Soil organic matter

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Soil Organic Matter

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2.1 Introduction and Definitions

Research pertaining to the organic fraction of soils can be traced back more than 200 yr. Achard (1786) isolated a dark amorphous precipitate upon acidification of an alkaline extract from peat. The effect of organic matter on soil N fertility (Liebig, 1840), and studies on the use of animal manures for maintaining soil fertility (Lawes, 1861) and the influence of soil and tree species on the development of humus form (Muller, 1887) demonstrated the importance of organic matter in soil processes. The advancement of organic chemical methodologies and confirmation of the presence of various chemical structures in soil organic matter (SOM) lead to theories that SOM was composed of a heterogeneous mixture of dominantly colloidal organic substances containing acidic functional groups and N. More recently, the polyphenol theory was proposed in which quinone structures of lignin and microbial origin polymerize in the presence of N containing groups (amino acids, peptides, and proteins) to produce nitrogenous polymers (Flaig et al., 1975). The early research pertaining to SOM has been reviewed by Stevenson (1994). While alkaline extraction of SOM is still practiced, modern analytical techniques, including solid-state ^{13}C nuclear magnetic resonance spectroscopy (^{13}C NMR), infrared spectroscopy (IR), and pyrolysis gas chromatography/mass spectroscopy (Py-GCMS) allow selective probing of the chemistry of SOM within samples of whole soil, and avoid the problems of incomplete extraction, lack of biological significance, and artifact synthesis often ascribed to alkaline extraction procedures. The combination of these techniques with novel approaches capable of identifying biologically important fractions of SOM has significantly advanced our knowledge of the organic fraction of soils and its dynamics over the last 20 years.

Despite such a long history of research and new methodological and technological advancements, many questions related to the genesis and chemical composition of organic materials in soils and their impacts on soil fertility, pedogenesis, and soil physical and chemical properties persist today. Many excellent texts and review papers have been written on the topic of SOM; some of the more recent of these are given in Table 2.1.

An examination of terms used to describe SOM and its components in the literature revealed a lack of precise definitions of what SOM and its various fractions represent. Such a problem exists because

Table 2.1 List of texts and review articles pertaining to the study of soil organic matter released since 1985. Individual review articles within texts have not been identified separately [modified from Hedges and Oades, 1997]

Texts

Humic substances in soil, sediment and water (Aiken et al., 1985)
Soil organic matter and biological activity (Vaughan and Malcolm, 1985)
Interactions of soil minerals with natural organics and microbes (Huang and Schnitzer, 1986)
Cycles in soil: carbon, nitrogen, phosphorus, sulfur, micronutrients (Stevenson, 1986)
Chemistry of soil organic matter (Kumada, 1987)
Soil organic matter (Tate, 1987)
Humic substances and their role in the environment (Frimmel and Christman, 1988)
Dynamics of soil organic matter in tropical ecosystems (Coleman et al., 1989)
Humic substances II: In search of structure (Hayes et al., 1989)
Soil microbiology and biochemistry (Paul and Clark, 1989)
Soil Biology and Biochemistry, Vol. 6 (Bollag and Stotzky, 1990)
Humic substances in soil and crop science (MacCarthy et al., 1990a)
Advances in soil organic matter research: The impact on agriculture and the environment (Wilson, 1991)
Soil Biology and Biochemistry, Vol. 7 - Vol. 9 (Stotzky and Bollag, 1992, 1993, 1996)
Soil organic matter dynamics and sustainability of tropical agriculture (Mulongoy and Merckx, 1993)
Environmental organic chemistry (Schwartzenbach et al., 1993)
Humic substances in the global environment (Senesi and Miano, 1994)
Humus chemistry: genesis, composition, reactions (Stevenson, 1994)
Soil organic matter management for sustainable agriculture (Lefroy et al., 1995)
Humic substances of soils and general theory of humification (Orlov, 1995)
Carbon forms and functions in forest soils (McFee and Kelly, 1995)
The role of nonliving organic matter in the earth's carbon cycle (Zepp and Sonntag, 1995)
Driven by nature: plant litter quality and decomposition (Cadisch and Giller, 1997)
Soil organic matter in temperate ecosystems (Paul et al., 1997)

Review Articles

The retention of organic matter in soils (Oades, 1988)
An introduction to organic matter in mineral soils (Oades, 1989)
Soil organic matter - the next 75 years (Schnitzer, 1991)
Physical fractionation of soil organic matter in primary particle size and density separates (Christensen, 1992)
A hierarchical model for decomposition in terrestrial ecosystems - application to soils of the humid tropics (Lavelle et al., 1993)
Organic matter in tropical soils - current conditions, concerns and prospects for conservation (Ross, 1993)
Modelling food webs and nutrient cycling in agro-ecosystems (Deruiter et al., 1994)
Towards a minimum data set to assess soil organic matter quality in agricultural soils (Gregorich et al., 1994)
The chemical composition of soil organic matter in classical humic compound fractions and in bulk samples - a review (Beyer, 1996)
Carbon in primary and secondary organo-mineral complexes (Christensen, 1996)
Applications of NMR to soil organic matter analysis - history and prospects (Preston, 1996)
Characterization of humic and soil particles by analytical pyrolysis and computer modeling (Schulten and Leinweber, 1996)
Life after death - lignin-humic relationships reexamined (Shevchenko and Bailey, 1996)
Stabilization and destabilization of soil organic matter - mechanisms and controls (Sollins et al., 1996)

of the heterogeneity of organic material found in soil in terms of its source, chemical and physical composition, diversity of function, and dynamic, ever changing character. The term SOM has been used to encompass all organic materials found in soil (Stevenson, 1994), excluding charcoal (Oades, 1988), or excluding nondecayed plant and animal tissues, their partial decomposition products, and the living soil biomass (MacCarthy et al., 1990b). As suggested by MacCarthy et al. (1990b), it is most important that readers establish how particular authors apply the various terms to fully understand and assess the implications of comments made. However, it is also important that a set of definitions for SOM and its components is derived and applied consistently. The definitions of SOM and its components to be utilized in this chapter (Table 2.2) have been derived from several sources (Oades,

Table 2.2 Definitions of soil organic matter and its components

Component	Definition
Soil organic matter (SOM)	The sum of all natural and thermally altered biologically derived organic material found in the soil or on the soil surface irrespective of its source, whether it is living or dead, or stage of decomposition, but excluding the aboveground portion of living plants.
Living Components	Living tissues of plant origin. Standing plant components which are dead (e.g., standing dead trees) are also considered as phytomass.
Phytomass	
Microbial Biomass	Organic matter associated with cells of living soil microorganisms.
Faunal Biomass	Organic matter associated with living soil fauna.
Nonliving Components	Organic fragments with a recognizable cellular structure derived from any source but usually dominated by plant derived materials.
Particulate organic matter	
Litter	Organic materials devoid of mineral residues located on the soil surface.
Macroorganic matter	Fragments of organic matter > 20 μm or > 50 μm (i.e., greater than the lower size limit of the sand fraction) contained within the mineral soil matrix and typically isolated by sieving a dispersed soil.
Light Fraction	Organic materials isolated from mineral soils by flotation of dispersed soil suspensions on water or heavy liquids of densities 1.5 - 2.0 Mg m^{-3}.
Dissolved organic matter	Water soluble organic compounds found in the soil solution which are < 0.45 μm by definition. Typically this faction consists of simple compounds of biological origin (e.g., metabolites of microbial and plant processes) including sugars, amino acids, low molecular weight organic acids (e.g., citrate, malate, etc.) but may also include large molecules.
Humus	Organic materials remaining in the soil after removal of macroorganic matter and dissolved organic matter.
Non-humic biomolecules	Identifiable organic structures which can be placed into discrete categories of biopolymers including polysaccharides and sugars, proteins and amino acids, fats, waxes and other lipids, and lignin.
Humic substances	Organic molecules with chemical structures which do not allow them to be placed into the category of non-humic biomolecules.
Humic acid	Organic materials which are soluble in alkaline solution but precipitate on acidification of the alkaline extracts.
Fulvic acid	Organic materials which are soluble in alkaline solution and remain soluble on acidification of the alkaline extracts.
Humin	Organic materials which are insoluble in alkaline solution.
Inert organic matter	Highly carbonized organic materials including charcoal, charred plant materials, graphite and coal with long turnover times.

1988; MacCarthy et al., 1990b; Stevenson, 1994) and are put forward in an effort to reduce existing variations in the use of the terms.

2.2 Functions of Soil Organic Matter

The organic fraction of soils often accounts for a small but variable proportion of total soil mass. Organic C concentrations ranging from < 5 g C kg^{-1} soil for desert loams (Aridisols) to > 130 g C kg^{-1} soil for alpine humus soils (Histosols and Mollisols) were presented for the 0–10 cm layer of the great soil groups of Australia (Spain et al., 1983). Sombroek et al. (1993) presented topsoil and subsoil organic C content values ranging from 0.5–3 g C kg^{-1} for Yermosols up to 310–555 g C kg^{-1} for Histosols using 400 soil profiles grouped according to FAO soil units. Contents of organic C on the order of 441–549 g C kg^{-1} and 440–550 g C kg^{-1} were measured for Canadian peats (Preston et al., 1989b) and German forest litter layers (Zech et al., 1992), respectively.

Despite its often minor contribution to the total mass of mineral soils, the organic fraction can exert a profound influence on soil properties, ecosystem functioning, and the magnitude of various obligatory ecosystem processes (Table 2.3). The soil properties which organic matter influences have been classified into three broad groups: biological, chemical, and physical properties. It should be noted that strong interactions and interdependencies exist between these groups. For example, the ability of organic matter to chelate multivalent cations can affect its potential to stabilize soil structure and also its biodegradability (Juste and Delas, 1970; Juste et al., 1975; Gaiffe et al., 1984; Muneer and Oades, 1989a,b,c). In addition, the effects of organic matter on soil properties often involve interactions with the soil mineral fraction, and variations in soil properties noted across different soils may not be solely a consequence of qualitative or quantitative variations in the soil organic component.

2.2.1 Biochemical Functions

2.2.1.1 Reservoir of Metabolic Energy

The most fundamental function of the organic fraction of soils is the provision of metabolic energy which drives soil biological processes and the direct and indirect effects which this has on other soil properties and processes. Photosynthesis fixes CO_2 into glucose which is then converted into a wide range of organic compounds (e.g., cellulose, hemicellulose, lignin, lipids, proteins, etc.) by various enzymatic processes. The C fixed into such compounds is deposited in or on the soil during plant growth and as the plant or a portion of its tissues senesce, thereby providing C substrates for soil macro- and microdecomposer organisms. As the organic C is utilized by decomposer organisms, it is either assimilated into body tissues, released as metabolic products, or respired as CO_2. Oades (1989) presented an estimate of the C flow through a fertile grassland where primary production via photosynthesis was 10 Mg C ha^{-1} yr^{-1}. Of the 3 Mg C ha^{-1} yr^{-1} that was added to the soil organic C fraction, the soil fauna were estimated to utilize 0.3–0.45 Mg C ha^{-1} yr^{-1}, while the soil microbial biomass was estimated to utilize 2.4 Mg C ha^{-1} yr^{-1}. The majority of organic matter processing is thought to be completed by the soil microbial biomass. However, other activities of the soil fauna enhance the ability of soil microbial decomposers to utilize organic residues added to soil. These include (1) fragmentation of plant debris, which enhances the surface area per unit weight of plant residue available to microbial attack, and (2) distributing organic materials throughout the soil matrix, which provides an avenue for greater contact between decomposer microorganisms and substrates.

