ORGANIC MATTER

Contents

Principles and Processes

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Introduction

The presence of organic matter (OM) distinguishes the soil from a mass of rock particles and allows it to become a living system. Soil organic matter (SOM) serves as a soil conditioner, nutrient reservoir, substrate for microbial activity, preserver of the environment, and major determinant for sustaining and increasing agricultural productivity. The OM content of soils ranges from less than 1% in desert soils to close to 100% in organic soils. A typical agricultural soil may contain between I and 5% OM in the top 15 cm. The main emphasis of this article is on the analytical characteristics of SOM fractions and on studies on their chemical structure. Based on the results of extensive researches, a two-dimensional humic acid (HA) model structure was formulated which has been subsequently converted, with the aid of computational chemistry, to a three-dimensional HA model structure.

The term 'SOM,' as used in this article, refers to the sum total of all organic carbon-containing substances in soils. The major components of SUM are humic substances, especially HA; other significant components are carbohydrates, proteinaceous materials, and lipids.

Extraction and Fractionation of Humic Substances

Extraction of Humic Substances from Soils

Because, in soils, humic substances and inorganic soil constituents are closely associated, it is necessary to separate the two before either can be examined in greater detail. The most efficient extractants for humic substances are either dilute base (0.1—0.5 mol l^{1} NaOH solution) or dilute neutral salt solutions such as aqueous 0.1 mol l^{1} $Na_4P_2O_7$.

Fractionation of Extracted Humic Substances

Most soil OM chemists partition the humic substances extract into the following three fractions: (1) HA, which is that fraction of the extract that coagulates when the extract is acidified to pH 2; (2) fulvic acid (FA), which is that fraction of the extract that remains in solution when the alkaline extract is acidified, that is, it is soluble in both alkali and acid; and (3) humin, which is that humic fraction that remains with inorganic soil constituents, that is, it is insoluble in both alkali and acid.

A number of objections have been raised to the use of alkaline extractants. The latter may extract silica from minerals, protoplasmic components from organic tissues, and bring about the auto-oxidation of some organic components, and the condensation of amino groups of amino acids with carbonyl groups of reducing sugars to form Maillard-type reaction products. Some of these changes can be minimized by doing the extractions in atmospheres of inert gases, but not all possible changes can be excluded.

In Situ Analysis of SOM

Cross-polarization magic angle spinning 13C nuclear magnetic resonance (CP-MAS ‘3C NMR)and pyrolysis-field ionization mass spectrometry (Py-FIMS) are used for the in situ analysis of OM in soils. These methods identify the major chemical components of SUM without extraction and fractionation and yield valuable information on the main chemical structures of these materials. The major chemical components of SUM that have so far been identified include carbohydrates, phenols, lignin monomers and dimers, saturated and unsaturated fatty acids, alkanes and alkenes, alkyl monodi- and triesters, alkyl benzenes, methyl naphthalenes, methyl phenanthrenes, amino acids, and heterocyclic N-compounds. While the in situ analysis of OM in whole soils by the two methods referred to above does away with the extraction of OM from soils and its subsequent fractionation into HA, FA, and humin, it defines instead SUM in terms of its chemical makeup. In contrast to earlier workers, who thought 86 ORGANIC MA TTERIPrinciples and Processes

that HA and FA were chemically pure substances that were well separated by the extraction procedure, we know now from chemical, 13C NMR, and mass spectrometric analyses that the assumptions of workers prior to the early years of the twentieth century are incorrect. HA, FA, as well as humin, are not distinct chemical substances. Each of these fractions consists of hundreds of compounds, which appear to be associated at molecular levels by mechanisms not yet well understood.

If soil chemists want to retain the extraction and fractionation approach, they need to define each fraction not on the basis of color and solubility or insolubility in base or acid, but by its ‘3C NMR spectrum, its infrared (IR) spectrum, its mass spectrum, its elemental and functional group analyses, and so on.

