

CHAPTER-6

CARBON TRANSFORMATIONS AND SOIL ORGANIC MATTER

Concern about high levels of carbon dioxide in the earth's atmosphere constitutes the public's pivotal interest in the global carbon cycle. For soil scientists, other pools and fluxes of carbon are of equally high interest. Particularly important is the balance between autotrophic fixation, primarily by green plants, which brings carbon from the atmosphere into the biosphere, and respiration, which releases carbon dioxide back to the atmosphere. Much of the respiratory activity on earth occurs in the soil. Soil respiration represents decomposition of organic residues, root respiration, and slow decay of soil organic matter (SOM). Currently soil scientists are refocusing considerable effort towards quantifying soil respiration. Beginning in the eighteenth century, land cleaning with accompanying cultivation accelerated soil respiration and was the largest contributor to carbon dioxide buildup in the atmosphere from that time until 1950. We now recognize that accelerated soil respiration occurs during the initial 50+ years of cultivation of virgin soils; during that period, top soil may lose 30 to 50% of their organic carbon. Nevertheless, SOM in mineral soils remains a major storehouse or sink of global carbon, containing about twice that in the atmosphere. Thus, any change in this pool can significantly influence the global carbon dioxide level.

Each of the two major biological fluxes of carbon dioxide in nature, namely, photosynthetic fixation and global respiration, transfers about 7% of atmospheric carbon annually, but in opposite directions (Bolin, 1983). Put another way, 15 years of photosynthetic fixation without renewal by respiration would exhaust the atmosphere of its carbon dioxide.

In an agricultural ecosystem, crop residues constitute the primary carbon source that furnishes substrate for the soil biota and gives rise to the respiratory release of carbon dioxide into the local atmosphere. Decomposition of organic residues is a major function of the vast soil microbial population. These residues, the bulk of which are of plant origin constitute a reservoir of energy stored in carbon compounds. Heterotrophic soil microorganisms need the energy in carbon sources derived through photosynthesis of green plants to grow, multiply, and survive.

The simplest diagram or form of the C cycle might look something like that shown in Figure 6-1. This is a gross oversimplification in terms of geochemical cycling. However, it demonstrates the essential points. Carbon dioxide is fixed via photosynthesis into carbohydrate and other reduced compounds. These, in turn, are ultimately metabolized aerobically to CH_4 and CO_2 .

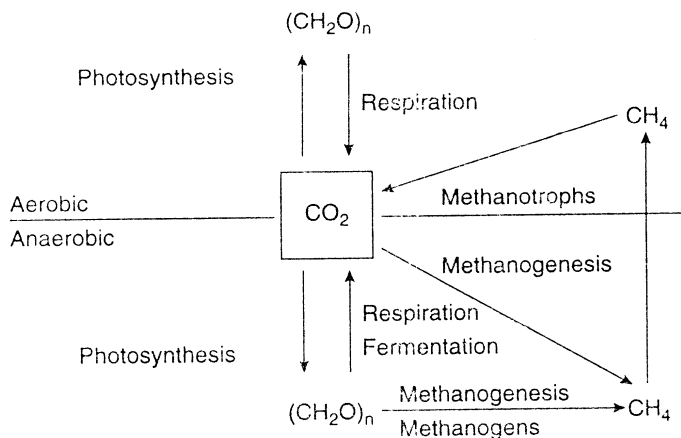


Figure 6-1: A simple diagram of the C cycle.

MICROBIAL CARBON CYCLING

Microorganisms play the central role in converting reduced C compounds to their elemental forms. Microorganisms are nature's garbage disposal agents. Without them, decomposition would be unbelievably slow. In their search for energy, microorganisms feed on reduced organic compounds. As a result, they are the driving force behind C cycling, and C cycling is the driving force behind nearly all nutrient cycling reactions involving organic S, N, or P.

