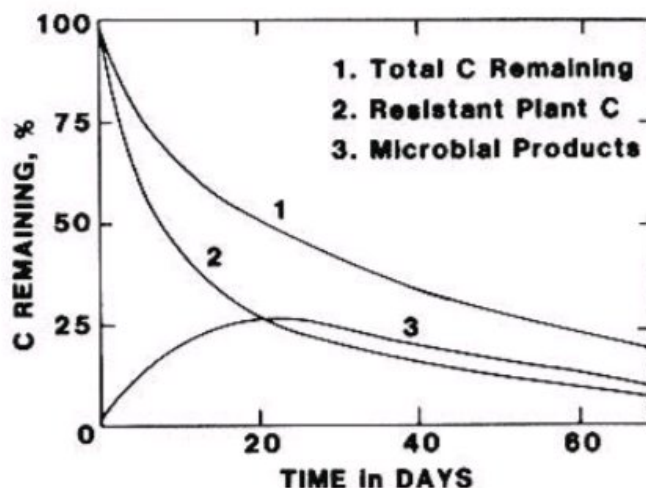


FIGURE 6.2. Idealized diagram for the decay of crop residues in soil under conditions that are optimal for microbial activity. (From F. J. Stevenson. 1982. *Humus Chemistry*. Wiley, New York.)

Figure 6.2 is an idealized graph of crop-residue decay with time in temperate regions. Plant residues are attacked rapidly at first, but the rate of decay soon slows. Considerable plant carbon remains in the soil at this point, but part of the residual carbon occurs as microbial by-products and part as the more resistant plant residues. Different plant components decompose at different rates. Lignin in wood is attacked much more slowly than cellulose. While most is converted into CO_2 , the more readily decomposable constituents are also partially resynthesized by the decomposer microbes into more resistant components. Decay also slows because microbes work on the surface of particles; the resistant material can coat the underlying material and protect it from further decay.

Figure 6.3 shows the course of carbon losses from soils in a temperate climate (England) and a humid tropical climate (Nigeria). The shapes of the curves are similar, but the time scale is four times faster in the tropical climate. The approximate half-life of fresh organic matter in temperate regions is about 3–4 months, but it is as little as 3–4 weeks in the humid tropics. The flatter portion of the curve represents the second stage of organic matter decomposition, with a half-life of about 1.6 years in the humid tropics and 6.2 years in temperate regions.

The final stage of decomposition is the gradual loss of the more resistant plant parts, such as lignin, in which the actinomycetes and fungi play a major role. A small fraction of the original carbon, however, persists for a very long time. When the age of soil organic carbon is measured by ^{14}C dating, a small but extremely old fraction raises the average age of carbon in SOM to about 1000 years in surface soils and to several thousand years in subsoils.

Results of field experiments confirm that carbon becomes increasingly resistant to decomposition with time. This has led some investigators to conclude that the organic component exists in three major fractions when considered on a dynamic basis: (1) decomposing plant residues and the associated biomass, which turn over every few years; (2) microbial metabolites and cell wall constituents that become stabilized in soil and have a half-life of 5 to 25 years; and (3) the smallest fraction, resistant organic matter, ranging in age from 250 to 2500 years or more.

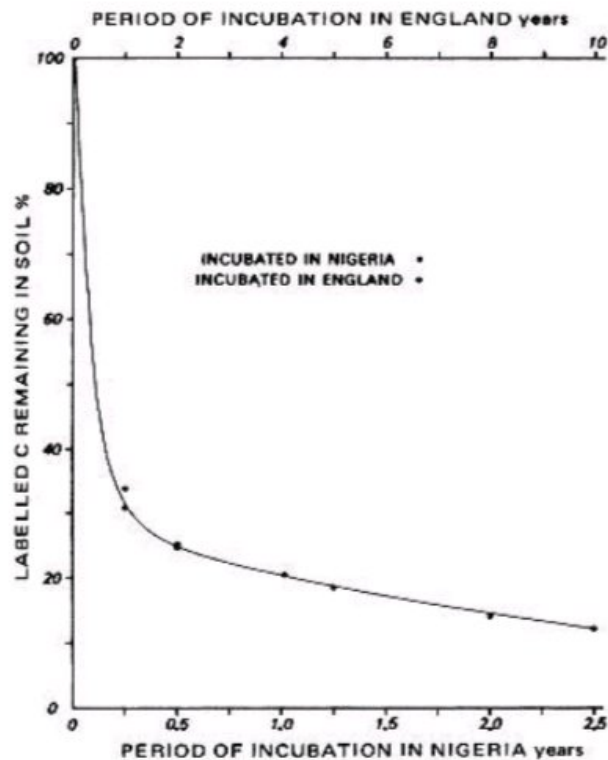


FIGURE 6.3. Decomposition rates of fresh organic matter in England and in Nigeria. (From D. S. Jenkinson and A. Ayanaba. 1970. *Soil Sci. Soc. Am. Proc.* 43:912.)