Analytical Characteristics of HAs and FAs

Elemental Composition and Functional Group Content

The elemental composition and oxygen-containing functional group analysis of a typical HA (extracted from the Ah horizon of a Haploboroll) and a FA (extracted from the Bh horizon of a Spodosol) are shown in Table 1.

A more detailed analysis shows that: (1) the HA contains approximately 10% more C, but 36% less 0 than the FA; (2) there are quantitatively smaller differences between the two materials in H, N, and

Table I Analytical characterist
and a Spodosol fulvic acid
cs of a Haploboro
II humic acid

HA
FA
Element (gkg 1)
C
H
N
S
0
Functional groups (cmolkg 1)
Total acidity
COOH
Phenolic OH
Alcoholic OH
Quinonoid C0
Ketonic 0=0
OCH3
E4/E6
564
55
41
11
329

660
450
210
280

250
190
30
4.3
509
33
7
3
448

1240
910
330
360
60
250
10
7.1

HA, humic acid; PA, fulvic acid.

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S contents; (3) the total acidity and COOH content of the FA are significantly higher than those of the HA; (4) both materials contain per unit weight significant concentrations of phenolic OH, alcoholic OH, and ketonic and quinonoid C=O groups; (5) the HA is richer than the FA in quinonoid C~=O groups, while both materials contain relatively few OCH3 groups; (6) about 74% of the total 0 in the HA is accounted for in functional groups, but all of the 0 in the FA is similarly distributed; and (7) the E4/E6 ratio (ratio of absorbances at 465 and 665 mm) of the FA is almost twice as high as that of the FA, indicating that the FA has lower molecular weight than the HA.

Infrared and Fourier Transform Infrared Spectrophotometry

IR and Fourier transform JR (FTJR) spectra of HAs and FAs show bands at 3400 cm_i (H-bonded OH) 2900 cm~’ (aliphatic stretch), 1725 cm~’(CO of COOH, C=O stretch of ketonic C=O), 1630 cmt (COO~, C=O of carbonyl and quinone), 1450 crn~1 (aliphatic C—H), 1400 cm~’ (COO~), 1200 cm~1 (C—O stretch or OH deformation of COOH), and

1050 cm~' (Si—O of silicates). The bands are usually broad because of extensive overlapping of individual absorhances. JR and FTIR spectra of HAs and FAs reflect the preponderance of oxygen-containing functional groups, i.e., COOH, OH, and C=O in these materials. Some FTIR spectra show the presence of C=C and polysaccharides. While JR and FTJR spectra provide useful information on the functional groups and their participation in metal—humic as well as pesticide—hu.mic interactions, they tell us little about the chemical structure of these materials.

Chemical Structure of SOM

13C NMR Spectroscopy

One of the most important methods currently available for elucidating the chemical structure of organic substances is 13C NMR. For the analysis of SOM and fractions derived from it such as HA, FA, and humin as well for the direct in situ analysis of OM in whole soils, CP-MAS or solid-state 13C NMR is especially useful. CP-MAS 13C NMR spectra of a Mollisol HA and a Spodosol FA are shown in Figure 1. Both the HA and FA show distinct resonances in the aliphatic (0—105 ppm), aromatic (106—iSO ppm), phenolic (1S5—l69ppm), and carboxyl (170—l9Oppm) regions. The signals in the HA spectrum at 17, 21, 25, 27, and 31 ppm are probably due to alkyl C. The resonance at 17 ppm is characteristic of terminal CH3 groups and that at 31 ppm of (CH2)~ in straight paraffinic chains. The peak at 40 ppm could include

ORGANIC MA TTER/Principles and Processes 87drate C than the FA.

However, on the whole, the main irradiation, or increases in pH.