Any biologically synthesized organic compound can be decomposed by soil microorganisms. If it is naturally made, it is decomposed. This is the Theory of Microbial Infallibility, first articulated in this form by Martin Alexander, a soil microbiologist at Cornell University of USA. We know this has to be true, otherwise in the course of geologic time there would be vast accumulations of undecomposed C compounds. Any organic compound that contains energy in reduced bonds is ultimately used as an energy source. In general, microbial life is limited by C.

ATMOSPHERIC CARBON

A rather small amount of C is actually available in the atmosphere, plants, and soil biomass, about 2.1×10^{15} kg (Schlesinger, 1991). The remaining available C is in soil (3.5×10^{15} kg) or is dissolved in the oceans (38.0×10^{15} kg). Most of Earth's C is locked up in fossil fuels or carbonate (43×10^{18} Kg). The CO_2 in the atmosphere has risen from about 250 ppm in 1850 to its present concentration of about 360 ppm (0.036% by volume). The increase in atmospheric CO_2 would have been more rapid except for the buffering capacity of the ocean (Schlesinger,

1991). About 40% of the CO₂ released through industrial and human activity dissolves in the oceans as carbonate and bicarbonate. Some immobilization in terrestrial biomass may have also occurred.

The increase in atmosphere CO₂ seems to have come from burning fossil fuels, which fits into the framework of the industrial revolution, but this is not the only cause. There have been other sources of CO₂ entering the atmosphere over the last 100 years. These sources are partly agricultural, due to the cultivation of forests and prairies, soil microbial respiration, forest clearing and burning, and the opening of new cropland. The increased cultivation of soil has resulted in a net loss of C from terrestrial ecosystems.

ORGANIC CARBON

Most organic C in soil comes from plants. This C represents the residue of plants on the soil surface and organic C coming from the decomposition of roots in soil. Plant C can be roughly characterized as follows:

1. Carbohydrates (30-75% of dry weight)

Cellulose (15-60%)

Hemicellulose (10-30%)

Sugars and starches (1-5%)

2. Lignin (10-30% of dry weight)
3. N-containing compounds (1-15% of dry weight) Proteins and amino acids
4. Waxes and pigments (1%)
5. Pectin (1%)
6. Others (5-20% of dry weight)

Fats, oils, organic acids, hydrocarbons

As the plants age, these values vary because the cellulose, hemicellulose, and lignin contents increase while the simple sugars, amino acids, proteins, fats and oil decrease.

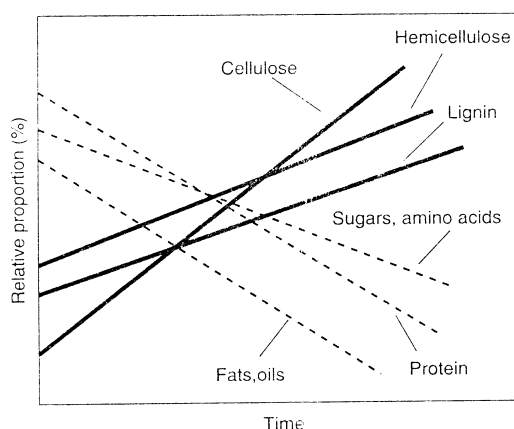


Figure 6-2: Changing composition of aging plant material. The proportion of soluble components in plant material decreases while the proportion of insoluble and resistant components increase.

MICROBIAL UTILIZATION OF PLANT CARBON

Utilization of plant structural components by soil microorganisms presents significant problems. Physical barriers are imposed by meshworks of cell wall components such as polysaccharides, cutins, and suberins. Relatively inaccessible, stable crystalline regions in molecules such as cellulose and chitin impede degradation. Lignin slows the rate of decomposition mostly by physical protection. Filamentous fungi are important in decomposition partly because they penetrate these physical barriers. The greater the polymerization and rigidity of the C building blocks, the slower the decomposition. Water is required for hydrolysis and to increase the surface area available for enzymatic degradation. Some plant products have bacteriostatic and fungistatic properties.

Most plant material contains mixtures of different polymers such as cellulose, hemicellulose, pectins, and lignin. Their decomposition requires the combined action of many microorganisms, none of which has all of the enzymes required to completely decompose plant material. In plant tissue, decomposition is generally initiated by fungi and continued by bacteria and actinomycetes so there is the combined action from a range of microorganisms and the combined action by the range of enzymes that these microorganisms produce.