Despite the stability of the resistant fractions of SOM, 50 to 80% of freshly added organic matter is lost from most temperate soils during the first year. The smaller the particle size, the faster the SOM is destroyed. Plant or animal residues must be added to soils continually if the favorable effects of organic matter on soil properties are to be maintained. To increase the SOM content by adding organic residues to soils is difficult. The decomposition rate of organic materials in soils increases in proportion to the addition rate. The more organic matter added, the more it is oxidized. An experiment in Rothamsted, England, has been adding ca. 30 tonnes ha^{-1} of organic manures to a cultivated soil annually since 1843, without bringing the SOM content back to its uncultivated level.

6.3 EXTRACTION, FRACTIONATION, AND COMPOSITION

Soil organic matter is a complex polymer that can be studied only after it is separated from the inorganic soil fraction and after it has been broken into smaller fragments. Recent advances have lessened the degree to which SOM has to be destroyed to be studied. The separation of organic matter from the inorganic matrix of sand, silt, and clay is not physically difficult, but the extracting agent (traditionally 0.1 to 0.5 M NaOH) is harsh and alters the organic matter through hydrolysis and autoxidation. The components in such extracts can be partially fractionated by precipitation with acids or metal salts, or by taking advantage of solubility differences in various organic solvents. Students interested in the extraction and fractionation procedures should consult the works of Stevenson (1982) and Schnitzer and Schulten (1998).

The classical procedure for fractionation of extracted organic matter involves acid precipitation of some fractions from an NaOH extract, and subsequent dissolution of part of the precipitated material with alcohol (Fig. 6.4). The *humic acids* and *fulvic acids* fractions so prepared are mixture of many different chemical compounds in various stages of polymerization. Stevenson defines them as humic acid, the dark-colored organic material that is extracted from soil by various reagents and that precipitates when dilute acid is added, and fulvic acid, the colored material that remains dissolved in the extracting solution after acidification. Schnitzer and Schulten define humic acid as the fraction soluble in dilute alkali or neutral salt but coagulated by acidification, and fulvic acid as that which remains in aqueous solution after acidification, and *humin* as the fraction that cannot be extracted from soils by dilute base, neutral salts, or acids. Humin is thought to be humic acid-like material that has reacted strongly with inorganic soil components and thereby resists attack by alkalis and acids.