200 .100 0

FA

L
ppm
200 100 0

Figure 1 Cross-polarization magic angle spinning 13C nuclear magnetic resonance (CP-MAS ‘3C NMR) spectra of HA (extracted from the Ah horizon of a Haploboroll and FA (extracted from the Bh horizon of a Spodosol). (Reproduced with permission from Schnitzer M (2000) A lifetime perspective on the chemistry of soil organic matter. Advances in Agronomy 68: 1—58, © Academic Press, San Diego.)

contributions from both alkyl C and amino acid C. The broad signal at 53 ppm and the sharper one at 59 ppm appear to be due to OCH3. Amino acid C may also contribute to this region. Carbohydrates in the HA would be expected to produce signals in the 60—65, 70—80, and 90—105 ppm regions; also other types of aliphatic C bonded to 0 could do so. The aromatic region contains a relatively sharp peak at 130 ppm due to alkyl aromatics. The signal at 155 ppm shows the presence of 0- and N-substituted aromatic C (phenolic OH andlor NH2 bonded to an aromatic C). The broad signal near 180 ppm is due to C in COOH groups, although amide C and C in esters could also contribute to this resonance.

The CP-MAS 13C NMR spectrum of the FA (Figure 1) consists of a number of aliphatic resonances in the 20- to SO-ppm region, followed by signals due to C in OCH3 groups, and C in amino acids. Signals due to carbohydrate C are present between 50 and 85 ppm. Broad signals between 130 and 133 ppm indicate the presence of C in alkyl aromatics. The strong signal between 170 and 180 ppm shows the presence of C in COOH groups. In general, fewer sharp signals are observed in the spectrum of the FA than that of the I-IA, possibly because of more H-bonding in the FA.

The CP-MAS 13C NMR data for the HA and FA are summarized in Table 2 in terms of the distribution of C in the different spectral regions. An examination of the data shows similar C distributions in the two humic materials. The HA is slightly more aromatic than the FA, but the PA is richer in COOH groups, which appears to be the main difference between the two substances. Other differences are that the HA is richer in paraffinic C but poorer in carbohy

Table 2 Distribution of C (%) in a
Spodosol FA as determined by 13C NMR

Haploboroll HA and a

	% of C	
Chemical shift range (ppm)	HA	FA
0—40	24.0	15.6
41—60	12.5	12.8
61—105	13.5	19.3
106—150	35.0	30.3
151—170	4.5	3.7
171—190	10,5	18.3
Aliphatic C (0—105 ppm)		

	50.0	47.7
Aromatic C (106—1 50 ppm)	35.0	30.3
Phenotic C (151—170 ppm)	4.5	3,7
Aromaticity[a]	44.1	41.6

~((Aromatic C + phenolic C)/(aromatic C ± phenolic C aliphatic C)) x 100.
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structural features, as well as the aromaticiry and aliphaticity, are similar so that the HA and P A have similar chemical structures.

As far as the CP-MAS ‘3C NMR spectrum of humin, that portion of SOM that stays behind after extraction of the soil with dilute alkali or neutral salt solution, is concerned, the spectrum, after extensive leaching, is very similar to that of HA. This indicates that humin is essentially HA-bound strongly to soil minerals.

Electron-Spin Resonance Spectroscopy

Humic substances contain free radicals that can participate in a wide variety of organic—organic and organic—inorganic interactions. The electron-spin resonance (F.SR) spectrum of a typical HA consists of a single line devoid of hyperfine splitting. From the magnitudes of the g-values (the spectroscopic splitting constant), the prominent free radicals in humic materials appear to be semiquinones or substituted semiquinones. The latter can be produced either by the reduction of quinones or the oxidation of phenols. Except for indicating the presence of phenols, semiquinones, and quinones in these materials, ESR spectroscopy has so far contributed little to our understanding of the structural chemistry of these substances. The main reason for this is that it has been difficult to split the signal.

It is also known that there are two types of free radicals in humic materials: (1) permanent free radicals with long lifetimes, and (2) transient free radicals with relatively short lives (several hours). Transient free radicals in humic substances can be generated in relatively high concentrations by chemical reduction,

OH OH OH

FIgure 2 Chemical structure of humic substances based on oxidation products. (Reproduced with permission from Schnitzer M (2000) A lifetime perspective on the chemistry of soil organic matter. Advances in Agronomy 68; 1—58, © Academic Press, San Diego.)