Any environmental factor that affects the activities of the soil biota may influence the decomposition of organic residues. These factors include moisture, temperature, pH, O₂, inorganic nutrients, and clay. For example, decomposition of organic matter is more rapid in tropical than temperate regions partly because it is warmer and also because the microorganisms have a higher metabolic rate for longer periods.

Substrate quality also has an effect on decomposition. Two-thirds of the C added to soil is lost in the first year. If the C:N ratio is much greater than 20-31:1, immobilization of N will result, but another consequence is that there could be inadequate N to sustain decomposition. Consequently, decomposition of C slows down. However, structural complexity is a more important determinant of substrate decomposition than is the C:N ratio. Lignin content slows decomposition because it has no N, but it is more important that lignins are structurally complex, large, and insoluble in water.

As a general rule, the ease with which C-compounds decompose is starch > hemicellulose > cellulose > lignin. Yet, surprisingly, soil carbohydrates are estimated to be 15% of the soil C even though in a free state they are readily degraded. Polysaccharides persist in soil for several

reasons. They adsorb to clay and become less available. They interact with multivalent cations such as Fe, Al, and Cu, which render them somewhat toxic to microorganisms. Probably the most important reason is that polysaccharides aggregate soil particles, and in doing so they form microaggregates that isolate them from microorganisms and become opened only when the soil is disturbed.

INCORPORATION OF ORGANIC CARBON INTO SOIL

After an extended incubation period, the proportions of different types of plant material retained in soil are usually similar, even though the initial plant composition may differ. If you add straw or glucose to soil, the glucose is used much faster than is the straw, but both substrates are ultimately incorporated into soil organic matter to about the same extent-about 20%. Some substrates are oxidized after a lag period. This could reflect their solubility, difficulty in decomposing, or novel structure. Others, such as ethanol and acetate, are oxidized immediately, suggesting that soil microorganisms are exposed to these simpler compounds repeatedly and are always ready to decompose them.

The pH of the soil environment affects the rate of organic C incorporation, but not the ultimate amount that is incorporated. As the pH of the soil decreases from neutral to acidic, the C remaining in plant material in soil decreases more slowly, but after 5 years, there is relatively little difference.

Complex materials that are added to soil undergo physical, biochemical, and biological changes during decomposition in which polymers are degraded to monomers, reduced compounds become increasingly oxidized, and rapidly growing microorganisms subsisting on easily degraded compounds are replaced by slower growing microorganisms subsisting on recalcitrant compounds. Figure 25-3 illustrates these changes.

SOIL ORGANIC MATTER (SOM)

Soil organic matter is composed of decomposing residues, by-products formed by decomposition, microorganisms, and resistant soil humic material. Different ecosystems have different amounts of soil organic matter, partly because of different temperature and decomposition rates. In some ecosystems, such as tropical rain forests, about as much C is above ground as is below ground, in other, particularly the tundra, far more C is below ground than is above ground.

The tropical ecosystems represent the greatest aboveground organic C pool while tundra represents the greatest below ground organic C pool. Decomposition of 1 peta gram (10^{15} g or 10^{12} Kg) is equivalent to enriching the CO_2 in the atmosphere by 0.47 ppm. So, rain forest destruction and global warming create a vicious cycle. As the tropical rain forests are cut down, CO_2 in the atmosphere increases. As CO_2 increases, the temperature warms. As the temperature warms, decomposition in tundra ecosystems increases, which leads to more CO_2 production, and so on.