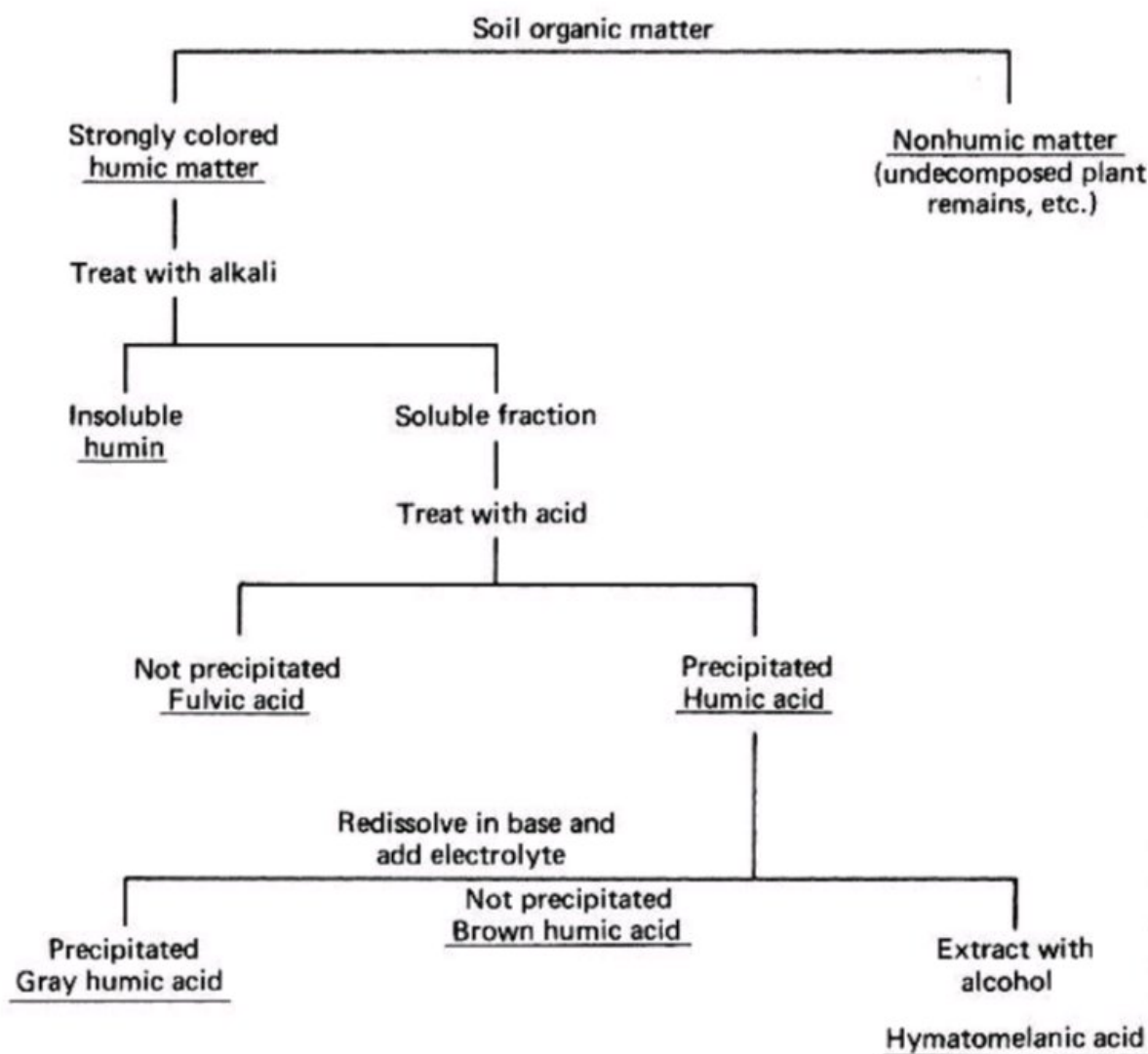


FIGURE 6.4. Fractionation of soil organic matter. (Modified from F. J. Stevenson. 1982. *Humus Chemistry*. Wiley, New York; and J. L. Mortenson and F. L. Hines. 1964. In *Chemistry of the Soil* (F. E. Bear, ed.). ACS Monograph Series No. 160.)

Organic materials undergo microbial enzymatic and chemical reactions in soils to form colloidal polymers called humus (Fig. 6.1). Humus is a complex and rather microbially resistant mixture of brown to almost black, amorphous and colloidal substances modified from the original plant tissues or resynthesized by soil organisms. Humus contains approximately 10% carbohydrates, 10% nitrogen components (proteins, amino acids, and cyclical N compounds), 10% "lipids" (including alkanes, alkenes, fatty acids, and esters), and 70% humic substances.

Chemists have attempted to unravel the details of humus composition for many years. Despite considerable progress in characterizing various extracts, much remains to be discovered. Humus contains primarily C, H, O, N, P, and S plus small amounts of other elements. Only a small but important portion is soluble in water, but much is soluble in strong bases. The various fractions of humus obtained on the basis of solubility characteristics are part of a heterogeneous mixture of molecules, which range in molecular weight from as low as several hundred to over 300 000 (Fig. 6.5). Carbon and oxygen content, acidity, and degree of polymerization all change systematically with molecular weight. The low molecular weight fulvic acids have higher oxygen contents and lower carbon contents than the high molecular weight humic acids. The more soluble fulvic acids are usually responsible for the brownish-yellow color of many natural waters. Humic acids precipitate with acids and polyvalent cations, thus tending to be insoluble.

Recently, SOM has begun to be analyzed by pyrolysis, which is destruction at high temperatures in the absence of oxygen, and analysis of the many volatile compounds that emanate from SOM. Carbohydrates, phenols, lignin and *n*-fatty acids are the