Oxidatnie Degradation

The oxidative degradation of HAs, FAs, humins, and whole soils under a wide variety of experimental conditions produces aliphatic carboxylic, phenolic, and benzene carboxylic acids. Among aliphatic oxidation products are mono-, di-, tn-, and tetracarboxylic acids. Major phenolic acids include aromatic rings substituted by one to three OH groups and by one to five COOH groups, while major henzene carboxylic acids are the di-, tn-, tetra-, penta-, and hexa-forms. From the oxidation products identified and from CP-MAS ^{13}C NMR spectra of humic substances, it appears that the aromatic rings are cross-linked by paraffinic chains. Oxidation converts CH_3 and CU_2 groups closest to the aromatic rings to COOH groups, whereas CH_2 groups in alkyl chains are oxidized to mono- and dicarboxylic acids and/or to CO_2. The formation of significant concentrations of CO_2 from the oxidation of side chains may explain the low oxidation yields of aliphatic acids compared with phenolic and benzene carboxylic acids.

The model structure shown in Figure 2 has an aromaticity of 50% if functional groups are excluded. Of special interest are the following: (1) isolated aromatic rings are important structural components of all humic substances; (2> aliphatic chains link aromatic rings to form an alkyl aromatic network; and (3) the structure contains voids of various dimensions that can trap organic and inorganic soil constituents. These characteristics are typical of soil humic substances.

Reductive Degradation

Relatively mild reduction of humic substances with Na amalgam produces phenols and phenolic acids. But the harsher Zn-dust distillation and Zn-dust fusion yield methyl-substituted naphthalene, anthracene, phenanthrene, pyrene, and perylene. The methyl groups on the polycyclics are probably the remains of longer alkyl chains linking the polycyclics in HA, FA, and humin structures.

Pyrolysis-Field Ionization Mass Spectrometry of HAs, FAs, and Humins

Compounds identified in the Py-FI mass spectra of a whole soil, an HA, an FA, and a humin are summarized in Table 3. The most abundant compounds identified in all three fractions are carbohydrates, phenols, lignin monomers, lignin dimers, n-fatty acids, n-alkyl diesters, and n~alkyl benzenes. Minor components include n-alkyl monoesters, methylnaphthalenes, methyiphenanthrenes, and N-compounds. HA tends to be enriched in n-fatty acids and the whole soil and the humin in n-alkyl diesters and n-alkyl benzenes.

Curie-Point Pyrolysis—Gas Chromatography/Mass Spectrometry of HAs and FAs

Curie-point pyrolysis—gas chromatography/mass spectrometry (Cp Py-GC/MS) of HAs and FAs indicates the presence of relatively high concentrations of aromatic rings substituted by alkyl chains. Of special significance is the identification of a series of C1—C22 n-alkyl benzenes. In addition, ethylmethyl benzene, methyipropyl benzene, methylheptyl benzene, methyloctyl benzene, and methylundecyl ben—zene are also detected. Other compounds identified

Table   Compounds
Armadale soil and in H
by
A, F A, and humin fraction isola

ted
from it
Compound identified
Soil
HA   F A

Hum/n
Carbohydrates
Lingin monomers
Lingindimers
n-Fatty acids
n-Alkyl monoesters
n-Alkyl diesters
ri-Alkyl benzenes
Methylnaphthalenes
Methyiphenanthrenes
N compounds
n-Alkanes
++a

-l-+
+±
±

+
-i-+
+
±
+
+
±
++   ++++   ++++   +++++ +±   ++   +   +

+

++

++

++

++

+
++
+-f
+
+
+
a+ weak (relative intensity <20%); +±, intense (relative intensity 20—60%); ++±, very intense (relative intensity >60%).
Reproduced with permission from Schnitzer M and Schulten H-R (1995) Analysis of organic matter in soil extracts and whole soils by pyrolysis-mass spectrometry Advances inAgronomy 55; 168—217, © Academic Press, San Diego. (CH3)0.3

are trimethyl- and tetramethyl benzenes, alkyl naphthalenes, and alkyl phenanthrenes. The alkyl substitution on the naphthalenes ranges from one to five methyls, whereas that on the phenanthrene rings ranges from one to four methyls.