2.2.1.2 Source of Macronutrients

A result of the utilization of organic materials by soil organisms is a conversion of macronutrients (N, P, and S) within organic chemical structures into inorganic forms, which are either immobilized and

Table 2.3 Properties and functions of organic matter in soil

Property	Function
Biological Properties	
Reservoir of metabolic energy	Organic matter provides the metabolic energy which drives soil biological processes.
Source of macronutrients	The mineralization of soil organic matter can significantly influence (positively or negatively) the size of the plant available macronutrient (N, P, and S) pools.
Ecosystem resilience	The build up of significant pools of organic matter and associated nutrients can enhance the ability of an ecosystem to recover after imposed natural or anthropogenic perturbations.
Stimulation and inhibition of enzyme activities and plant and microbial growth	The activity of enzymes found in soils and the growth of plants and microorganisms can be stimulated or inhibited by the presence of soil humic materials.
Physical Properties	
Stabilization of soil structure	Through the formation of bonds with the reactive surfaces of soil mineral particles, organic matter is capable of binding individual particles and aggregations of soil particles into water-stable aggregates at scales ranging from < 2μm for organic molecules through to mm for plant roots and fungal hyphae.
Water retention	Organic matter can directly affect water retention because of its ability to absorb up to 20 times its mass of water and indirectly through its impact on soil structure and pore geometry.
Low solubility	Ensures that the bulk of the organic materials added to the soil are retained and not leached out of the soil profile
Color	The dark color which soil organic matter imparts on a soil may alter soil thermal properties.
Chemical Properties	
Cation exchange capacity	The high charge characteristics of soil organic matter enhance retention of cations (e.g., Al^{3+}, Fe^{3+}, Ca^{2+}, Mg^{2+}, NH_4^+, and transition metal micronutrients).
Buffering capacity and pH effects	In slightly acidic to alkaline soils, organic matter can act as a buffer and aids in the maintenance of acceptable soil pH conditions.
Chelation of metals	Stable complexes formed with metals and trace elements enhance the dissolution of soil minerals, reduce losses of soil micronutrients, reduce the potential toxicity of metals, and enhance the availability of phosphorus.
Interactions with xenobiotics	Organic matter can alter the biodegradability, activity and persistence of pesticides in soils.

used in the synthesis of new tissues within soil organisms or mineralized and released into the soil mineral nutrient pool. With the exception of intensively managed soil receiving significant inputs of macronutrients in the form of fertilizers, organic matter provides the largest pool of macronutrients in the soil. McGill and Cole (1981) proposed that the mineralization of C, N, P, and S followed a dichotomous system involving both biological and biochemical mineralization. Biological mineralization is driven by the need of decomposer organisms for C as an energy source and accounts for the mineralization of N and C bonded S. Biochemical mineralization refers to the release of phosphate and sulfate from the P and S ester pool via enzymatic hydrolysis outside of the cell

membrane. As a result and in contrast to organic N, organic P and S accumulation and mineralization in soils can occur independently of C and N dynamics. This leads to the potential for large variations in C:N:P:S ratios in SOM. An average C/N/P/S ratio of 107:7.7:1:1 was presented by Stevenson (1986) for SOM. In the next several paragraphs, the contents and chemical structures of soil organic N, P, and S and ratios of organic C/N, C/P, and C/S will be discussed to provide an indication of the organic forms and potential stores of macronutrients within SOM. More detailed presentations of the forms and availability of organic N, P and S, can be found in Section C, Chapters 3 and 4.

Nitrogen

The soil N pool is dominated by N found in organic structures. In soils with significant contents of K^+-containing clay minerals (e.g., illite) capable of fixing NH_4^+, approximately 90% of the soil N is contained in organic structures, 8% exists as fixed NH_4^+, and 1–3% can be found in the inorganic plant available pool (NO_3^- and NH_4^+). In soils with little capacity to fix NH_4^+ in clay minerals, the proportion of organic N is > 97% and the inorganic fraction is 1–3%. On a global scale, Söderlund and Svensson (1976) estimated that the organic N fraction of soils accounted for 95% of the total soil N pool, which is equivalent to the average value presented by Bremner (1967). The C/N ratio of SOM depends on the C/N ratio of the vegetational inputs and the degree to which they are decomposed. Organic materials that have cycled through the decomposer biomass generally have C/N ratios of 12–16, whereas undecomposed fragments of plant litter and organic materials in peat deposits, where decomposition is hindered by anaerobic conditions, can have much higher C/N ratios.

Soil organic N has been traditionally divided into the following five fractions based on a variety of acid hydrolysis procedures: (1) acid insoluble N, (2) ammonia N recovered after hydrolysis, (3) amino acid N, (4) amino sugar N, and (5) hydrolyzable unidentified N. Data summarized by Stevenson (1994) for 11 studies where acid hydrolysis procedures were applied to different soil types showed that there was as much variation in the contents of each form of N within similar soils as between different soil types. The proportions of each form of organic N were 7–44% acid insoluble N, 9–37% ammonia N, 13–50% amino acid N, 1–14% amino sugar N, and 4–40% hydrolyzable unidentified N. Although methodological differences may account for a portion of the large variations noted in the composition of soil organic N, it is evident that approximately 50% of the total soil N cannot be identified by acid hydrolysis procedures (acid insoluble N + hydrolyzable unidentified N).

Initial attempts to identify the chemical composition of unidentifiable organic N utilized gel filtration followed by acetylation and gas chromatography/mass spectroscopy (GC/MS) (Schnitzer, 1985; Schnitzer and Spiteller, 1986). Schulten et al. (1995, 1997) utilized Curie point pyrolysis-GC MS with N selective detection of the pyrolysis products. These studies suggested that heterocyclic N compounds represented an important component of unidentified soil organic N (Schulten et al., 1997 presented examples of the chemical structure of the heterocyclic N compounds). The formation of heterocyclic N compounds via nonbiological fixation of $^{15}NH_3$ by humic substances (IHSS Suwannee River fulvic acid and peat and leonardite humic acids) and by reacting ^{15}N labeled analine with humic materials was noted by Thorn and Makita (1992) and by Thorn et al. (1996), respectively. In contrast to these results, studies utilizing solid-state ^{15}N nuclear magnetic resonance (NMR) spectroscopy have failed to observe substantial contributions from heterocyclic N, and spectra tend to be dominated by signals arising from amides and terminal amino groups (Knicker and Ludemann, 1995; Knicker et al., 1995; Clinton et al., 1995). Further effort is required to address these inconsistencies, and to quantitatively characterize the composition of the fraction of N, which cannot be identified by conventional acid hydrolysis procedures.

Phosphorus

The composition and cycling of soil organic P have been recently reviewed by Stevenson (1986, 1994), and Sanyal and DeDatta (1991). As a result of potential adsorption and inorganic precipitation reactions capable of reducing the availability of P in soils, mineralization of organic P is important to soil fertility (Tiessen et al., 1984; Beck and Sanchez, 1994). The relative importance of organic P as a nutrient source tends to be greater on highly weathered soils (Duxbury et al., 1989). The principal organic P-containing compounds in soils and their approximate proportions include inositol phosphates (2–50%), phospholipids (1–5%), nucleic acids (0.2–2.5%), trace amounts of phosphoproteins, and metabolic phosphates (Stevenson, 1994). Soil organic P accounts for a variable proportion of the total soil P. Halstead and McKercher (1975) and Uriyo and Kessaba (1975) presented soil organic P values ranging from 4–1400 μg g^{-1} soil which accounted for 3–90% of the total soil P. Uriyo and Kessaba (1975) derived the relationship between organic P and organic C given in Equation [2.1] which produces an organic C/P ratio of 115 and is consistent with the average value of 117 proposed by Stevenson (1994). However, large variations in the organic C/P ratio (61–526) have been noted for Finnish soils (Kiala, 1963).

$$\text{Organic C (mg g}^{-1}\text{ soil)} = 4.9 + 0.059\ \text{Organic P (μg g}^{-1}\text{ soil)}\ (R^2 = 0.49) \qquad [2.1]$$

Sulfur

Reviews of the cycling and chemical composition of soil organic S include Stevenson (1986, 1994), Germida et al. (1992), and Nguyen and Goh (1994). Sulfur-containing organic compounds found in soils are generally grouped into two pools: compounds in which the S can be reduced to H_2S by hydroiodic acid (HI), and compounds in which the S is directly bound to C. The HI reducible fraction consists mainly of ester sulfates (C-O-S bonds) and some ester sulfamates (C-N-S bonds). The C bonded S fraction contains amino acid S (C-S bonds) or sulfonates ($C\text{-}SO_3^-$ bonds). The ester sulfates and sulfamates are typically associated with aliphatic side chains of soil organic compounds (Bettany et al., 1979), while the C bonded S is incorporated along with C and N into the core of soil organic compounds and is generally less biologically accessible (McGill and Cole, 1981; Stewart and Cole, 1989). Organic S typically accounts for > 90% of the total S found in non-saline and non-tidal soils (Nguyen and Goh, 1994; Stevenson, 1994).

2.2.1.3 Ecosystem Resilience

The resilience of an ecosystem is defined as its capacity to return to its initial state after being subjected to some form of disturbance or stress. The important role played by SOM in determining the resilience of an ecosystem can be exemplified by a comparison of the contents of chemical energy and nutrients stored within the soil organic fractions in several ecosystems. In temperate grasslands, high organic matter levels are built up in soils as a result of large below-ground additions of photosynthate, limited leaching, and slow decomposition rates. Storage of C in such ecosystems is greater in the soil than in the vegetation (Szabolcs, 1994). The large store of chemical energy and nutrients contained in the soil organic fraction offers resistance to the loss of soil fertility induced by natural or by agricultural disturbance. Temperate grassland soils, typically Mollisols, have remained agriculturally productive with limited inputs for many years, despite the mining of energy and nutrient reserves contained within the soil organic fraction (Janzen, 1987; Tiessen et al. 1994b). Such systems can be considered resilient, at least initially, but one must question for how long such systems can be sustained. This was exemplified by Tiessen et al. (1983), who showed that rates of organic P mineralization in a grassland soil were in excess of crop requirements over the first 60 years of agricultural production, but that

subsequent to 60 years, only the less labile, low energy providing forms of organic matter remained, and organic P mineralization rates decreased below crop demands. In temperate forests, SOM contents are less than those of temperate grasslands and more C and nutrients are stored in aboveground vegetation than in the readily available soil organic materials (Szabolcs, 1994). As a result, the impact of a natural disturbance such as fire can significantly deplete ecosystem stores of energy and nutrients, and ecosystem recoveries (resilience) are slow due to low residual contents of SOM and associated nutrients. Where temperate forests are cleared and agricultural production is initiated, SOM and nutrient losses must be minimized; however, production systems which increase SOM and nutrient reserves (e.g., crop rotations including legume pastures) can lead to highly productive and sustainable agriculture. In tropical forest ecosystems, the storage of energy and nutrients in vegetation dominates, and the rapid utilization of plant residues by decomposer organisms and cycling of nutrients maintain ecosystem stability. This, when coupled with the low stores of energy and nutrients in organic matter of tropical soils, indicates a reduced importance of SOM in ecosystem resilience (Anderson, 1995). A comparison of a temperate grassland Mollisol with a tropical Oxisol (Tiessen et al. 1994b) demonstrated the important contribution of organic matter to the resilience of the grassland soil and its reduced significance in the tropical soil.

2.2.1.4 Stimulation and Inhibition of Enzyme Activities and Plant and Microbial Growth

Research pertaining to the impacts of SOM on plants, microorganisms and enzyme activities has typically utilized humic substances (e.g., humic and fulvic acids) as surrogates for SOM. The influence of humic and fulvic acids, tannins, and melanins on the activity of various enzymes was summarized by Ladd and Butler (1975), Müller-Wegener (1988), and Gianfreda and Bollag (1996). Based on earlier studies, Ladd and Butler (1975) concluded that the effect of humic acids on the activity of proteolytic enzymes varied and that the mechanism of humic acid-enzyme interaction involved primarily the carboxyl groups of humic acids. Inhibition of nonproteolytic enzyme activities by humic acids have also been demonstrated (Sarkar and Bollag, 1987). Müller-Wegener (1988) indicated that possible humic acid-enzyme interactions which could impact on enzyme activity included (1) a direct interaction of the humic acid with the enzyme resulting in a modification of enzyme structure or changes in the functioning of active sites, (2) interference in the equilibrium of the enzyme reaction via the humic substances acting as analog substrates, and/or (3) a reduction in the availability of cations, which often act as cofactors required for enzyme catalysis or structural stabilization of the protein molecule by fixation on the humic acid molecule.

The effect of soil humic substances on plant and microbial growth involves the absorption or adsorption of the humic species and their impacts on biochemical properties at cell walls, cell membranes, and/or in the cytoplasm. Information on the impacts of humic materials in field studies is scarce and often confounded with other impacts of humic materials on soil properties (e.g., CEC, nutrient status, etc.). The effects of humic materials on plant growth were reviewed by Chen and Aviad (1990). Favorable effects on plant growth included (1) increased uptake of water and germination rate of seeds, (2) enhanced growth of shoots and roots as assessed by measurements of length and fresh and/or dry mass, and (3) increased root elongation, number of lateral roots, and root initiation. These effects result from increased permeability of cell membranes, increased chlorophyll content and rates of photosynthesis and respiration, enhanced protein synthesis resulting from a stimulation of ribonucleic acid synthesis, and enhanced enzyme activity (Vaughan and Malcolm, 1985). The influence of humic substances on the growth of microorganisms (bacteria and fungi) also involves a penetration and alteration of cell membranes. Addition of humic substances at concentrations ≤ 30 mg L^{-1} to a nutrient solution increased growth rates in microbial cultures (Visser, 1995), and *in vitro*

growth and activity of nitrifying bacteria have been increased by the addition of humic acid (Valdrighti et al., 1996; Vallini et al., 1997).

2.2.2 Physical Functions

2.2.2.1 Stabilization of Soil Aggregates

Organic matter is considered important to the maintenance of the structural stability of a wide range of soil types including Mollisols, Alfisols, Ultisols and Inceptisols. Its importance tends to be less in Oxisols and Andisols, where hydrous oxides play an important stabilizing role, and in self-mulching soils (e.g., some Vertisols) that contain clays with a high shrink/swell potential. In soils where organic matter is an important agent binding mineral particles together, a hierarchical arrangement of soil aggregates exists in which aggregates break down in a stepwise manner as the magnitude of an applied disruptive force increases (Tisdall and Oades, 1982; Oades and Waters, 1991; Oades, 1993). Golchin et al. (1998) and others have proposed the existence of three levels of aggregation: (1) the binding together of clay plates into packets < 20 μm, (2) the binding of clay packets into stable microaggregates (20–250 μm), and (3) the binding of stable microaggregates into macroaggregates (> 250 μm).