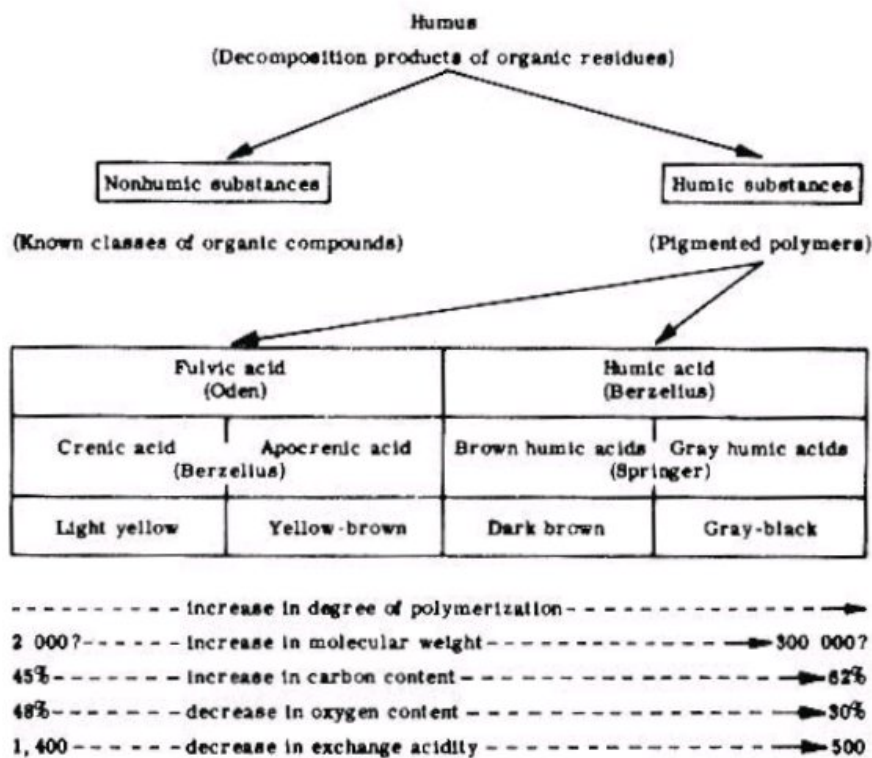


FIGURE 6.5. Classification and chemical properties of humic substances. (From F. J. Stevenson, 1982. *Humus Chemistry*. Wiley, New York.)

major products volatilized. Pyrolysis is a destructive technique but the compounds evolved may lead to a better understanding of humus and soil organic matter.

The composition and structure of soil humus probably varies with the material from which it was derived and with the species of microbe. Although there is no reason to believe that humus from different soils is the same, several researchers agree on a "type" structure for humic acid (Fig. 6.6). Two types of polymers, humic acid (50 to 80% by mass) and polysaccharides (10 to 30% by mass), can constitute up to 90% or more of the total humus in soils. A typical humic acid molecule probably consists of polymers of a basic six-carbon aromatic ring structure of di- or trihydroxyl phenols linked by —O—, —NH—, —N—, and —S— bonds, and containing —OH groups and quinone (—O—C₆H₄—O—) linkages. This structure contains a high density of reactive functional groups. Individual humic acid molecules vary in the structure and density of functional groups, but the basic structure is thought to remain approximately the same.

The chemical origin of humus components is not yet resolved. Some workers consider humus to be microbially resistant plant materials (lignin, suberin, cutins, paraffins, etc.) that are awaiting oxidation to humic acid and further oxidation to fulvic acid. Some have thought that humic materials were the largely nondegraded plant materials, which would account for the aromatic content; microbiologists thought that producing large amounts of aromatic groups was too exotic for soil microbes. A lignin origin for humus, however, would not account for the nitrogen content of humus or for the large amount of alkanes (paraffins) found in recent studies. Lignin in wood is nitrogen-free and synthesis of alkanes (aliphatic hydrocarbons) was thought to be rare. The aromatic (alkene) components have received high attention: They are present in lignin and make up about half of the carbon in SOM. Recent studies indicate that alkanes are also present in SOM and may play a role in binding the aromatic groups together.

6.4 COLLOIDAL PROPERTIES

Most of the colloidal properties of SOM are due to humus. Humus is highly colloidal and is x-ray amorphous rather than crystalline. The surface area and adsorptive capacities of humus per unit mass are greater than those of the layer silicate minerals. The specific surface of well-developed humus may be as high as $900 \times 10^3 \text{ m}^2 \text{ kg}^{-1}$; its exchange capacity ranges from 1500 to 3000 mmol(+) kg^{-1} .

The negative charge (and hence the CEC) of humus is generally agreed to be due to the dissociation of H⁺ from functional groups. All charge on humus is strongly pH dependent, with humic and fulvic acids behaving like weak-acid polyelectrolytes (polyprotonated weak acids). Figure 6.7 shows typical titration curves for peat and soil humic acids. Both buffer soil pH over a wide range. The slopes of humic and fulvic acid titration curves do not change as sharply as for monomeric acids, because of electrostatic effects on the high molecular weight polyacids and because of configurational changes that occur at higher pH.