Other Characteristics

From surface pressure, surface tension, and viscosity measurements at different pHs and varying concentrations of HA and neutral electrolytes, it appears that, under conditions normally prevailing in most agricultural soils, HA behaves like a flexible, linear polyelectrolyte. Additional support for this view comes from transmission electron micrographs of HA which show that in dilute aqueous solution HA forms flat, elongated, multibranched filaments, 20—100 nm in width. With increasing pH or HA concentration, a finely woven network of elongated fibers is formed which then coalesces into a sheet-like structure, perforated by voids of varying dimensions. The overall impression is that of a relatively flexible and open structure.

Model Structures of HA

Two- and Three-Dimensional Model Structures of HA

The two-dimensional HA model structure of HA shown in Figure 3 is based on long-term chemical, l3~ NMR spectroscopic, degradative, electron -

microscopic, X-ray, Py-FIMS, and Cp Py—GC!MS studies. In this structure, n-alkyl aromatics play a significant role. Oxygen is present in the form of COOH, phenolic and alcoholic OH, ester, ethers and ketones, whereas nitrogen occurs in nitriles and hetercyclic structures. The carbon skeleton contains voids of various dimensions which can trap and bind other organic and inorganic soil constituents as well as water. The molecular formula of the HA is C308H328C90N5, its molecular weight is 5540 Da, and its elemental analysis is 66.8% C, 6.0% H, 26.0% 0, and 1.3% N. It is assumed that carbohydrates and proteinaceous materials are adsorbed on external HA surfaces and in internal voids and that hydrogen bonds play an important role in their

Figure 3 Two-dimensional HA model structurO, (Reproduced with permission from Schulten H-R and Schnitzer M (1993) A state of the art structural concept for hurnic substances, Naturwissenschaften 80: 29—30, Fig. 1 ~ Springer-Verlag, Heidelberg.)

Figure 4 Three-dimensional humic acid model structure. Element colors are: carbon (light gray), hydrogen (white), oxygen (black), and nitrogen (dark gray). (Reproduced from Schulten H-B and Schnitzer M (1997) Chemical model structures for soil organic matter and whole soils. So//Science 162: 115—130, © Lippincott, Williams & Wilkins, Baltimore.)

immobilization. Aside from carbohydrates and proteinaceous materials, the voids can also trap and bind lipids and biocides, as well as inorganics such as clay minerals and hydrous oxides.

The conversion, with the aid of HyperChern software, of the two-dimensional HA structure (Figure 3) to a three-dimensional HA structure is shown in Figure 4. The three-dimensional HA model structure has a molecular weight of 5547 and an elemental analysis of 66.7% C, 6.1% H, 26.0% 0, and 1.3% N.

It is likely that applications of computational chemistry to the development of SOM structural models will increase in the future and lead to a better understanding of the spatial arrangements of the molecular constituents of SOM. A more comprehensive knowledge of the chemistry and reactions of SUM will certainly be beneficial to a sustainable agriculture and help to protect the environment.

Reactions of SOM with Metals and Organics

Formation of Water-Soluble Metal-Organic Complexes

Reactions in water near pH 7 between di- and trivalent metal ions and HAs and FAs are likely to proceed via one or more of the mechanism shown in Figure 5, taking a divalent metal ion M2~ as an example. According to eqn [1] in Figure 5, one COOH group on the HA or FA reacts with one metal ion to form an organic salt or monodentate complex. Equation [2] in Figure 5 describes a reaction in which one COOH and one adjacent OH group react simultaneously with the metal ion to form a bidentate complex or chelate. According to eqn [3] in Figure 5, two adjacent COOH groups interact simultaneously with the metal ion to form a bidentate chelate. Equation [4] shows the metal ion M2~ linked to the HA or FA not only by electrostatic bonding, but also through a water molecule (water bridge) in its primary hydration shell to a C=O group of the ligand. The latter type of interaction is especially important when the cation has a high solvation energy and so retains its primary hydration shell. Equations [21 and [3] in Figure 5 describe the formation of strong, inner-sphere complexes, whereas eqn [4] refers to the formation of a weaker, outer-sphere complex. While a number of workers have published stability constants of water-soluble metal—HA and metal—FA complexes, problems have been encountered with the analysis and interpretation of the data. Probably the most serious obstacle to progress in this area is our lack of knowledge of the chemical structures of HAs and FAs, the ligands.