The importance and nature of the organic materials associated with each level of aggregation vary. At the scale of packets of clays, aggregation is primarily dictated by soil mineralogical and chemical properties important in controlling the extent of dispersion, and is often a function of pedological processes. The binding together of clay packets to form microaggregates occurs via a range of mechanisms. The dominant mechanism is proposed to involve polysaccharide-based glues (mucilages or mucigels) produced by plant roots and soil microorganisms (Ladd et al., 1996). Emerson et al. (1986) presented transmission electron micrographs showing mucilage located between packets of clay plates. Small microaggregates (< 53 μm) held together by humified organic matter and biologically processed materials are bound together around a particulate organic core (Oades, 1984; Elliott, 1986; Beare et al., 1994b; Golchin et al., 1994b) to produce larger microaggregates and small macroaggregates < 2,000 μm. Macroaggregates > 2,000 μm are stabilized by the presence of roots, fungal hyphae and larger fragments of plant residues, which interconnect soil aggregates via bonding to aggregate surfaces, penetration into or through aggregates, and/or physical enmeshment (Tisdall and Oades, 1982; Churchman and Foster, 1994; Foster, 1994). Additional information pertaining to the involvement of organic matter in stabilizing soil structure is presented in Section A, Chapter 7.

2.2.2.2 Water Retention

Organic materials can influence soil water retention directly and indirectly. SOM can absorb and hold substantial quantities of water, up to twenty times its mass (Stevenson, 1994). This direct effect, however, depends on the morphological structure of the organic materials and will not impart any beneficial effect to the soil unless it serves to enhance the ability of soil to hold water at potentials within the plant available range. Organic matter in the form of surface residues can also influence water retention directly by reducing evaporation and increasing the infiltration of water.

The indirect effect of organic matter on water retention arises from its impact on soil aggregation and pore size distribution, and thus on the plant available water holding capacity (AWHC) of soil (the difference between volumetric water content at field capacity and at permanent wilting point). This effect is best exemplified by the inclusion of soil organic C content as a significant parameter in pedotransfer functions which predict pore size distribution (Vereecken et al., 1989; da Silva and Kay, 1997; Kay et al., 1997). Equation [2.2] presents the pedotransfer function derived by da Silva and Kay

(1997) to describe the relationship between volumetric water content, θ_v ($m^3\ m^{-3}$), and matric potential; ψ (MPa), clay content, CL (%); organic C content, OC (%); and bulk density, BD ($Mg\ m^{-3}$). Using this equation Kay et al. (1997) calculated predicted changes in AWHC for soils ranging in clay content from 7 to 35% when organic C content was increased by 0.01 kg kg^{-1}. Increases in AWHC of 0.039 and 0.020 ($m^3\ m^{-3}$) were obtained for the soils with 7 and 35% clay, respectively, at a relative bulk density of 0.75. Application of the same equations to a data set acquired by Wegner et al. (1989) for 80 South Australian red brown earths (Alfisols) showed that the increase in AWHC induced by increasing organic C content by 0.01 kg kg^{-1} soil could be expressed by Equation [2.3]. These results indicate that the presence of additional organic matter enhances AWHC of soils; however, the magnitude of the increase decreases with increasing clay content.

$$\theta_{\varpi} = \varepsilon^{(4.15 + 0.68 \ln CL + 0.42 \ln OC + 0.27 \ln BD)} \psi_m^{(-0.54 + 0.11 \ln CL + 0.02 \ln OC + 0.10 \ln BD)} \quad (R^2 = 0.94) \qquad [2.2]$$

$$\text{Change in AWHC} = -0.0012\ (\%\text{clay}) + 0.055 \quad (R^2 = 0.82) \qquad [2.3]$$

2.2.2.3 Soil Thermal Properties

The typical dark color of SOM contributes to the dark color of surface mineral soils and can enhance soil warming and promote biological processes related to temperature in cooler climates (e.g., plant growth and mineralization of C and nutrients contained in SOM). However, the presence of litter layers or organic horizons can insulate a soil against fluctuations in air temperature and solar heating. On several Canadian forest soils subject to cold winters and cool springs, average soil temperatures and the growth of fertilized seedlings were greater where the litter layers were removed compared to where they were left intact (Burgess et al., 1995a,b). Similar effects have been observed in a comparison of cropping systems that leave different amounts of crop residue on the surface of mineral soil (Fortin, 1993).

2.2.3 Chemical Functions

2.2.3.1 Cation Exchange Capacity

Organic matter contributes 25–90% of the cation exchange capacity (CEC) of surface layers of mineral soils and practically all of the CEC of peats and forest litter and humus layers (Stevenson, 1994). The contribution is greatest for soils with low clay content or where the clay fraction is dominated by minerals with a low charge density, such as kaolinite, and is lowest for soils with high contents of highly charged minerals such as vermiculite or smectite. In sandy soils, organic matter plays a critical role in providing CEC. As a general rule of thumb, each weight percentage of organic matter in soils contributes approximately 3 $cmol_c\ kg^{-1}$ soil to the CEC of neutral permanent charge soils (McBride, 1994) and approximately 1 $cmol_c\ kg^{-1}$ soil to the CEC of variable charge soils (Oades, 1989). The CEC of organic matter is derived principally from carboxyl functional groups but also from phenol, enol and imide groups, and is, therefore, dependent on soil pH. However, because of potential organo-mineral interactions in soils and the ability of organic matter to complex cations, the contribution of organic matter to soil CEC values is often much less than could be expected based on its carboxyl content. For example, the protonation of carboxylate groups, interaction with positively charged sites on inorganic colloids, and complexation of Al^{3+} and Fe^{3+} can reduce the ability of organic matter to contribute to the CEC of acidic soils (McBride, 1994). Measurements of the CEC of SOM have yielded values ranging from 60–300 $cmol_c\ kg^{-1}$ (Leinweber et al., 1993; Stevenson, 1994).

2.2.3.2 Buffering Capacity and Soil pH

The presence of weakly acidic chemical functional groups on soil organic molecules, that can act as conjugate acid/base pairs, makes SOM an effective buffer. The diversity in chemical composition of the functional groups (e.g., carboxylic, phenolic, acidic alcoholic, amine, amide and others) provides organic matter with the ability to act as a buffer over a wide range of soil pH. James and Riha (1986) reported buffer capacities of 18–36 and 1.5–3.5 $cmol_c\ kg^{-1}$ $(pH\ unit)^{-1}$ for the organic and mineral horizons of forest soils, respectively. Starr et al. (1996) obtained a good correlation between acid buffer capacity and organic matter content for 29 organic and 87 mineral soil horizons (E, B, and C horizons) exhibiting buffering capacities of 9.8–40.8 and 0.1–5.2 $cmol_c\ kg^{-1}$ $(pH\ unit)^{-1}$, respectively. For 59 agricultural soil samples taken from the 0–15 cm layer of cultivated fields, Curtin et al. (1996) noted that titratable acidity could be described by Equation [2.4] in which the terms OC and Clay represent the soil organic C and clay contents expressed in units of kg kg^{-1} soil and ΔpH is the reference pH (e.g., 8) minus the initial pH. Assuming that the organic C content of SOM is 58%, Equation [2.4], indicates that the buffering capacity offered by organic matter was approximately 34 $cmol_c\ kg^{-1}$ $(pH\ unit)^{-1}$ and is an order of magnitude greater than that offered by clay [34 versus 3 $cmol_c$ kg^{-1} $(pH\ unit)^{-1}$]. The average clay/organic C ratio for the soils studied by Curtin et al. (1996) was 7.9/1, indicating that even though most soils contained much more clay than organic C, organic C accounted for about two-thirds of the soil buffering capacity.

$$\text{Titratable acidity to pH 8} = 0.02 + 59\ \text{OC}\ \Delta\text{pH} + 3.0\ \text{Clay}\ \Delta\text{pH} \quad R^2 = 0.95 \qquad [2.4]$$

Addition of organic matter to soil may result in increases or decreases in soil pH, depending on the influence that the addition has on the balance of the various processes that consume and release protons. A detailed presentation of these soil processes and their ability to release or consume protons is given by van Breeman et al. (1983). Factors which need to be considered include the chemical nature of the soil and that of the organic materials added as well as environmental properties including water content and extent of leaching. The net effect of adding organic matter to acidic soils is generally an increase in pH values (e.g., Yan et al., 1996; Pocknee and Sumner, 1997) with the main processes leading to the increase being (1) a decomplexation of metal cations, (2) mineralization of organic N, and (3) denitrification. Pocknee and Sumner (1997) found that on the acid Cecil soil, the extent of the increase in pH was controlled by the N content to basic cation content ratio. The decarboxylation of organic acids has also been shown to increase the pH of acid soils (Yan et al., 1996). Under alkaline soil conditions, however, these processes would be ineffective and would contribute to a reduction in soil pH as a result of their influence on soil CO_2 concentrations. The addition of organic matter to alkaline soils tends to acidify them especially under waterlogged and leaching conditions (Nelson and Oades, 1998). The main processes involved in the acidification of alkaline soils on addition of organic materials include (1) mineralization of organic S and P, (2) mineralization followed by nitrification of N, (3) leaching of the mineralized and nitrified organic N, (4) dissociation of organic ligands, and (5) dissociation of CO_2 during decomposition.

2.2.3.3 Complexation of Inorganic Cations

The presence of various functional groups on soil organic materials provides the capacity for interaction with inorganic cations. The possible interactions can take the form of simple cation exchange reactions, such as those between negatively charged carboxyl groups and monovalent cations, or more complex interactions where coordinate linkages with organic ligands are formed, such as occur between amino acids and Cu^{2+}. The mechanisms involved in the complexation of

inorganic cations by soil organic materials are discussed in detail in Section B, Chapter 8. The influence that the complexation of inorganic cations by soil organic materials has on soil properties and processes includes the following: (1) increased availability of insoluble mineral P through complexation of Fe^{3+} and Al^{3+} in acid soil and Ca^{2+} in calcareous soil, competition for P adsorption sites, and displacement of adsorbed P (Stevenson, 1994; Cajuste et al., 1996), (2) the release of plant nutrients through the weathering of rocks and soil parent materials by the removal of structural cations from silicate minerals (Tan, 1986; Robert and Berthelin, 1986), (3) enhanced availability of trace elements in the upper portion of the soil profile as a result of upward translocation by plant roots and subsequent deposition on the soil surface and complexation during residue decomposition (Stevenson, 1994), (4) facilitated adsorption of organic materials to soil minerals which aids in the generation and or stabilization of soil structure (Oades, 1984; Emerson et al., 1986), (5) buffering of excessive concentrations of otherwise toxic levels of metal cations (e.g., Al^{3+}, Cd^{2+}, and Pb^{2+}) (Anderson, 1995), and (6) pedogenic translocation of metal cations to deeper soil horizons (McKeague et al., 1986) and the formation of minerals (Huang and Violante, 1986).

2.3 Quantifying Soil Organic Matter Contents

Soil organic matter contents are difficult to measure directly. Most methods measure organic C content, and multiply the resultant values by conversion factors ranging from 1.72 to 2.0 to obtain organic matter contents. The value of the conversion factor used is determined by the C content of SOM, which is assumed to range from 50 to 58%. Recent studies have suggested that the C content of SOM is variable and that no single factor is appropriate for all soils. As a result, researchers are encouraged to determine and report organic C contents.

Methods currently used to estimate soil organic C contents have been reviewed recently by Nelson and Sommers (1996) and include dry and wet combustion methods for total C and dichromate wet oxidation methods for organic C. Total C analyses involve the complete conversion of all C in the soil to CO_2 and quantification of the evolved CO_2 by various means (e.g., infrared detection, increased mass of an Ascarite trap, or others). Corrections for the presence of inorganic C must be performed when using total C methods if carbonates are present in the soil. Where organic C contents are measured using dichromate methods (e.g., Walkely and Black, 1934; and subsequent modified methods), an excess of dichromate is added. The unused dichromate is titrated with $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ to determine the amount of dichromate used during the reaction and thus the amount of organic C present. A basic assumption of the dichromate procedure is that soil organic C has a valance of 0. In addition, dichromate oxidation methods are subject to interferences from Cl^-, Fe(II) or Fe(III) oxides, and Mn. The presence of significant amounts of Cl^- and Fe^{2+} will lead to an overestimation, while the presence of MnO_2 will result in an underestimation of organic C levels. The extent of heating used in the analysis is also important. Where the heat of dilution or minimal external heating is used, complete oxidation of soil organic compounds does not occur and correction factors must be applied to the results of the oxidation procedure. Correction factors ranging from 1.0 to 2.86 have been noted in the literature and an average value of 1.3 is recommended if an experimentally derived value is not available (Nelson and Sommers, 1996). Dichromate methods that incorporate extensive heating (Tinsley, 1950) do not require a correction factor as oxidation of the soil organic C is considered complete. Heating has also been implicated in the ability of dichromate oxidation procedures to recover the organic C contained in carbonized materials (charcoal, charred plant materials, etc.); however, the impact of heating is variable and Nelson and Sommers (1996) suggest that recovery is highly dependent on the characteristics of the carbonized materials. Recent results obtained by J. Skjemstad (Personal communication) show that the particle size of charcoal is an important factor

determining its susceptibility to oxidation by dichromate, with increased detection as particle size decreased. Of the methodologies currently available, a dry combustion automated analyzer which measures CO_2 evolution with an infrared detector is the preferred methodology for determining soil organic C, provided accurate estimates of inorganic C contents can be obtained where required.