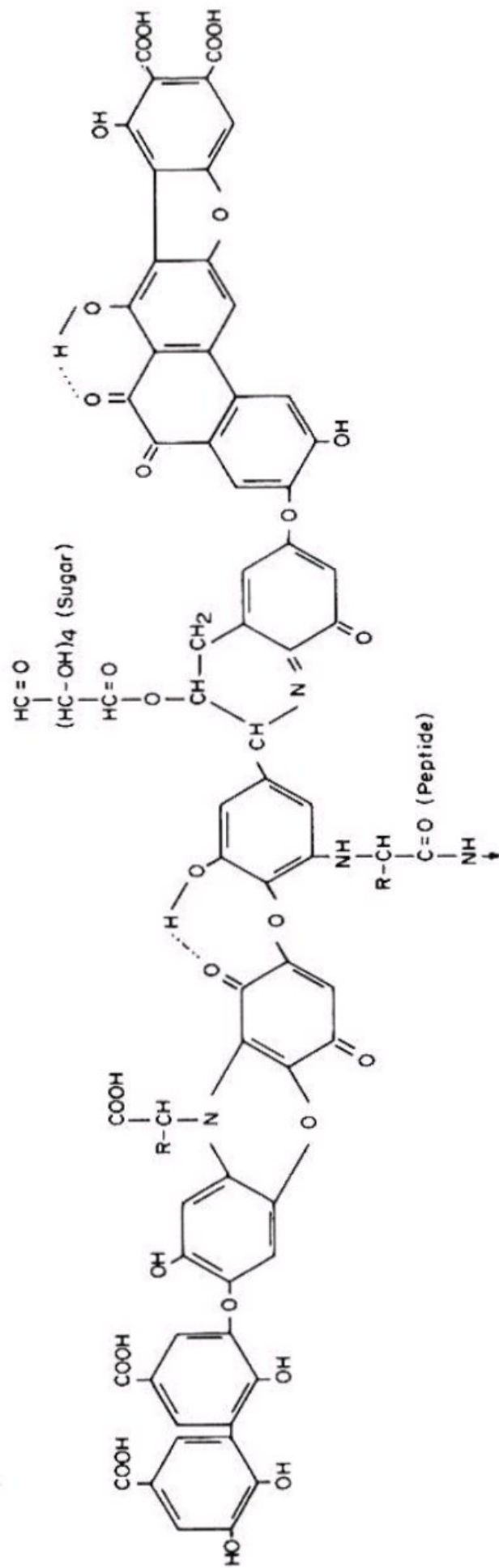


FIGURE 6.6. Hypothetical structure of humic acid. (From J. J. Mortvedt, P. M. Giordano, and W. L. Lindsay, eds. 1972. *Micronutrients in Agriculture*. American Society of Agronomy, Madison, WI.)

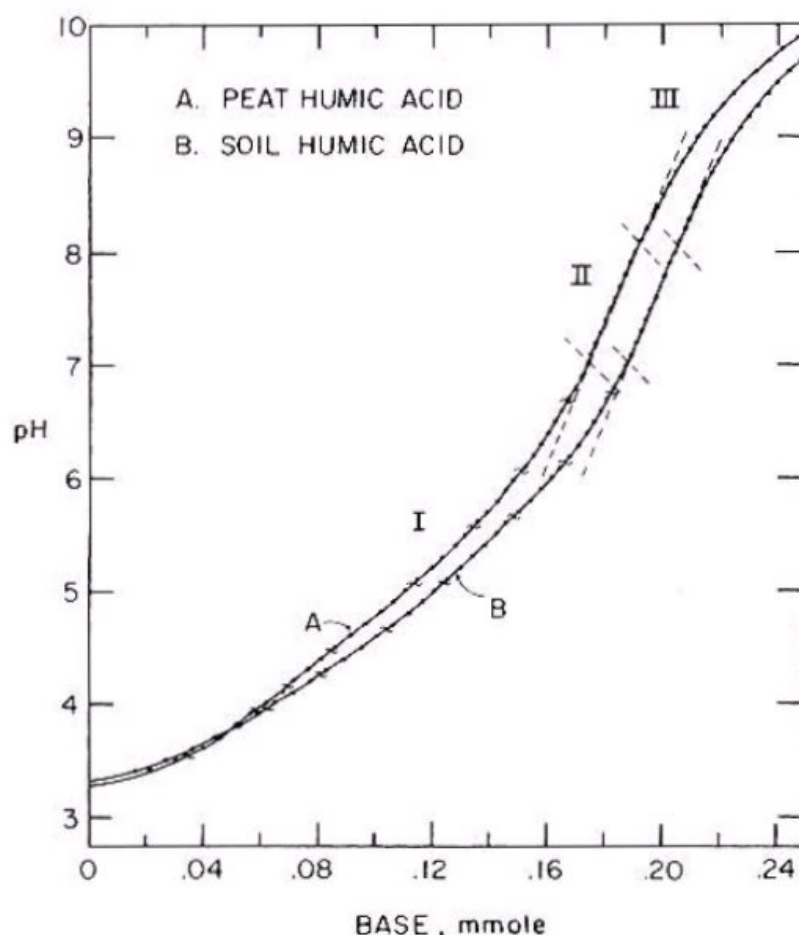
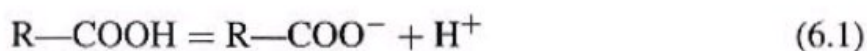