0 0
ft

÷M2~H2O =
0
‘S

—b
I 0
~ /M
C -
+

OH

C_O
+ M2~

C-OH

o — Na~
C~O

C- 0

M+W

0

OH

Figure 5 Major metal—HA and —FA reaction mechanisms. (Reproduced with permission from Schnitzer M (1986) Binding of humic substances by soil colloids. In: Huang PM and Schnitzer M (eds) interactions of Soil Minerals with Natural Organ/cs and Microbes, pp. 77—101. Special Publication No. 17. Madison, WI: Soil Science Society of America.)

Other Types of Metal SOM Interactions

The formation of mixed-ligand complexes of the type M2~—FA — secondary ligand (Y) is known to occur in soils. Secondary ligands (Y) can be citrate tartrate, salicylate, phosphate, bicarbonate, sulfate, aspartate, glycinate, etc. In neutral to weakly acid solutions, these complexes are more stable than simple complexes. The formation of mixed ligand complexes prevents the precipitation of metal ions by hydrolysis at elevated pHs.

Due to their ability to complex di-, tn-, and tetravalent metal ions, dilute aqueous FA solutions and aqueous HA solutions at pH >6.5 can attack and degrade minerals to form water-soluble and water-insoluble metal complexes. Thus, the weathering of minerals in soils and sediments is often enhanced by the action of naturally occurring organic substances, especially FA. Because of its abundance in soils, its solubility in water, and its ability to complex with metal ions and interact with silica, the latter may increase the concentrations of these soil constituents in aqueous solutions to levels that far exceed their normal solubilities. In this manner, aqueous FA solutions may not only bring about the dissolution and degradation of existing minerals, but also lead to the synthesis of new minerals by permitting the complexed and dissolved metals and silica to form new combinations. Conversely, active surfaces of inorganic soil constituents may catalyze either the degradation or synthesis of HAs and FAs.

The extent of adsorption of HA and FA on mineral surfaces depends on the characteristics of the surface,
the pH of the system, and its water content. For
[2] example, sepiolite, which has a channel-like surface, readily adsorbs FA. In untreated sepiolite, these channels are filled by bound and/or zeolitic water, which can be displaced by undissociated FA in aqueous solution at pH 3.

The interlayer adsorption of FA by expanding clay
[3] minerals is pH-dependent, being highest at low pH
but no longer occurring at pH >5. The FA cannot be displaced from the clay interlayers by leaching with 1 molY’ NaC1; an inflection is observed in the adsorption—pH curve near the pH corresponding to the
pK of the acid species of FA so that the adsorption
[4] can be classified as a ligand-exchange reaction. In this type of reaction, the anion (FA) is thought to penetrate the coordination shell of the dominant cation in the clay and displace water coordinated to the dominant cation in the clay interlayer.

Nitrogen In Soils and SOM

Almost 95% of total soil N is associated with SOM. This N occurs in the forms of amino acids, peptides, proteins, amino sugars, heterocyclic N compounds, and ammonia. The amino acid composition of soils and SOM from widely differing origins is remarkably similar and resembles that of bacteria. This appears to indicate that microbes play a major role in the synthesis of amino acids, peptides, and proteins in soils. The most prominent amino sugars in soils and SOM are D-glucosamine and o-galactosamine. Present in smaller amounts are muramic acid, D-mannosamine, N-acetylglucosamine, and D-fucosamine.