2.4 Factors Determining Soil Organic C Levels

The amount of organic C contained in a particular soil is a function of the balance between the rate of deposition of plant residues in or on soil and the rate of mineralization of the residue C by soil biota. Losses by erosion or leaching may be significant in some cases. With the exceptions of peatland and wetland soils (Histosols), which have been estimated to accumulate 0.1–0.3 Pg C yr^{-1} globally (Post et al., 1990), organic C levels in soil do not increase indefinitely but rather tend to equilibrium values dictated by the soil forming factors of climate, biota (vegetation and soil organisms), parent material, time, and topography. During the initial phases of soil development, a lack of available nutrients places a ceiling on the amount of organic C which can be fixed by photosynthetic organisms. The low rates of C addition and low nutrient status are not capable of supporting large populations of decomposer organisms. Thus, soil organic C accumulates slowly, aided by mechanisms capable of biologically stabilizing organic C against processes of decomposition. The mechanisms through which soil organic C can be biologically stabilized depend on the composition of the soil mineral phase and the chemical structure of the organic residues added to the soil. Thus, each soil could potentially offer a different protective capacity. With continued soil development, organic C content and the activity of decomposer organisms increase to a point where a continued supply of nutrients in a plant available form is reached. At this point, the rate of organic C synthesis and deposition is much greater than mineralization, and organic C accumulates at an exponential rate. With increasing organic C content, the proportion of potential sites of biological stabilization which remains vacant decreases, and an increasing proportion of added organic C cannot be biologically stabilized. As a result, the increase in organic C per unit time proceeds through an inflection point and then begins to decrease. Once the capacity for biological stabilization offered by soil mineral components is approached, the rate of mineralization of organic materials tends toward the rate of deposition of fresh organic residues and soil organic C levels approach an equilibrium value.

It is important to note that biological protection rarely equates to a permanent and complete removal of organic C from the decomposing pool, but rather to a reduction in its rate of decomposition when compared to similar materials existing in an unprotected state. As the older protected C is slowly mineralized, its position in the biologically protected pool is replaced with younger modern organic C, but the proportion of such modern organic C in the protected pool remains low. It is possible that some forms of soil organic C may be rendered unavailable to decomposition for prolonged periods (potentially on a geologic time scale) through mechanisms such as entrapment between layers of clay plates (Theng et al., 1986) or burning to create charred plant residues and/or charcoal. Pieces of charcoal selectively removed from soil and unassociated with soil minerals have been shown to have radiocarbon ages equivalent to or greater than soil humin fractions (Pressenda et al., 1996). Typically, the proportion of the total soil organic C held in such more highly stable forms would be minor. However, in recent soil fractionation/ultraviolet oxidation studies, J. Skjemstad (Personal communication) has estimated that charcoal C can account for 0–40% of the total organic C found in Australian soils.

The progression of soil organic C content with soil development and the magnitude of the equilibrium level of soil organic C will depend on interactions which occur between the factors of soil formation. Where cold and water saturated soil conditions persist, decomposition is confined to slow

anaerobic processes and organic C contents may continue to increase leading to the formation of Histosols. In sandy soils, the extent of biological protection offered by the soil mineral component will be much different than that offered by clay rich soils and large differences in organic C content of the two textural classes of soil develop.

An independent evaluation of the influence of any single soil-forming factor on soil organic C content is difficult because of the requirement that all other factors remain constant. Variations in the soil-forming factors experienced on a landscape scale and the interdependence of these factors contribute to the large variability noted for soil organic C contents, even within localized areas. Computer simulation models of soil organic C dynamics (e.g., Parton et al., 1987) can be used to provide valuable information pertaining to the interaction of soil-forming factors on soil organic C levels and thus, ecosystem functioning, but field data are still required to validate predictions (Burke et al., 1989).

An additional factor which must be considered in an examination of factors influencing soil organic C contents in disturbed soils (those used for agriculture and forestry) is management. Management can induce rapid and drastic changes to equilibrium contents of soil organic C attained under natural undisturbed conditions and completely override the influence of soil-forming factors. Combining this observation with early results presented by Jenny (1930) indicates that the relative importance of the soil-forming factors on SOM content can be viewed as: management > climate > biota (vegetation and soil organisms) > topography = parent material > time.

2.4.1 Climate

Climate impacts on soil organic C content primarily through the effects of temperature, moisture, and solar radiation on the array and growth rate of plant species, and on the rate of soil organic C mineralization. Post et al. (1982) found that amounts of soil organic C were positively correlated with precipitation and, at a given level of precipitation, negatively correlated with temperature. In the Great Plains of North America, precipitation controls net primary productivity and temperature controls rates of soil organic C mineralization (Parton et al., 1987; Sala et al., 1988; Burke et al., 1989; USDA-SCS, 1994). Ladd et al. (1985) compared the mean loss of ^{14}C-labeled plant residues from four soils in South Australia with those obtained by Jenkinson and Ayanaba (1977) for soils in England and Nigeria and observed a doubling of the rate of substrate C mineralization for an 8–9 °C increase in mean annual temperature. An influence of temperature on decomposition can also be inferred from ^{14}C signatures of soil organic C, which showed a latitudinal gradient in the mean residence time of soil organic C (Bird et al., 1996).

The observed trend of decreasing soil organic C content with increasing temperature implies that the relative temperature sensitivity of decomposition is greater than that of net primary productivity. Because of the strong interactions between temperature, water availability and substrate quantity, it is difficult to assess the temperature dependence of decomposition without confounding effects. In a compilation of data extracted from controlled incubation studies where water limitations were avoided and a common substrate was used at all temperatures, Kirschbaum (1995) showed that the Q_{10} value of C mineralization from soil was greater than that for net primary productivity developed by Lieth (1973), especially at temperatures < 15 °C. Increases in temperature, particularly when starting from temperatures < 15 °C, will enhance decomposition more than net primary productivity.

Climate has also been shown to affect the chemical structure of soil organic C. Using pyrolysis-gas chromatography to characterize the chemical structure of soil organic C in a climosequence of nine New Zealand soils, Bracewell et al. (1976) observed significant correlations between changes in the intensity of peaks in the chromatograms and mean annual precipitation and temperature. By including both temperature and precipitation in a regression analysis, the resultant regression line explained

90% of the variation in chromatogram peak intensities. Amelung et al. (1997) used ten grassland samples originating from different climatic zones of the North American Great Plains to investigate the impacts of mean annual temperature and precipitation on the chemical structure of soil organic C using a combination of chemical methods and ^{13}C NMR. Mean annual precipitation was capable of accounting for only 10% of the variation in alkaline CuO oxidizable lignin. Higher precipitation tended to favor an accumulation of polysaccharide C; however, at a given mean annual precipitation, polysaccharide C tended to decrease with increasing temperature. Amelung et al. (1997) suggested that the increased content of polysaccharide C in more humid conditions may have resulted from (1) a positive feedback mechanism in which increased plant production enhanced microbial activity and soil structural conditions, thereby offering the potential for stabilizing microbial polysaccharides within aggregates, and/or (2) an enhanced activity of earthworms increased polysaccharide content relative to the surrounding soils (Guggenberger et al., 1995b) and offered organic C some physical protection against mineralization (Lavelle and Martin, 1992). Accompanying the decrease in polysaccharide C noted with increasing temperature, Amelung et al. (1997) noted an increase in aliphatic C content. Accumulation of alkyl C at high temperature may be explained by (1) enhanced mineralization of carbohydrates and selective preservation of plant or microbially derived alkyl structures by adsorption onto clay particles (Baldock et al., 1989, 1992), and/or (2) higher inputs of plant-derived alkyl C in plant residues due to the presence of thicker cuticles on plants growing in warmer climates.

2.4.2 Soil Mineral Parent Materials and Products of Pedogenesis

The mineral phase of soils can exert a strong influence on soil organic C contents as a result of mechanisms capable of stabilizing organic materials against biological attack. As noted above in Section 2.4, each soil has a given capacity to protect soil organic C dictated by the following soil characteristics: (1) the chemical nature of soil minerals, (2) the presence of multivalent cations and their ability to form complexes with organic molecules in soils, (3) the adsorptive capacity of soil minerals for organic materials as governed by particle size and surface area, (4) physical protection mechanisms which restrict access of organic materials to biological attack. As with other aspects of soil organic C dynamics addressed so far in this review, strong interactions can exist between these characteristics (e.g., the presence and type of multivalent cations will undoubtedly be related to the chemical nature of the minerals present).

2.4.2.1 Chemical Nature of the Soil Mineral Fraction

An analysis of different soil types indicates that soils with high contents of active $CaCO_3$ and amorphous Al and Fe tend to have higher organic C contents (Sombroek et al., 1993). In a study of the influence of soil properties on soil organic C genesis, Duchaufour (1976) suggested that the presence of $CaCO_3$ in a Rendzina could stabilize fresh and humified organic materials. Thin carbonate coatings visible under stereoscan examination, and a precipitation of organic molecules induced by Ca^{2+} complexation were implicated in the stabilization of fresh and humified organic residues, respectively, and helped to explain the observed impedance of mineralization. Stabilization of organic C in high base status soils with less reactive or low contents of $CaCO_3$ results predominantly from the formation of Ca organic linkages. In such soils, the initial decomposition of plant residues is rapid, but the subsequent utilization of initial decomposition products is slow leading to higher soil organic C contents, lower C/N ratios and longer retention times. Soils with high base status typically have higher clay contents, are more fertile, and have greater annual vegetative inputs than similar low base status soils. Establishment of causative relationships between base status and organic C contents must,

therefore, be examined carefully because of the potential confounding effects of increased vegetative inputs and stabilization mechanisms involving clay minerals.

Soils derived from volcanic ash (Andisols) are typically characterized by large accumulations of organic C, high C/N ratios, and high allophane contents. The formation of Al organic complexes is considered to be important to the biological protection of organic C in Andisols. Boudot et al. (1986, 1988) obtained a significant correlation between the amount of native C mineralized from 10 French highland soils and the contents of amorphous Al and allophane, without observing significant correlations with clay content, exchangeable Al^{3+}, or crystalline Fe oxides. Decreased organic C mineralization rates from ^{14}C-labeled organic substrates in allophanic and nonallophanic soils amended with allophane, relative to that noted in unamended nonallophanic soils, also demonstrated a protective effect of allophanic material on soil organic C (Zunino et al., 1982; Boudot et al., 1988; Boudot et al., 1989). Zunino et al. (1982) demonstrated that the influence of allophane on mineralization of C from an organic substrate varied with the chemical structure of the substrate. The presence of amorphous Fe compounds and Fe^{3+} cations has been shown to have a similar effect to that of allophane and Al^{3+} cations on the mineralization of C from organic materials; however, the magnitude of the protective effect was reduced (Boudot et al., 1989).

2.4.2.2 Impacts of Multivalent Cations

The presence of multivalent cations in soil has important implications on the behavior of clays and organic materials, and the biological availability of organic C. When saturated with multivalent cations, clays remain flocculated, which reduces exposure of organic materials adsorbed onto their surfaces (Section 2.4.2.3) and macromolecular organic materials bearing functional groups become more condensed, and thus, less susceptible to biological attack. The dominant multivalent cations present in soils include Ca^{2+} and Mg^{2+} in neutral and alkaline soils and hydroxypolycations of Fe^{3+} and Al^{3+} in acidic, ferrallitic and andic soils. A stabilizing effect of Ca^{2+}, relative to Na^{+}, on organic C mineralization was effectively demonstrated by Sokoloff (1938), where the extent of mineralization and solubility of organic C in two soils was reduced by addition of Ca^{2+} salts and enhanced by addition of Na^{+} salts. Other studies have also shown a decreased solubility of organic C in the presence of Ca^{2+} (Muneer and Oades 1989c) and reduced mineralization of native organic materials and organic substrates on addition of Ca^{2+} in incubation studies (Linhares, 1977; Muneer and Oades, 1989a,b). In such studies, the question remained as to whether the effect of Ca^{2+} addition on mineralizable C resulted from an indirect effect on colloidal dispersibility or from a direct effect of Ca^{2+} complexation on the biodegradability of organic molecules.