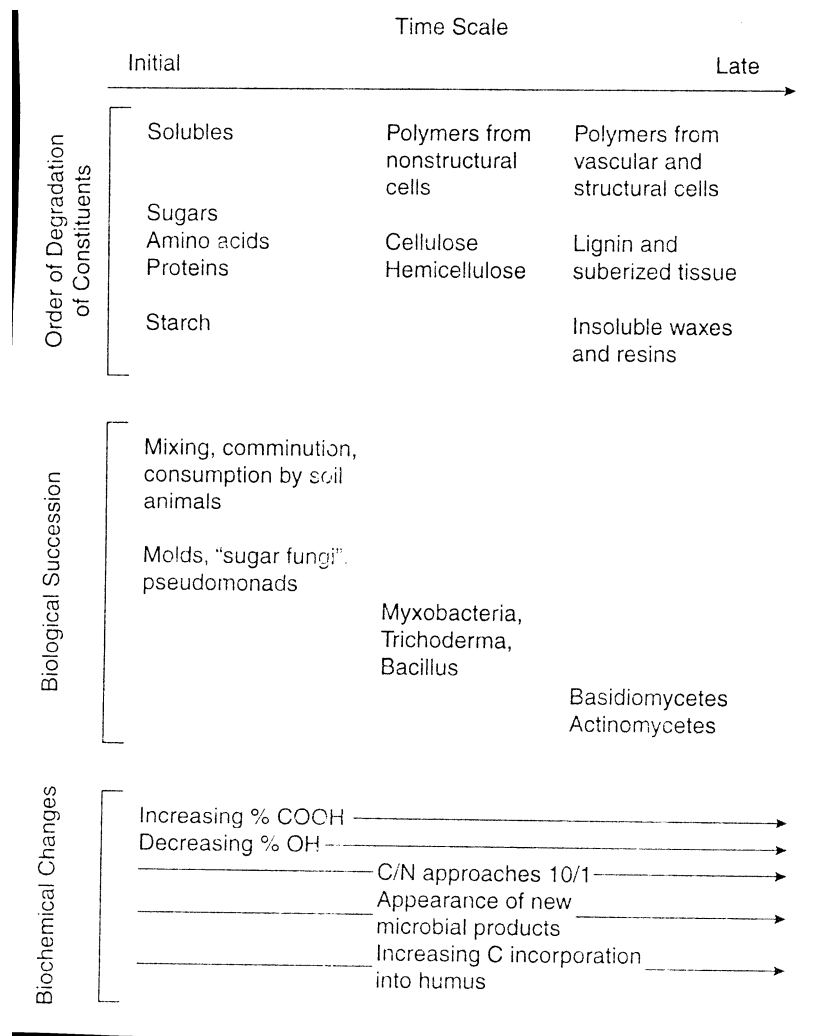


Figure 6-3: Physical, chemical and biological changes that occur during the decomposition and incorporation of organic carbon into soil organic matter.

The most important concept to learn from this chapter is that the greatest single factor controlling productivity in cultivated and uncultivated soil is the amount and depth of soil organic matter. This concept has its limitations in the sense that a Histosol, or peat soil, even though it has

abundant organic matter, is not necessarily the most productive soil for physical reasons. Likewise, although wetland soils have a lot of organic matter, they aren't necessarily productive for agriculture because they contain too much water. It's always possible to have too much of a good thing.