By Py-FIMS and Cp Py-GE/MS, more than 100 heterocyclic N compounds have been identified in soils and SOM. These N compounds include nonsubstituted and substituted pyrroles, pyrrolidines, imidazoles, pyrazoles, pyridines, pyrazines, nitriles, indoles, quinolines, isoquinolines, benzothiazoles, and pyrimidines. Low-mass N-compounds detected are hydrocyanic acid, dinitrogen, dinitrogen monooxide, isocyanomethane, acetamide, and hydrazoic acid. N-derivatives of benzene detected include benzamine, benzonitrile, and isocyanomethylbenzene. According to the latest estimates, the distribution of total N in soils and SOM is as follows: proteinaceous materials (amino acids, peptides, proteins), 40%; amino sugars, 5—6%; heterocyclic N (including purines and pyrimidines), 35%; and NH_3-N, 19%. Thus, proteinaceous materials and N heterocyclics are the major N components. While there are indications that the

0 0
ft

÷M2~H2O =
0
‘S

—b
I 0
~ /M
C -
+

OH

C_O
+ M2~

C-OH

o — Na~
C~O

C- 0

M+W

0

OH

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Genesis and Formation

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Introduction

The primary sources of soil organic matter (SOM: all organic C-containing compounds in the soil) are dead plant materials in the form of leaves, straw, twigs, roots, and other plant litter materials. The global biomass of higher plants amounts to approximately 500—700 Gt C (1 Gt 1 ~ t) and contributes approximately 100 Gt C in litter annually in the soil, either on the surface or deposited belowground as rhizodeposition. About the same amount of carbon is annually released from soil as CO2. The dead plant material consists of lignocelluloses with an average composition of 15—60% cellulose, 10—30% hemicelluloses, 5—30% lignin, and 2—15% protein. Minor components are phenols, sugars, amino acids, and peptides, as well as numerous secondary metabolites. Most of the compounds are used as nutrient and energy sources for microbial growth.

SOM is a natural product resulting from microbial activity in the inorganic and/or organic soil environment. The amount and accumulation of SOM are controlled by the composition and amounts of the plant residues, by climatic conditions, and soil texture. Other important factors are microbial activity, soil redox conditions, and other soil chemical and physical properties.

Soils may contain several tons of SOM per hectare. Most of it can be only slowly degraded and metabolized by soil organisms as a consequence of both its physical and chemical stabilization. Plant debris, with structural relationship to its origin, may become resistant to microbial degradation by interaction with minerals, whereas its completely humified products are produced by random condensation of refractory plant and microbial products. Their diversity and lack of regular polymeric structures do not favor efficient enzymatic degradation and energy production. Therefore, chemical composition and structure of the humified residues and their physical protection by spatial distribution are equally important for accumulation of soil carbon, which amounts to approximately 1400—1600Gt C on a global scale.

Combining the concepts of chemical stability and physical protection, it is assumed that there are two categories of natural organic matter: labile (readily degrading) and resistant (slowly degrading). Furthermore, there are three categories of microenvironments: free unprotected particles, particles occluded or entrapped in an inorganic or organic microenvironment, and particles attached or adsorbed to surfaces by physical or chemical mechanisms. This gives rise to six categories of SOM:

1. Free particulate, intrinsically labile;
2. Free particulate, intrinsically resistant;
3. Occluded particulate, potentially labile but currently protected as a result of inaccessibility;
4. Occluded particulate, intrinsically resistant and further protected by its inaccessibility;
5. Adsorbed, potentially labile, but currently protected by adsorption;
6. Adsorbed, intrinsically resistant and further protected by adsorption.

Soil Fabric and its Impact on SOM Stabilization

Transformation and Stabilization Processes of Free and Occluded Particulate Organic Matter

The location of organic matter within the soil structural units has been demonstrated to control SOM dynamics by physical or chemical mechanisms. Crushing of macroaggregates (greater than 250 jsm) provides plant-derived material from roots or leaves colonized by microorganisms, which decompose