FIGURE 6.7. Titration curves of a soil and peat humic acid. The small wavy lines on the curves indicate endpoints for ionization of weak-acid groups having different, but overlapping, ionization constants. (From F. J. Stevenson. 1982. *Humus Chemistry*. Wiley, New York.)

The dissociation of carboxyl and phenol groups yields perhaps 85 to 90% of the negative charge of humus. Many carboxylic groups are sufficiently acid to dissociate below pH 6 (zone I, Fig. 6.7)



leaving a negative charge on the functional group. Here R represents any number of organic species whose differing electronegativities alter the tendency for H^+ to dissociate. Thus, the various $\text{R}-\text{COOH}$ units dissociate at different pH values. As the pH of a system increases above 6, still weaker carboxylic groups and other very weak acids dissociate (zone II, Fig. 6.7). Zone III represents dissociation of phenolic OH and other very weak acids at $\text{pH} > 8$. Dissociation of H^+ from acid groups throughout the pH range adds to the total negative charge of humus. Dissociation of H^+ from enolic OH, imide ($=\text{NH}$), and possibly other groups also contribute to the negative charge.

No SOM fraction possessing a net positive charge has been found at normal soil pH values (Table 6.2). Protonated groups such as $(\text{R}-\text{OH}_2)^+$ and $(\text{R}-\text{NH}_3)^+$ can yield positive charges, but the overall charge on humus is negative.

Charged sites (primarily COO^-) enable SOM to retain cations in nonleachable but exchangeable forms that are available to plants. The bonding is primarily coulombic

Table 6.2. Effects of pH on cation exchange capacity (CEC) for 60 Wisconsin soils^a

pH	CEC (mmol(+) kg ⁻¹ , Means for 60 Soils)			% CEC from SOM
	Organic Matter	Layer Silicates	Whole Soil	
2.5	360	380	58	1
3.5	730	460	75	28
5.0	1270	540	7	37
6.0	1310	560	108	36
7.0	1630	600	123	40
8.0	2130	640	148	45

^aData of C. S. Helling, G. Chesters, and R. B. Corey. 1964. *Soil Sci. Soc. Am. Proc.* 28:517-520.

or electrostatic (e.g., $-\text{COO}^- \text{K}^+$). The bonding is also partly covalent, particularly when the charge is neutralized by transition-metal cations (Fe^{2+} , Zn^{2+} , Cu^{2+} , Ni^{2+}).

6.5 FUNCTION OF ORGANIC MATTER IN SOIL

Table 6.3 summarizes the general properties of humus and its associated effects on soil. SOM contributes to plant growth through its effects on the chemical, biological, and physical properties of soil. The SOM supplies N, P, and S for plant growth, serves as an energy source for soil microorganisms, and promotes good soil structure. Humus also indirectly affects the plant uptake of microelement and heavy metal cations, and the performance (availability) of herbicides and other agricultural chemicals. SOM is highly porous so that pesticide and other organic compounds added to soils can be enveloped by SOM. In that form they are much less active. Soils with high amounts of SOM require higher dosages to herbicides and pesticides to achieve the desired result.

The SOM supplies nearly all the N, 50 to 60% of the P, perhaps as much as 80% of the S, and a large part of the B and Mo adsorbed by plants from unfertilized, temperate region soils. Indirectly, SOM affects the supply of essential elements from other sources. The amount of N_2 fixation by the free-living bacterium *Azotobacter*, for example, is related to the amount of readily available energy sources in the soil, such as the carbohydrates in SOM.

In humid soils, C, N, and S are found predominantly in SOM. With increasing aridity, the amount of organic matter decreases and the fractions of the inorganic forms of the elements (carbonate, sulfate, and nitrate) tend to increase.