A direct effect of multivalent cation complexation on biodegradability in soil was demonstrated by the following results: (1) a reduced oxygen absorption on incubation of humic acids saturated with Ca^{2+}, Al^{3+}, or Fe^{3+} in the same soil, relative to that noted for Na^{+}-saturated humic acids (Juste and Delas, 1970; Juste et al., 1975), (2) an increased stability of Al^{3+} and Fe^{3+} forms of plant and microbial polysaccharides (Martin et al., 1966, 1972), and (3) a three-fold increase in the amount of C mineralized from an organic soil after replacing Ca^{2+} cations with K^{+} during a 25-week incubation (Gaiffe et al., 1984). Indirect evidence for the involvement of cations in the accumulation of organic C in soils can also be obtained through a comparison of the organic C contents of a variety of soil types. Using data derived from Spain et al. (1983) for the organic C contents of 29 Australian great soil groups, Oades (1988) showed that, excluding soils subject to waterlogging, there was a positive correlation between organic C contents and either high base status or the presence of substantial contents of Al and Fe oxides. Of interest was the comparison of siliceous and calcareous sands which have little or no clay, but indicate an increased soil organic C content in the presence of Ca^{2+}-containing mineral fractions (< 0.5–1.5% versus 1.5–> 4% organic C, respectively.)

2.4.2.3 Adsorption of Organic Materials onto Mineral Surfaces

Clay particles provide a reactive surface onto which organic materials can be adsorbed and it is generally accepted that such adsorption reactions provide a mechanism of stabilizing soil organic C against microbial attack. Correlations between soil organic C and clay contents have been observed (Schimel et al., 1985a,b; Spain, 1990; Feller et al., 1991) and the various interactions between soil clays and organic materials have been summarized by Oades (1989). Such interactions are principally defined by the chemical nature of organic materials (functional group content, molecular size, etc.) and the type of clay mineral (kaolinite, illite, smectite, etc.). Numerous studies utilizing isotopically labeled organic substrates have shown a positive relationship between the contents of residual substrate C and soil clay content (Amato and Ladd, 1992).

In a field experiment where ^{14}C-labeled plant residues were added to four cultivated soils varying in clay content (5–42%) but having similar clay mineralogy, climatic conditions, and no other organic inputs, the amounts of residual ^{14}C and total organic C in the topsoil (0–10 cm) remaining after 8 years of decomposition were nearly proportional to soil clay content (Ladd et al., 1985). Saggar et al. (1996) completed a similar study in which the decomposition of ^{14}C-labeled ryegrass was monitored over six years in four soils having variable clay content (16–60%) and clay mineralogy. The mean residence time of the ^{14}C-labeled ryegrass was not related to clay content but rather to surface area as measured by adsorption of *p*-nitrophenol. The increase in mean residence time with increasing soil surface area suggested that the protective capacity of the soils toward transformed metabolites derived from plant residues was principally controlled by adsorption onto soil surfaces. Since the data presented by Ladd et al. (1985) were derived from soils with a similar clay mineralogy, soil surface areas would have been well correlated with clay content. The importance of available surface area was also suggested by the results of Sørensen (1972, 1975) where the addition of high surface area montmorillonite to a soil/sand mixture stabilized microbial metabolites, but addition of low surface area kaolinite had little influence. These results suggest that the potential protective capacity of soil clay minerals is more a function of the surface area available for adsorption of organic C than the actual amount of clay.

2.4.2.4 Physical Protection Within Soil Matrix Offered by Soil Architecture

The architecture or structural condition of a soil can exert significant control over processes of biological decomposition by limiting the accessibility of soil organic C to decomposer microorganisms and of microorganisms to their faunal predators. This limitation results from the ability of clays to encapsulate organic materials (Tisdall and Oades, 1982), the burial of organic C within aggregates (Golchin et al., 1994b, 1997b), and the entrapment of organic C within small pores (Elliott and Coleman, 1988). As outlined by van Veen and Kuikman (1990) and Hassink (1992), evidence of the importance of these processes in the protection of organic C in soils can be inferred from the following observations: (1) a faster turnover rate of organic substrates in liquid microbial cultures relative to that of similar substrates in mineral soils, (2) an enhanced mineralization of C and N when soils are disrupted prior to incubation, and (3) a more rapid mineralization of organic C and plant residues in sandy soils than clay soils.

A continuum of pore sizes exist in soils, starting with large macropores (> 20 μm) and decreasing to micropores (< 0.1μm). Kilbertus (1980) suggested that bacteria can only enter pores > 3 μm, which suggests that a significant proportion of the soil pore space may not be accessible to microbial decomposers. Organic materials adsorbed onto clay particles contained in pores < 3 μm would only be decomposed as a result of diffusion of extracellular enzymes released by microorganisms. With increasing soil clay content, the proportion of the total soil pore space contained in micropores increases, and the potential for stabilization due to the exclusion of soil microorganisms increases. This concept of exclusion can be extended to the predation of microorganisms by soil fauna. Van der

Linden et al. (1989) suggested that Protozoa and nematodes are excluded from pores < 5 μm and < 30 μm, respectively. Killham et al. (1993) showed that although placing glucose into pores < 6 μm or < 30 μm did not impact on the rate of glucose decomposition, the turnover of glucose C incorporated into the microbial biomass was slower where glucose was only added to pores < 6 μm.

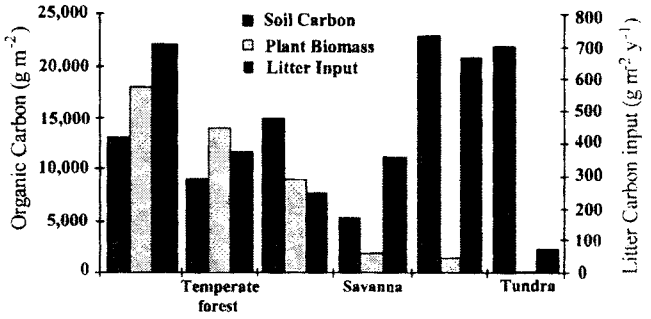
The ability of clay particles to adsorb organic materials can also contribute to a biological stabilization of soil organic C through an encapsulation of organic residues in soils and the formation of stable aggregates. Encapsulation of particulate organic residues in soils not only places a physical barrier between decomposer organisms indigenous to soils and substrates, but can also can limit the movement of water and O_2 to sites of potentially active decomposition. A similar situation develops within soil aggregates. Relative to the larger pores between aggregates, the smaller pores within aggregates are more likely to remain filled with water during drying events, and therefore, restrict O_2 movement into the aggregate. The presence of organic cores in aggregates (Beare et al., 1994a,b; Golchin et al. 1994, 1997a,b) will serve to increase this effect by enhancing O_2 consumption within the aggregate. It has been found that anaerobic conditions can exist in the core of moist aggregates even under well-aerated conditions (Sexstone et al., 1985). In native grasslands, Amelung and Zech (1996) demonstrated that the exterior 0.5 mm of > 2 mm diameter peds contained less organic C and had a higher C/N ratio, less lignin, and more microbial derived saccharides than ped interiors. The organic C associated with ped surfaces, therefore, appeared to turn over more rapidly, and exhibit a greater degree of decomposition than that contained within peds.

2.4.3 Biota: Vegetation and Soil Organisms

2.4.3.1 Vegetative Inputs: Variations across and within Ecosystems

Vegetation can influence soil organic C levels as a result of the amount, placement and biodegradability (chemical recalcitrance) of plant residues returned to the soil. The greatest effects of vegetation on soil organic C contents are confined to the A horizon. Concentrations of organic C detected below the A horizon result from pedogenic processes, which occur over much longer time scales than the lifetime of current vegetation. Volkoff and Cerri (1988) showed that for Brazilian soil profiles, current vegetative cover was only in direct equilibrium with topsoil (A horizon) organic C, while that in subsoils was largely unaffected by the nature of vegetative cover. Once the organic C moves to depth (e.g., argillic or spodic horizons), it becomes less accessible to decomposer organisms, as exemplified by the increased radiocarbon ages of soil with depth (Pressenda et al., 1996).

Scharpenseel et al. (1992) provided estimates of the amount of organic C contained in the vegetation, soil, and annual litterfall associated with various ecosystems (Fig. 2.1). Across the tropical, temperate, and boreal forests, a continuous decrease in the amount of plant biomass and litter C is noted, with little change in the amount of organic C stored in soils. The decrease in the ratio of plant biomass C: soil organic C was associated with an increase in turnover time from 18 to 60 yr. Presumably, most of this variation was related to the effect of temperature on litterfall decomposition; however, significant changes in litterfall quality and morphology are also evident. On the basis of the information reviewed in Section 2.4.1, the amount of residue returned to the soil under similar types of vegetation appears to be a function of climatic factors, principally the amount of precipitation; however, this will depend on the nature of the factor most limiting plant growth. Where ample water is available, the amount of residues returned to the soil may be a function of some other factor such as nutrient supply. Where climatic and soil factors are constant, residue placement may become important. A comparison of the amounts of organic C contained in the plant biomass and soils of temperate grassland and forest ecosystems reveals that despite a much smaller amount of plant biomass in the grassland, annual litter C inputs and soil organic C contents were approximately twice



Plant biomass C / Soil organic C	1.38	1.55	0.60	0.33	0.06	0.01
Turnover time (y^{-1})	18	24	60	15	34	293

Fig. 2.1 Variations in mean soil organic C contents, plant biomass C contents and rate of litter deposition in various ecosystems [Drawn from data of Scharpenseel et al., 1992]

that of the forests (Fig. 2.1). The occurrence of deep organic rich mineral horizons in temperate grassland soils (e.g., Mollisols), in comparison to the concentration of organic materials in litter layers in boreal forest soil (e.g., Spodosols), is an example of the influence which vegetation can have on soil organic C content and distribution within the soil profile. The apparent larger input of belowground residues in grassland soils, compared to forest soils, places organic C in close proximity to the soil mineral components, thereby enhancing the potential for biological stabilization via the mechanisms discussed in Section 2.4.2. Turnover times in grassland soils are greater than in forest soils (34 versus 24 yr, respectively).

The fate of surface deposited residues depends on the activity of soil microorganisms and fauna and their ability to mix these residues into the surface mineral horizons. In well-drained soils with high Ca status, the activity of earthworms and other soil fauna is high, leading to a mixing of organic residues through processes of particle size diminution, ingestion and casting, and bioturbation. Under such conditions, a mull type humus layer is formed and litter layers do not develop. Plant residues and their decomposition products are intimately mixed with soil mineral particles, which facilitates potential biological stabilization through organomineral interactions (Section 2.4.2). Soils low in Ca do not support as active soil faunal populations and plant residues tend to accumulate on the soil surface forming organic rich, mor-type humus layers. Within mor-type humus little potential exists for biological stabilization other than that due to the chemical recalcitrance of highly decomposed residues. The intermediate form of humus is referred to as a moder.

2.4.3.2 Composition of Plant Materials: The Parent Material for Soil Organic C

Plant materials can be viewed as the parent material for soil organic C in much the same manner as one views primary minerals as the parent materials of soil mineral components. Plant materials are altered by soil fauna and microorganisms, predominantly after deposition in or on the soil, resulting in changes in the original chemical structure and in the synthesis of new compounds, just as some soil minerals dissolve and others precipitate during pedogenesis. An understanding of the chemical nature of plant materials is, therefore, important to studies of soil organic C genesis and composition.

Plant materials consist of a range of different compounds varying in concentration across plant species, plant components (e.g., conducting, supporting or photosynthetic tissues), growth stages, and space (distribution in the landscape). Plant cells can be divided up into three components: the

cytoplasm, cell membranes and cell walls. The cytoplasm contains the simple sugars, organic acids, amino acids, and enzymes essential to maintain metabolic activity. Cell membranes consist of globular proteins embedded within a lipid bilayer. Plant cell-wall components include hemicelluloses, celluloses, lignins, proteins, cuticular and root waxes. Oades (1989) presented the following average contents for the major types of organic C in plant residues: (1) extractable materials including water extractables (simple sugars, amino acids and organic acids) and organic solvent extractables (free and bound alkyl molecules including fats, oils and waxes) – 200 g kg^{-1}, (2) hemicelluloses – 200 g kg^{-1}, (3 celluloses – 300 g kg^{-1}, (4) lignins – 200 g kg^{-1}, and (5) proteins – 60 g kg^{-1}.

The organic components of plant cell walls account for the majority of the mass of plant residues deposited in soils. Carbohydrate structures consist mainly of the polysaccharides cellulose and hemicellulose. Cellulose is the primary component of cell walls with a dominant structure of D-glucopyranose residues linked into a polymer via β-1,4 linkages (Fig. 2.2). Cellulose can exist in either a crystalline or amorphous state as indicated by X-ray diffraction (Atalla and van der Hart, 1984) and solid-state ^{13}C nuclear magnetic resonance (van der Hart and Atalla, 1984). The crystalline state is more highly resistant to microbial and enzymatic degradation than the amorphous form (Ljungdahl and Eriksson, 1985). Hemicellulose is defined as the polysaccharides extractable in alkali solution. The hemicelluloses exist as linear and branched polymers of D-xylose, L-arabinose, D-mannose, D-glucose, D-galactose, and D-glucuronic acid monomers, which may be acetylated or methylated. Most hemicelluloses are composed of 2 to 6 of these monomers linked together primarily via a β–1,4 linkage backbone as shown in Fig. 2.2 for pectin, a glucuronic acid polymer.