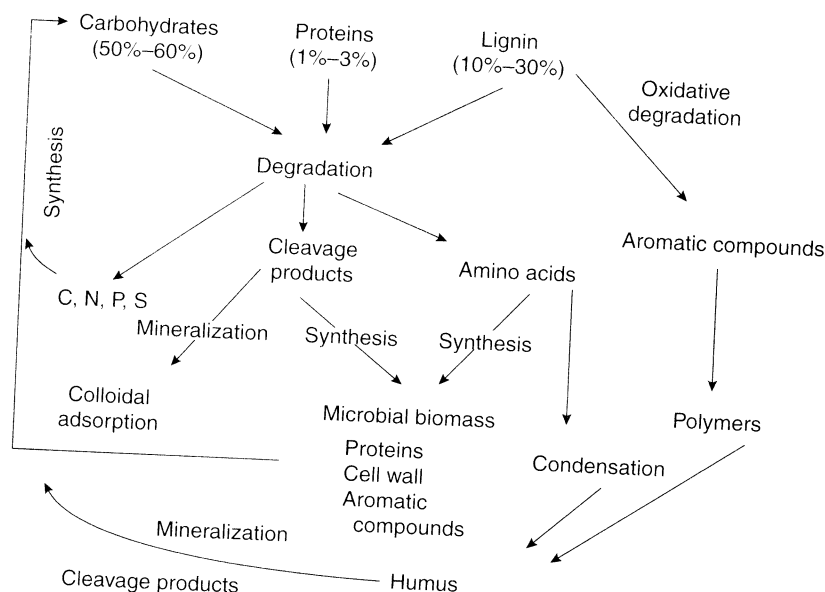


Figure 6-4: Steps in the cycling of soil C and the formation of soil organic matter.

Soil organic matter is formed by the decomposition of plant components into low-molecular-weight compounds that then repolymerize. The C in soil organic matter comes from carbohydrates, which are primarily of microbial origin once decomposition has been completed, or from nitrogen-containing compounds, aliphatic fatty acids and alkanes, oily compounds, and aromatic compounds that generally come from the decomposition of lignin (6-4). Thus, the exact nature of soil organic matter is not clear. It has no definite chemical formula, no defined structure, and no defined shape.

HUMUS:

The more ambiguous, less clearly defined fraction of soil organic matter is known as humus. Humus is the amorphous, colloidal, microbially altered, and relatively stable portion of soil organic matter. Humus forms from condensation of phenolic and amino-quinone intermediates (Figure 6-5). In the polyphenol theory of humus formation, lignin degrades to polyphenols such as catechol (this can be spontaneous in alkaline environments, but most likely is caused by enzymes), which are oxidized to quinones (Paul and Clark, 1996). The quinones, in turn, react

with amino compounds and amino acids to form nitrogenous polymers that combine to form larger nitrogenous polymers.

The primary characteristic of soil humus is its resistance to degradation. Humus removed from soil degrades more slowly than do most other organic compounds, but faster than humus in soil. Humus is resistant to degradation in soil because of its physical protection during the formation of micro-aggregates and micropores and its extensive interactions with soil minerals (clays, oxides, and amorphous material). The interactions directly reduce the availability of humus.

Humus also resists degradation because it can be very large. It forms immobile, sometimes hydrophobic, complex globular structures of low solubility. Because humic materials can be large and insoluble, they must first be attacked by extracellular enzymes. In addition, humus has a polyaromatic character with highly cross-linked, random, varied, and disordered structures that are due to chemical condensation reactions. This material can bind and inactivate attacking enzymes.

Fractionation of Humus

Humus is generally fractionated into three components following extraction in NaOH: *humin*, *fulvic acid*, and *humic acid*.

Humin:

Humin is the non-NaOH dispersible fraction.

Humic acid:

It is a NaOH soluble fraction of humus that is insoluble at pH2. The molecular weight of humic acid varies from 10,000 to 100,000 and it is composed of aromatic rings, cyclic nitrogen compounds, and peptide chains of indeterminate structure. Humic acid has an overall composition of 57% C and 4% N. The functional groups of humic acid are COOH, phenolic OH, alcoholic OH, and ketones.

Fulvic acid:

Fulvic acid is soluble in NaOH and soluble at pH2. It is smaller than humic acid, with molecular weight ranging from 1,000 to 30,000. Fulvic acid contains highly oxidized aromatic rings with numerous side chains. Fulvic acids in lower soil horizons are formed by the leaching of organic constituents from horizons above.