The mass ratio of C/N/S in the SOM of temperate region soils is roughly 100/10/1. Carbon supplies the energy for N and S reduction, as well as the matrix of compounds into which reduced N and S are incorporated and stabilized. Nitrogen

Table 6.3. General properties of humus and associated effects in soil^a

Property	Remarks	Effect on Soil
Color	The typical dark color of many soils is caused by organic matter	May facilitate warming
Water retention	Organic matter can hold up to 20 times its weight in water	Helps prevent drying and shrinking; improves moisture retention in sandy soils
Combination with clay minerals	Joins soil particles into structural units called aggregates	Permits gas exchange; stabilizes structure; increases permeability
Chelation	Forms stable complexes with Cu^{2+} , Mn^{2+} , Zn^{2+} , and other polyvalent cations	Buffers the availability of trace elements to higher plants
Solubility in water	Insolubility of organic matter results partially from its association with clay; salts of divalent and trivalent cations with organic matter are also insoluble; isolated organic matter is partly soluble in water	Little organic matter is lost by leaching
pH relations	Organic matter buffers soil pH in the slightly acid, neutral, and alkaline ranges	Helps to maintain a uniform reaction (pH) in the soil
Cation exchange	Total acidities of isolated fractions of humus range from 3000 to 14 000 mmole kg^{-1}	Increases the cation exchange capacity (CEC) of the soil; from 20 to 70% of the CEC of many soils is caused by organic matter
Mineralization	Decomposition of organic matter yields CO_2 , NH_4^+ , NO_3^- , PO_4^{3-} , and SO_4^{2-}	A source of nutrient elements for plant growth
Combination with organic molecules	Affects bioactivity, persistence, and biodegradability of pesticides	Modifies the application rate of pesticides for effective control

^aFrom F. J. Stevenson. 1982. *Humus Chemistry*. Wiley, New York.

and sulfur, in turn, are among the elements that govern the rate of plant growth and photosynthesis. The result under natural conditions is a relatively constant C/N/S ratio in SOM.

The availability of many microelement cations is strongly affected by SOM. Various low molecular weight and somewhat water-soluble components of SOM, such as fulvic acid, form stable complexes (chelates) with Fe^{2+} , Cu^{2+} , Zn^{2+} and other polyvalent cations. These shield the cations from hydrolysis and precipitation reactions

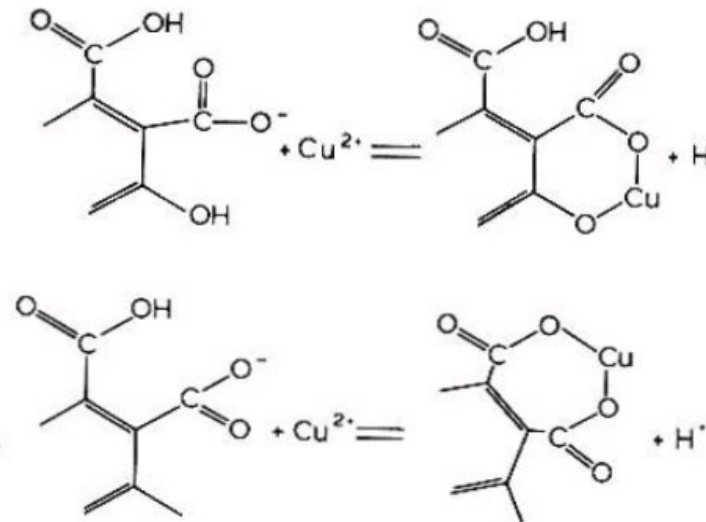


FIGURE 6.8. Postulated reaction between Cu^{2+} and fulvic acid function groups. (After D. S. Gamble et al. 1970. *Can. J. Chem.* 48:3197.)

and therefore increase their water solubility. A typical reaction between Cu^{2+} and the functional groups of fulvic acid is given in Fig. 6.8. Inorganic precipitation, particularly in soils of high pH, greatly reduces the solubility and availability of many of the essential microelements. Organic amendments (manure, sewage sludge, etc.) can improve microelement availability in alkaline soils and correct Fe and Zn deficiencies in particular. The amendments apparently release microelements in chelated form or release (mineralize) fulvic acid compounds that chelate the inorganic Fe and Zn present in the soil. SOM also combines with toxic ions such as Cd^{2+} and Hg^{2+} , as well as with microelement cations at high concentrations, and reduces their availability. Organic amendments to soils often decrease cation toxicities in acid soils.