Lignin represents the second most abundant organic compound in plant residues, and accounts for approximately 5% of the mass of grasses and up to 30% of the mass of hardwood forest species (Haider, 1992). The basic building block of lignin, coumaryl alcohol, can be substituted with zero,

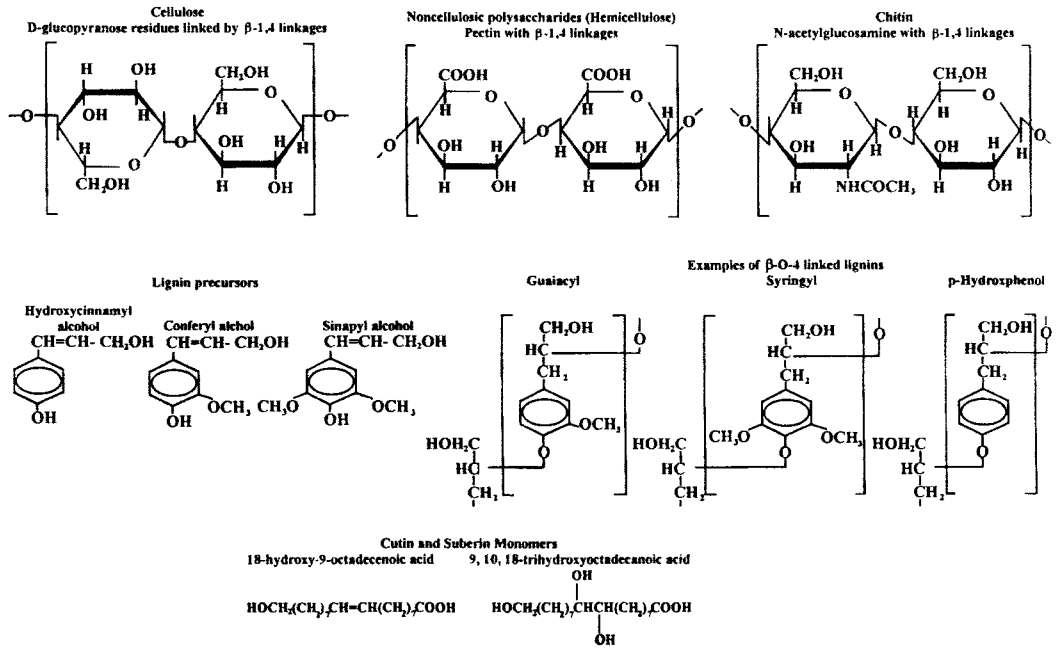


Fig. 2.2 Representative chemical structures of the organic macromolecules found in plant and microbial residues entering the soil.

one, or two methoxyl groups at the C-3 and C-5 positions on the benzene ring to produce the *p*-hydroxyphenol, guaiacyl and syringyl lignin monomeric units, respectively (Fig. 2.2). The units are then linked together by more than 12 possible interunit linkages based on C-O or C-C bonds (McDougall et al., 1993). The major interunit linkage, accounting for about 60% of the linkages, is the β-O-4 linkage depicted in Fig. 2.2 for the three lignin monomeric units. The nature of the lignin molecule changes with plant type: softwoods (gymnosperms) are dominated by guaiacyl-based lignin, hardwoods (angiosperms) contain a mixture of guaiacyl- and syringyl-based lignin, and grasses are dominated by syringyl lignin. Results presented by Hedges et al. (1985) suggested that such changes in lignin composition can affect its biodegradability, with syringyl lignin being more susceptible to decomposition than guaiacyl lignin.

The protein and water soluble components of plant residues, unless stabilized against biological attack, provide a readily decomposable substrate capable of supplying the chemical energy and nutrients required to drive soil biological processes. Enzymatic cleavage of the peptide linkages to form amino acids and mineralization of amino acid N to form NH_4^+ provide sources of N for soil biological processes, and the abiotic chemical processes, to be discussed subsequently.

Alkyl components of plant materials include free and bound lipids, polyesters, and nonsaponifiable alkyl C-dominated biopolymers. Free and bound lipids represent a heterogeneous group of neutral and polar molecules which are classified together based on their solubility in organic solvents (Tegelaar et al., 1989). The neutral component consists of triacylglycerols and waxes, which serve to protect external plant surfaces and to store energy. The polar component is dominated by the esterified fatty acids found in cell membranes. Insoluble polyesters derived from hydroxy fatty acids are found in cutin in plant cuticles and in suberin in roots. Cutin and suberin are composed of various long-chain (C_{16} and C_{18}) substituted fatty acids. The main substituent group is hydroxyl with lesser amounts of epoxy, ketone and carboxyl groups also present (Holloway, 1982). Two examples of cutin and suberin monomers are presented in Fig. 2.2 and Tegelaar et al. (1989) have presented figures showing additional monomeric chemical structures and a proposed model of the structure of intact cutin and suberin. Plant cuticles and roots have also been shown to contain nonsaponifiable aliphatic biopolymers which have been labeled cutan and suberan (Nip et al., 1986a,b, 1987). Cutan and suberan are considered similar to cutin and suberin with the exception that they are highly crosslinked by nonester bonds.

In order to assess the influence of plant residue composition on decomposition and mineralization, it is essential to remove other confounding effects such as climatic, soil and biological parameters. In field studies, this can be accomplished by examining decomposition of all residues of interest at a single site. Vedrova (1997) assessed the impact of forest species on litter decomposition rates by placing litter collected from each species on small plots located within a single unforested site. Mean rates of mineralization measured for cedar, pine, larch, spruce, aspen, and birch litter over ~ 2 years were 1.93, 1.57, 1.85, 2.20, 2.56, and 2.57 mg C g^{-1} litter C d^{-1}, respectively. A limitation of such studies is demonstrated, however, by the work of Elliott et al. (1992), in which the decomposition of four different forest litters (mixed hardwood, red pine, beech, and hemlock) was examined in each of the oril four forest types. The rates of decomposition were principally a function of litter type, with mixed hardwood litter decomposing the fastest and hemlock litter the slowest. However, with the exception of the mixed hardwood litter, decomposition rates of the individual litter types were highest when they were placed in the forest type from which they were derived (i.e., decomposition of the hemlock litter was greatest in the hemlock forest). This interaction between litter type and forest type suggests that decomposition pathways in any given ecosystem may be tailored to the type of litter deposited. Thus, the results of decomposition studies where litters are removed from their ecosystem

of origin, or where the community structure of the decomposer organisms is altered, may not accurately reflect the relative effects of residue composition on decomposibility.

2.4.3.3 Relative Impacts of Soil Fauna and Microorganisms

The requirement of soil organisms for chemical energy and nutrients drives processes of heterotrophic decomposition in soils, which account for the major pathways through which soil organic C is mineralized. Abiotic chemical oxidation is unlikely to account for > 20% of total C mineralization (Moorehead and Reynolds, 1989) and more often accounts for < 5% (Lavelle et al., 1993). Microorganisms are the major contributors to soil respiration and are responsible for 80–95% of the mineralization of C. Hassink et al. (1994) calculated that the contribution of the fauna to C mineralization in two sandy and two loam grassland soils ranged from 5–13% of the total C mineralization. The pattern of C mineralization by the soil fauna through time, noted by Hassink et al. (1994), differed from that of total C mineralization, suggesting that the activity of the soil fauna did not contribute substantially to the differences in total C mineralization observed between the soils. Hassink et al. (1993) concluded that soil protozoa and nematodes did not significantly influence soil C mineralization despite a positive response of bacterivorous nematodes on the amount of N mineralized. Several other studies have shown that soil fauna enhanced nutrient mineralization, and had both positive and negative effects on soil organic C mineralization (Griffiths, 1994; Kajak, 1995; Alphei et al., 1996). In a study including protozoa, nematodes and earthworms, Alphei et al. (1996) noted that none of the fauna studied significantly affected basal respiration.

The role of soil fauna in decomposition processes should not be based only on their direct contribution to C mineralization. Soil fauna also act to reduce the particle size of litter, distribute it within the soil, transport otherwise immobile microorganisms to new sites within the soil matrix, and prime microorganism activities by the production of easily metabolizable substrates (e.g., earthworm intestinal mucus). In so doing, soil fauna generally enhance microbial activity and rates of decomposition. Soil conditions which limit (e.g., water saturation and the development of anaerobic conditions) or enhance (e.g., tillage or installation of drains in imperfectly drained soils) the activity of soil microorganisms or fauna will also impact significantly on organic C mineralization rates and thus, alter soil organic C levels.

2.4.3.4 Composition of the Microbial Community

The population of decomposer microorganisms in soil is extensive; densities up to 1010 bacteria and several km of fungal hyphae per gram of soil have been measured in a wide range of soils (Lavelle et al., 1993). As a result of the diversity of decomposer organisms, the existence of interactions between specific types of organic residue and species of decomposer organisms can have pronounced effects on the chemical structure and biological availability of residual organic materials. The decomposition of woody materials provides an excellent example of how the species composition of the decomposer population can influence the chemical nature of decomposition products. Laboratory incubations of Eucryphia cordifolia wood with a brown rot fungus (unidentified species) and a white rot fungus (Ganoderma australe) showed a more selective utilization of carbohydrate C by the brown rot fungus and a delignification by the white rot fungus (Martínez et al. 1991). Using the same white rot fungus in a solid-state fermentation procedure with beech wood, Martínez et al. (1991) noted little change in the chemical composition of the wood, despite a 36% mass loss. Barrassa et al. (1992) obtained similar results in an ultrastructural study. Selective delignification of *Laurelia philippiana* wood by the white rot fungus *Phlevia chrysocrea* was noted, but decomposition of the same wood by *Ganoderma*

australe resulted in increased lignin contents. The selective degradation of carbohydrates by brown rot fungi appears to occur independently of the fungal or wood species involved. However, the presence of a selective or nonselective degradation process for white rot fungi appears to depend on interactions between the species of fungus and wood. Under anaerobic conditions, the activity of obligate aerobes such as wood degrading fungi is limited and bacterial decomposition processes dominate. In examinations of buried woods, it has been found that decomposition processes invariably result in a preferential utilization of carbohydrates and a concentration of lignin (Bates and Hatcher, 1989; Bates et al., 1991). Such data indicate that changes in species composition of the decomposer community can significantly alter the decomposition processes and thus, rates of accumulation or loss of organic C from soils. At present, insufficient data exist to extend the results obtained for woody residues more generally to nonwoody organic materials, but the governing principle would be expected to be similar.

2.4.3.5 Relationship Between Organic Residue Composition and Chemical Recalcitrance

All organic C in soils can serve as a substrate. In addition to the potential mechanisms of biological stabilization of organic materials offered by the soil mineral fraction, chemical structure can also impart a degree of chemical recalcitrance. Rates of decomposition of known organic substances in soils were reviewed by Paul and van Veen (1978). Although variations in decomposition rates for any single substrate were evident as a result of differences in soils and incubation conditions, simple organic molecules and monomeric compounds decomposed most rapidly. Oades (1989) showed that the extent and rate of mineralization of C for a series of polysaccharides (glucose, dextran, cellulose) and a fungal polysaccharide) decreased with increasing molecular complexity and branching. Similar results were obtained by Martin and Haider (1975) for the mineralization of C from specifically ^{14}C-labeled benzoic and caffeic acid monomers and polymers. C mineralization was most extensive from carboxylic acid groups, less extensive from the aromatic ring C of the monomers, and least extensive from the polymeric aromatic ring C. Of the polymeric materials contained in plant residues, lignin and other polyphenolic C and aliphatic C appear to be the most recalcitrant, but as discussed in the previous section, the stability of lignin C will be related to the species composition of the decomposer community.

Many studies have demonstrated a relationship between decomposition and plant residue characteristics thought to be indicative of residue quality (Edmons and Thomas, 1995; Hobbie, 1996; Cortez et al., 1996; Ågren and Bosatta, 1996). Included in these residue characteristics are N concentration, C:N ratios, lignin and/or polyphenol concentration, lignin:N ratios, and acid soluble carbohydrates. In a laboratory incubation experiment, examining the impact of temperature on decomposition of six species of tundra vegetation, patterns of decomposition were better correlated with substrate C composition than nutrient; mass losses were positively correlated with acid-soluble carbohydrate content and negatively correlated with lignin content (Hobbie, 1996). In a separate incubation study, mass loss from four types of one-year-old mediterranean ratio of the litter (Cortez et al., 1996; Ågren and Bosatta, 1996). Included in these residue characteristics are N concentration, C:N ratios, lignin and/or polyphenol concentration, lignin/N ratios and acid soluble carbohydrates. In a laboratory incubation experiment, examining the impact of temperature on decomposition of six species of tundra vegetation, patterns of decomposition were better correlated with substrate C composition than nutrient; mass loss from four types of one year old Mediterranean deciduous leaf litter as well correlated with the %N, C:N ratio, lignin concentration and lignin:N ratio of the litter (Cortex et al., 1996). Ågren and Bosatta (1996) found that the proportions of extractable, acid soluble, and acid insoluble C obtained from a conventional chemical fractionation could be used to assess the quality of forest litter, particularly when the acid insoluble fraction did not dominate. During the decompisition of plant residues, significant changes in chemical composition of residual C are evident

(Baldock et al., 1997). In response to such changes, Berg and Staaf (1980) proposed a model of litter decay in which decomposition was controlled initially by N content, but subsequently, by lignin concentration. This was supported by the results of Edmonds and Thomas (1995), which showed that organic C mineralization rates from green needles of western hemlock and pacific silver fir were initally similar, but became more a function of litter chemistry (e.g., lignin:N ratio) as decomposition progressed.