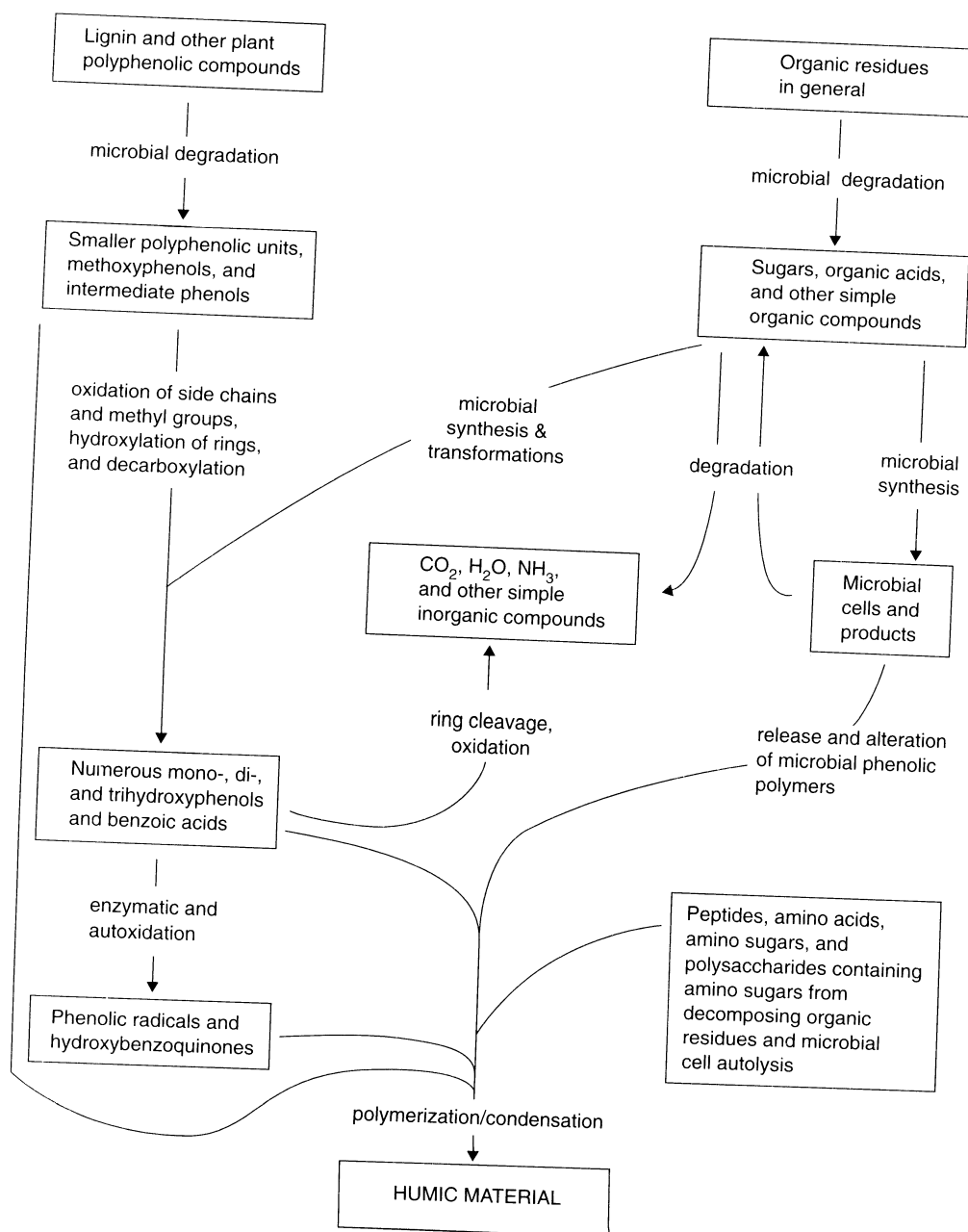


Figure 6-5: A schematic representation of humic acid synthesis in soil.

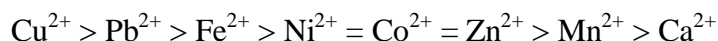
Fulvic acids are more acidic than humic acids. Humic materials are absorbed to clay by polyvalent cations such as Ca^{2+} and Fe^{3+} . They also form association with hydrous oxides. At low pH, the humus contributes to anion exchange capacity. We say that humic materials have pH-dependent charge because their overall charge alters in response to the change in the environment's pH - positive in acidic environments and negative in alkaline environments.