Soil organic matter is involved with soil acidity. In mature Swedish forests, for example, the soil pH is perhaps 3.5. After harvest and while the succeeding trees are young, the pH is >4 . The pH then decreases steadily as the forest matures, only to rise again when those trees are harvested. This pH cycle is thought to be due to organic acids formed by increasing litter fall. When litter production stops or slows and the organic acids decay or are leached away, the soil pH rises. In New England, part of the pH decline in formerly cultivated fields may be due to increased organic acids produced by greater leaf litter as trees invade the fields. In both cases, the pH is too low to be caused by Al^{3+} hydrolysis, and Al hydrolysis would not account for the cyclical pH change.

Humus affects soil structure and thus soil tilth, aeration, and moisture retention. The deterioration of structure that accompanies intensive tillage is usually less severe in soils adequately supplied with humus. When humus is lost, soils tend to become hard, compact, and cloddy.

Aeration, water-holding capacity, and permeability are all improved by humus. The frequent addition of easily decomposable organic residues leads to the synthesis of complex organics (e.g., polysaccharides) that bind soil particles into aggregates. The intimate association of clay-sized particles (layer silicates) with humus via cation (e.g., calcium, magnesium, aluminum, iron) bridges also promotes aggre-

gation. The water-insoluble salts of humic acid with polyvalent cations are called *humates*. They tend to be amorphous and glue-like. Heavy (clayey) soils, in particular, benefit from organic matter additions by promoting particle aggregation. Aggregation yields a loose, open, granular structure for good water and air permeability.

Humus also absorbs large quantities of water. The fully synthesized humus of a mineral soil contains as much as 80 to 90% water by weight. Additionally, micropores within larger soil aggregates hold available water for plants. This increase in plant-available water-holding capacity is a major benefit of organic matter additions to sandy soils.

The data in Table 6.2 point out important characteristics of the CEC of SOM. All of the charge of humus is pH dependent, even at low pH. The CEC of both organic matter and layer silicates increases with increasing soil pH, but the CEC of SOM increases faster with pH than that of the layer silicates. In one soil, for example, the SOM contributed only 1% of the total CEC at pH 2.5, but 45% at pH 8.0. In soils dominated by low-CEC layer silicates, such as kaolinite, the relative contribution of organic matter to whole-soil CEC can be even greater. A large fraction of the CEC in most soils is due to SOM.

The functional groups responsible for the high CEC of humus also buffer soil pH over a wide range. This buffering contributes significantly to the lime requirement of acid soils (Chapter 8). Total acidities of isolated fractions of humus vary from 3 to 14 mol kg⁻¹.

6.5.1 Organic Chemical Adsorption

Organic matter content is the soil factor most directly related to the sorption of most herbicides and organic compounds by soils. The manner in which organic matter sorbs organics is discussed more fully in Chapter 7. The SOM content strongly influences pesticide behavior in soil, including effectiveness against target species, phytotoxicity to subsequent crops, leachability, volatility, and biodegradability. Recommended herbicide application rates are often higher for soils high in organic matter content, to compensate for greater adsorption in these soils. The soil behavior of organic chemicals, and particularly their interaction with SOM, is an active area of current soil chemistry research.

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QUESTIONS AND PROBLEMS

1. Distinguish between soil organic matter, humus, and soil biomass.
2. Give representative SOM contents for Mollisols, Aridisols, Oxisols, and Histosols. Justify the SOM content of each in terms of the factors of soil formation.
3. Explain why the SOM content of soils in a given climatic zone tends to be higher in fine-textured soils than in coarse-textured soils.
4. Describe the overall decay process of SOM, including discussions of the organisms involved, the decomposition products, and the time necessary for the process.
5. If increased SOM contents are so beneficial to soils, why don't farmers manage their soils to increase SOM?
6. What are the chemical properties of humus that make it special?
7. How does SOM contribute to the chemical, physical, and biological properties of soil as a medium for plant growth?
8. How may SOM alter micronutrient and trace metal availability in soils?
9. What is the buffering capacity of humus expressed in terms of CaCO_3 equivalent? Assume 50% dissociation of humus acidity over the pH range of 4 to 7.
10. How may SOM affect pesticide recommendations, and why?
11. Explain how only a few percent organic matter can exert a profound influence on soil properties.
12. Assuming that layer silicates and organic matter exist independently in a soil, calculate a reasonable cation exchange capacity of a soil containing 40% montmorillonite and 3% organic matter. Repeat the calculation for a soil that
 - (a) Contains 40% kaolinite and 3% organic matter.
 - (b) Contains 20% kaolinite and 1.5% organic matter.
 How realistic are such calculations?
13. Is SOM amphoteric? Explain.
14. What are the primary functional groups responsible for charge development in SOM?