2.4.4 Topography

Topography exerts its major control over soil organic C contents through a modification of climate and soil textural factors, and through its impacts on the redistribution of water within a landscape. Soils in downslope positions are often wetter, have warmer average temperatures, and have finer textures than soils in upslope positions or at the top of knolls. Burke et al., (1995) examined the extent to which soil organic C varied at a landscape scale at two sites differing in soil texture, but having similar climatic characteristics. Burke et al. (1995) noted increased organic C contents (and clay and silt contents) in downslope positions relative to the summits at both sites. Such a finding has been attributed to the downslope movement of organic C and organic rich clay (Reiners, 1983). However, additional gradients in available water along slopes, especially in water limited systems, influence plant production (Peterson et al., 1988) with greater biomass inputs and a greater potential biological stabilization of organic C via higher clay contents at the base of slopes. Where excessive water exists, drainage of depressions in the landscape can be restricted, leading to the development of anaerobic conditions and preservation of organic C relative to the better drained higher landscape elements during wetter times of the year.

2.4.5 Land Management Practices

Paustian et al. (1997) have comprehensively reviewed the influence of agricultural management practices on soil organic C levels. The influence of forestry management practices has been reviewed by Johnson (1992). The most dramatic influence of agricultural practices occurs when soils are first brought into production. Typically, soil organic C levels decrease for the first few years after cultivation and then stabilize at a new equilibrium level which is dictated principally by the ability of the soil to stabilize organic C and amount, quality, and distribution of plant residues inputs. For example, 28–59% of the soil C was lost following 30 to 43 yr of cropping at 11 sites within the North American prairies (Haas et al., 1957). The following characteristics of cereal production systems, in comparison to those of native grasslands, help to explain the observed losses of soil organic C induced by cultivation: (1) 80% lower allocation of organic C to soils (Buyanovsky et al., 1987), (2) reduced below ground allocation of photosynthate (Anderson and Coleman, 1985), (3) enhanced aggregate disruption and exposure of physically protected organic C due to cultivation (see Section 2.4.2.4), and (4) enhanced rates of decomposition of available organic C substrates due to more favorable abiotic conditions (e.g., aeration, temperature and water content).

The intensity with which soil is cultivated can impact both the total amount of soil organic C and its distribution with soil depth. No-till systems tend to concentrate residue inputs at the soil surface and generally enhance soil organic C and N contents in soil surface layers. Therefore, to accurately evaluate the influence of tillage practices on soil organic C stores, it is important to sample at least to the depth of tillage, and preferably, deeper. Paustian et al. (1997) presented data from a number of long-term field trails indicating that soil organic C retention is typcally enhanced under no-till relative to more intensive conventional tillage systems. The selection of annual crops and the inclusion of annual and perennial pastures or mechanical fallows in rotation with annual crops can significantly

impact on soil organic C levels. In a long-term crop rotation trial located at the Waite Institute in Australia, soil organic C contents have increased under permanent pasture and declined to varying degrees under cropping systems, with the extent of the delcine being related to the intensity of soil cultivation (Tisdall and Oades, 1982). Field trials set up to examine the impact of fertilizer additions on soil organic C content have revealed that the addition of N fertilizers typically enhances soil organic C contents. Explanatory mechanisms suggest that N fertilizer additions result in a greater return of plant residues to soils, a reduction in decomposition rates due to enhanced soil drying (Andrén, 1987), a promotion of soil acidification (Thurston et al., 1976), a repression of lignilytic enzymes, and a formation of recalcitrant humic materials through a reaction of amino acides with humic precursors (Fog, 1988).

In tropical systems, the establishment of pastures after clearing of forests is becoming increasingly widespread (Sombroek et al., 1993). Pasture establishment immediately after deforestation, using species with high proportions of below-ground biomass, may increase soil organic C contents as demonstrated in the Brazilian Amazon (Serrâo et al., 1979), Latin America (Ligel, 1992) and East Africa (Boonman, 1993). If pastures are installed after one or more cycles of shifting cultivation, productivity is low and soil organic C levels remain low (Sombroek et al., 1993).

2.5 Chemical Structure of Soil Organic Matter

2.5.1 Characterizing the Chemical Structure of Soil Organic C

2.5.1.1 Wet Chemical Methods of Extraction and Characterization

Classical approaches to chemical characterization of soil organic C involved the use of water- and organic solvent-based chemical extractants, and various degradative procedures considered selective in their attack on specific molecular structures. After the removal of macroorganic materials via sieving or flotation and extraction of dissolved organic C (DOC), the remaining organic C was partitioned into humic substances and nonhumic biomoleculres. The distinction between these two forms of organic C is based on structural chemistry (Table 2.2). Several of the potential methodologies capable of being used to quantify and examine the composition of different classes of nonhumic biomolecules are indicated in Fig. 2.3. Although not indicated in Fig. 2.3, such selective methodologies can be applied equally to the macroorganic and DOC fractions and to the humic fractions to selectively remove nonhumic biomolecule contamination.

In the classical extraction scheme (Fig. 2.3), humic substances are differentiated simply on the basis of their extractability in alkali solution at pH values ranging from 10–13, and subsequent solubility on acidification of the alkali extract of pH 2. The unextracted alkali insoluble fraction is referred to as humin. The material which remains soluble in the acidified alkaline extract is the fulvic acid fraction while that which precipitates is the humic acid fraction. All three humic fractions are not discrete compounds, with each fraction containing a multitude of different chemical structures which can be further fractionated and purified. Each fraction typically contains nonhumic biomolecules as a result of the nonspecific nature of the alkaline extraction procedure. Purification of the humic and fulvic acid fractions, by removal of the nonhumic biomolecules, results in the isolation of humic and fulvic acids.

The use of alkaline reagents to extract soil organic fractions prior to the application of characterization procedures has been criticized of late, especially with the development of techniques which allow the chemical composition of soil organic C to be assessed *in situ*. Prior to the development of such spectroscopic techniques, extraction of soil organic materials from the mineral components was a prerequisite to their selective characterization. The main criticisms put forward include (1) the

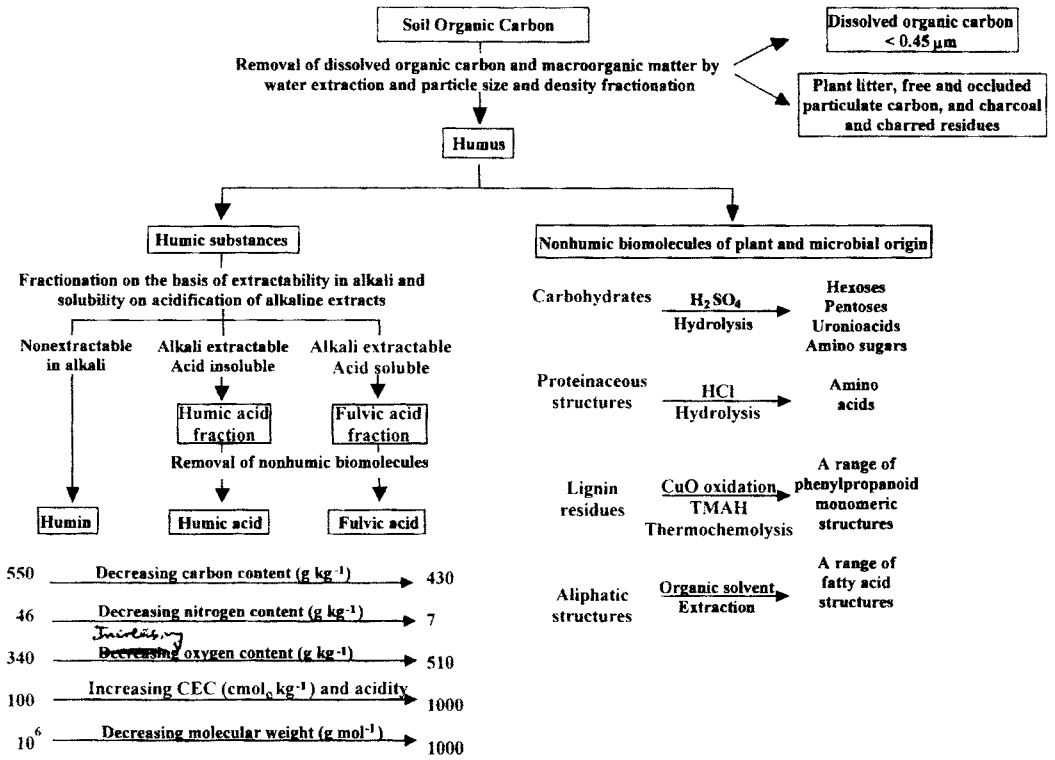


Fig. 2.3 Fractionation of soil organic matter based on chemical and physical properties [Modified from Oades, 1989]

questionable ability of the alkaline extractable organic matter to represent the composition of the non-extracted and whole soil organic fractions, (2) the apparent lack of a relationship between the biological functioning of organic C in soils and its extractability in alkaline reagents based on C and N isotopic tracer studies (Oades, 1995), (3) differences in the chemical characteristics displayed by the extracted organic molecules when compared to those of the same materials existing in soils in an adsorbed state (e.g., conformation, cation binding capacity, hydrophobicity, etc.), and (4) the creation of artifacts during the extraction procedure.

Of greatest concern is the creation of artifacts during the alkaline extraction procedure. A recent study by Zuman and Rupp (1995) used differential pulse polarography (DPP) and spectrophotometry to examine the impact of alkaline solutions on the cleavage of lignin. The rate of lignin cleavage and release of soluble aromatic aldehydes were shown to follow first order kinetics, with the magnitude of the rate constant describing lignin cleavage increasing exponentially over the pH range of 7.5 –10.5. Negligible release was noted at pH values < 7.5. A similar effect of solution pH was noted for the rate constant associated with the release of aromatic aldehydes directly from a sandy loam. The maximum release of aromatic aldehydes occurred within 1 or 2 h for the sandy loam and the lignin, respectively. Therefore, under the recommended conditions of alkaline extraction of humic materials from soils, namely, the exposure of soil to a solution of pH 13 for 4 h (Swift, 1996), a significant release of aromatic aldehydes, and potentially of many other aromatic species from lignin may occur. Acidification of alkaline solutions containing aromatic fragments of lignin results in an acid-catalyzed polymerization, and the formation of polymers having chemical structures and molecular masses different from those of lignin. The release of aromatic aldehydes from humic acids extracted from the

sandy loam used by Zuman and Rupp (1995) was found to differ from that of the whole soil and lignin in two ways: (1) release of aromatic aldehydes was initiated at pH 3; and (2) the kinetics of release were much faster (maximum release was attained in 10–20 min). The presence of two different mechanisms of release was suggested from the polarographic data. The similar patterns of aromatic aldehyde release from the whole soil and lignin and the contrasting pattern noted for humic acids suggested that the predominant aromatic components found in the whole soil were derived from unaltered lignin and/or partially degraded lignin fragments, and not from humic acids. This observation, taken in conjunction with the potential acid catalyzed polymerization of lignin fragments extracted by alkaline reagents, suggests that at least a portion, and potentially a significant component, of the humic acid fraction of soil organic materials is not representative of materials naturally present in soils, but is an artifact of the extraction procedure, especially when high pH extractants (pH > 10) are used. In addition, the cleaved aromatic species which do not polymerize on acidification of the alkaline extract end up in the fulvic acid fraction. Therefore, some of the organic species that end up in the fulvic acid fraction may also be a result of the alkaline extraction procedure employed.

Swift (1996) suggested that the problem of artifact production can be reduced by using mild extraction reagents (e.g., neutral sodium pyrophosphate); however, the pH of the extractant would have to be decreased to < 7.5. In doing so, the efficiency of organic C extraction would decrease to the point where the extracted organic C would no longer be an adequate representation of the entire soil organic C fraction. It is strongly suggested that the use of alkaline extractants be avoided, and that a combination of modern spectroscopic techniques and/or wet chemical degradative procedures known to be selective in their action (molecular techniques) be utilized to characterize soil organic C.

2.5.1.2 Spectroscopic Methods of Characterization

Modern spectroscopic techniques that can be used to probe the chemical structure of soil organic C *in situ* include solid-state ^{13}C MNR, analytical pyrolysis, and Fourier transform infrared spectroscopy (FTIR). Selected review and research articles addressing the details of the techniques, recent developments, and their application to the study of organic materials in soils are presented in Table 2.4. Modern spectroscopic methods are complementary and, where possible, efforts should be made to utilize combinations of these methods to confirm and enhance data pertaining to the chemical structure of soil organic materials.