SOIL CONDITIONERS

Soil conditioners are used to improve soil physical and chemical conditions by treatment with chemical or biological materials. These materials include adhesive polymers such as polyvinyl acetate, polyacrylamide, polyvinyl pyrrolidone, polyethylene glycol, and polyvinyl alcohol. Well-rotted compost, to use the organic farmer's terminology, provides the same functions as a soil conditioner. The aim of adding soil conditioner to soil is to complement natural processes of soil aggregation by enhancing all factors that favor aggregation. The strategy is to enhance the strength of soil aggregates.

INTERACTION WITH METALS

Soil organic matter reacts with metals in soil. Plants growing in soil with high organic matter show less aluminum (Al) toxicity than do plants in soil at the same pH with lower organic matter. It's thought that Al is exchanged from organic matter binding sites. The amount of Al adsorbed by peat increases with increasing pH. This is not surprising if you remember that the cation exchange capacity (CEC) of humic acids increases with increasing pH. Humic substances at a pH of 6.0 to 7.0 have an overall negative charge. Aluminum binding is probably due to carboxyl groups ($-\text{COO}^-$) on the humic substances. Humic substances bind divalent cations (M^{2+}) preferentially over monovalent cations (M^+). Their preference for binding divalent cations is something like this:



A quick method of immobilizing heavy metal such as Cu^{+2} and Pb^{2+} in soil is to mix the soil with a lot of organic material. This only works temporarily because the metals can be released again once the organic matter mineralizes.

BENEFICIAL EFFECTS SOIL ORGANIC MATTER

Following list illustrates the importance of adopting soil management systems, such as no-tillage, crop rotation, and manure addition, which maintain, if not augment, the level of organic matter in soil.

Biological properties

- Provides a slowly available carbon and energy source to support a large, diverse, metabolically active microbial population
- Source of certain compounds that may exert plant growth-promoting effects

Chemical properties

- Increases cation exchange capacity of soil (often 20 to 80% of the total CEG is due to organic matter)
- Buffers pH change
- Provides a slow release supply of organically bound nutrients such as nitrogen, phosphorous, and sulfur.
- Enhances chelation and thus bioavailability of trace elements to plants
- Accelerates mineral weathering and aids in solubilization of plant nutrients (such as phosphorus) from otherwise insoluble minerals
- Has a high adsorptive capacity for organic compounds and thus reduces the bioavailability of toxic xenobiotics

Physical properties

- Contributes to improving soil structure and aggregation
- Decreases bulk density and thus increases percentage pore space
- Increases total water holding capacity, but may also increase the strength with which water is held
- Increases heat absorption in early spring due to dark color, but soil often holds more water which requires more energy to heat

SOIL CARBON SEQUESTRATION

Since the industrial revolution began about 150 years ago, the atmospheric level of carbon dioxide has increased by an estimated 30%. As the carbon dioxide concentration in the atmosphere increases, there is worldwide concern about the impact of potential global climate change. In order of their importance, the increase in atmospheric carbon dioxide level has been attributed to:

1. fossil fuel combustion;
2. agricultural activities including deforestation with associated biomass burning when converting natural ecosystems to agricultural along with subsequent soil cultivation; and
3. Industrial manufacturing of cement, ammonia-N fertilizers, and lime.

It is estimated that most agricultural soils and severely eroded soils have lost 30-50% and 70-80% of their original organic carbon, respectively. One way to reduce the amount of atmospheric carbon dioxide is carbon sequestration, whereby the carbon dioxide is removed by

photosynthesis and dissolution and the carbon is stored in the soil as organic matter or secondary carbonates. Sequestration of soil organic carbon is primarily the conversion of plant and microbial carbon into soil organic matter. Such practices as no-till or conservation tillage have been shown to result in increased soil organic matter levels. Restoration and protection of wetlands would also be expected to reduce organic matter decomposition. The limited potential for carbon sequestration in inorganic forms is based upon formation of secondary carbonates and leaching into ground water. Soils have the potential to accommodate a substantial amount of carbon. Photosynthesis would remove the atmospheric CO₂-C, and the soil organic matter levels in cropland, grassland, and forests would be increased if appropriate soil management technology is adopted.