Solid-State ^{13}C Nuclear Magnetic Resonance Spectroscopy (^{13}C NMR)

Only the application of solid-state ^{13}C NMR to soils will be examined in this chapter; however, other forms of NMR including solid-state ^{15}N NMR and solution state ^{13}C, ^{15}N, and ^{31}P NMR have potential applications to the study of organic materials in soils (see Table 2.4 for indicative studies). The greatest positive aspect of the application of solid-state ^{13}C NMR to soils and soil fractions is its ability to characterize the chemical structure of soil organic C *in situ* and nondestructively. A typical spectrum acquired by applying the conventional solid-state cross-polarization magic angle spinning (CPMAS) ^{13}C NMR pulse sequence to soil humus is presented in Fig. 2.4a (Skjemstad et al., 1997). Organic C found in different chemical environments can be differentiated on the basis of chemical shift (the x axis in Fig. 2.4a expressed in units of ppm of the applied magnetic field). A review of the solid-state ^{13}C NMR chemical shift values of organic C found in a wide variety of known chemical structures has been presented by Duncan (1987). Solid-state ^{13}C NMR spectra acquired for most mineral soils with < 50 g C kg^{-1} soil are typically divided into four regions of chemical shift because of the large heterogeneous mixture of different types of organic C: alkyl C (0–45 ppm), O-alkyl C (45–110 ppm), aromatic C (110–165 ppm), and carbonyl C (165–220 ppm). The labels given to each chemical shift region are only indicative of the dominant form of organic C present, and there will undoubtedly be a range of

Table 2.4 List of review and research articles pertaining to the application of and recent developments in modern spectroscopic techniques to the characterization of the chemistry of soil organic materials

Title
Nuclear Magnetic Resonance Spectroscopy (NMR)
Applications of NMR to soil organic matter analysis - history and prospects (Preston, 1996)
N.M.R. techniques and applications in geochemistry and soil science (Wilson, 1987)
Characterisation of soil organic matter by solid-state ^{13}C NMR spectroscopy (Skjemstad et al., 1997)
Nuclear magnetic resonance in agriculture (Pfeffer and Gerasimowicz, 1989)
^{13}C NMR studies of soil organic matter in whole soils: I. Quantitation possibilities (Kinesch et al., 1995)
Pyrolysis-gas chromatography-mass spectrometry (PyGCMS)
Characterization of humic and soil particles by analytical pyrolysis and computer modeling (Schulten and Leinweber, 1996)
Thermal degradation of humic substances relevant to structural studies (Bracewell et al., 1989)
Analytical pyrolysis of humic substances and soils: geochemical, agricultural and ecological consequences (Schulten, 1993)
Pyrolysis and soft ionization mass spectrometry of aquatic/terrestrial humic substances and soils (Schulten, 1987)
Infrared spectroscopy (IR)
Characterization of humic acids, composts, and peat by diffuse reflectance Fourier transform infrared spectroscopy (Niemeyer et al., 1992)
Vibrational, electronic, and high energy spectroscopic methods for characterising humic substances (Bloom and Leenheer, 1989)

structures within each region. Spectra acquired for mineral soils with > 50 g C kg^{-1}, peats, forest litter, and other materials with high C contents such as particulate soil organic fractions can often be divided into narrower chemical shift regions indicative of more discrete types of C, because of higher signal to noise ratios.

The relative contribution of each type of C can be estimated by expressing the integral of signal intensity under a given peak or across a given chemical shift region as a proportion of the total integrated area of the entire spectrum. Such an approach to assessing the distribution of chemical structures within a sample should be considered as a semiquantitative analysis unless detailed NMR experiments are performed which examine the relative rates of signal generation (T_{CH}) and decay ($T_1\rho H$) and the rates of relaxation (T_1H) for each type of carbon present in the sample (Wilson, 1987; Baldock et al., 1989; Pfeffer and Gerasimowicz, 1989; Kinesch et al., 1995). Even with the completion of such detailed experiments, however, nonquantitative results can be obtained when paramagnetic materials are present or where ^{13}C nuclei are separated from ^{1}H nuclei. The presence of paramagnetic species (metal cations with unpaired electrons or organic free radicals) can drastically reduce the spin-lattice relaxation time (T_1H) such that signals from C in close proximity to such species are not observed. Of principal concern in the application of solid-state NMR to soil is the ratio of organic C to Fe in the samples (Arshad et al., 1988; Skjemstad et al., 1994). Arshad et al. (1988) suggested that, at organic C:Fe ratios > 1, adequate spectra can be obtained, but at ratios < 1, steps must be taken to remove the Fe prior to acquisition of NMR spectra. Skjemstad et al. (1994) showed that organic C:Fe ratios > 1 do not necessarily indicate that reasonable spectra can be accumulated if samples have high magnetic susceptibilities, and that the relative visibility (RV) (integrated spectral area g^{-1} organic C in the sample) of soil organic C could be estimated by Equation [2.5], where OC/Fe is the ratio of the gravimetric percentages of organic C to that of Fe in the sample. RIF is the remaining inorganic

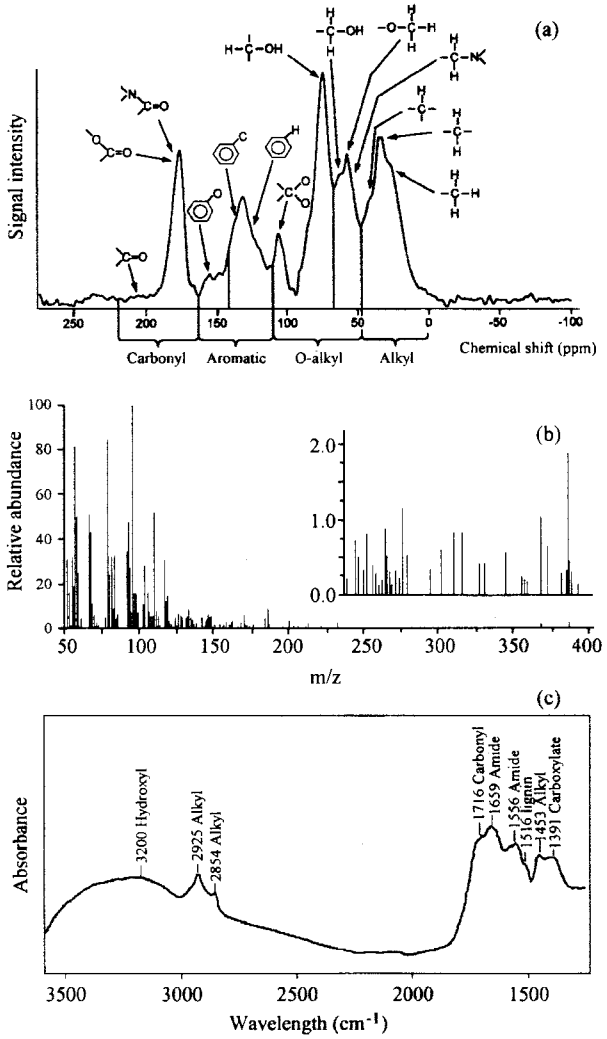


Fig. 2.4 Examples of data obtained using modern spectroscopic techniques to study the chemical structure of soil organic matter. a) Solid-state ^{13}C NMR spectrum of soil humus showing four general chemical shift regions and typical chemical shift assignments (modified from Skjemstad et al., 1997). b) Pyrolysis-field ionization mass spectrum of a humic acid (Schulten, 1987). c) Diffuse reflectance Fourier transform infrared spectrum acquired for the 0-2.5 cm layer of a mineral soil (52 g C kg^{-1}) by subtraction of the spectrum obtained for a sample heated at 350 °C from that of the unheated whole soil.

fraction expressed as a gravimetric percentage of the total mass of the sample after HF treatment, and χ is the mass magnetic susceptibility ($\mu m^3 kg^{-1}$). Repeated pretreatment of soils with a 2% HF solution reduced Fe concentrations and concentrated organic C through the dissolution of a portion of the inorganic matrix, thus enhancing the NMR visibility of the organic C in soil samples considerably. The use of such pretreatments must be examined carefully, since the HF pretreatment may remove significant quantities of organic C.

$$RV = 5.33 + 0.375\ (OC/Fe - 0.147\ RIF + 0.043\ \chi^{-1}) \quad [2.5]$$

The issue of the proximity of ^{13}C to ^{1}H nuclei arises because of the use of cross-polarization in solid-state ^{13}C NMR analyses. Cross-polarization can be used to enhance signal intensity by a factor of 4 under optimum conditions, but organic C that is separated from hydrogen by > 5 bond lengths cannot cross-polarize and will not be observed (Snape et al., 1989). Organic C in soils which contain appreciable contents of highly carbonized organic materials such as charcoal, charred plant material and coal will not be detected quantitatively using the conventional CPMAS analysis, and a Bloch decay pulse sequence must be used. Use of the Bloch decay pulse sequence is restricted because of the exceedingly long accumulation times required to obtain spectra with reasonable signal-to-noise ratios.

Additional chemical information on soil organic C can be obtained through the use of interrupted decoupling (ID), proton spin relaxation editing (PSRE), and mixing of proton spins (MOPS), techniques. The ID pulse sequence (Opella and Frey, 1979), also known as the dipolar dephasing pulse sequence, is capable of differentiating immobile protonated C from nonprotonated C or mobile protonated C. It has been used to assess the proportion of protonated versus nonprotonated aromatic C (Hatcher, 1987), to differentiate between methoxyl and N-alkyl C in the 45–60 ppm chemical shift region (Hatcher, 1987), and to examine the nature of the soil alkyl C fraction (Baldock et al., 1990a,b; Kögel-Knabner et al., 1992a,b). PSRE utilizes differences in T_1H values within a solid sample to derive subspectra associated with fast and slow relaxing hydrogen (Newman and Hemmingson, 1990). The presence of different T_1H values within a single sample implies a spatial separation of organic materials associated with each subspectrum on a scale of > 30 nm. Results from PSRE analyses have demonstrated a spatial separation of polymethylene from aromatic and carbohydrate C in HF-treated humin (Preston and Newman, 1992), plant residue C from humified C (Golchin et al., 1997a,b), and charcoal-like C from humified C (Tate et al., 1990; Golchin et al., 1997b). MOPS represents an extension of the PSRE technique to include differentiation of C on the basis of both T_1H and $T_1\rho H$, which provides information pertaining to the chemistry of C separated by > 30 nm and 2–30 nm, respectively. In applying the MOPS technique to wood, Newman (1992) was able to demonstrate that cellulose microfibrils with a diameter of approximately 14 nm were surrounded by a lignin hemicellulose mixture.

Analytical Pyrolysis

Analytical pyrolysis refers to the characterization of a material by instrumental analysis of its pyrolysis products and encompasses a group of methodologies including offline pyrolysis, pyrolysis-mass spectrometry, derivatization pyrolysis-mass spectrometry, and pyrolysis-gas chromatography/mass spectrometry. A detailed description of these techniques is presented by Schulten and Leinweber (1996).

Application of thermal energy to organic materials results in a cleavage of the weaker bonds in the organic molecules present, and a release of a range of reaction products. The thermal energy can be applied using two techniques: quasi-instantaneous heating (Curie point pyrolysis) or a controlled temperature programmed heating. Temperature programmed methods have been criticized because of the potential to form secondary reaction products unrelated to the organic materials present in the sample. Curie point pyrolysis methods are rapid, sensitive, highly reproducible and can be applied to small samples.

In offline pyrolysis, the loss of C and/or N from a sample during pyrolysis is measured with no attempt to characterize the chemical nature of the pyrolysis products. Using a set of 64 soil samples with organic C contents ranging from 1 to 460 g kg^{-1}, Schulten and Leinweber (1996) showed that the amount of volatilization was proportional to the soil organic C content. It was also shown that the

proportions of organic N which volatilized were often greater than those of organic C. In pyrolysis-mass spectrometry (Py-MS), the pyrolysis reaction products pass directly into a mass spectrometer that is capable of separating the products on the basis of m/z values (mass/charge ratios). Several methods of ionization are available to promote the movement of reaction products through the mass spectrometer: field ionization (FI), chemical ionization (CI), fast atom bombardment (FAB), and laser ionization (LI). Irrespective of the method of ionization utilized, distinctive patterns of pyrolysis products, often referred to as fingerprints, are produced (Fig. 2.4b). Signals located at various m/z values within these fingerprints can be considered diagnostic for particular types of organic molecules. For example, based on the work of Schulten et al. (1987), Schnitzer (1990) tentatively identified several of the signals in Fig. 2.4b as follows: polysaccharides (m/z values of 60, 82, 96, 110, and 126), heterocyclic N-containing structures (m/z values of 79, 92, and 117), and lignin (m/z values of 212, 302, 344). After normalization of the m/z peak intensities, a qualitative assessment of changes in the chemical nature of the organic C in samples of whole soils or soil fractions can be determined. For example, differences in the chemical composition of organic C contained in particle size fractions isolated from two mineral soils were presented by Baldock et al. (1991). Lists of other applications of Py-MS and the appropriate references are presented by Schnitzer (1990) and Stevenson (1994).

A cautionary note regarding the comparison of different of m/z signal intensities is required. First, the intensities observed at any single m/z value may result from multiple pyrolysate fragments if they have the same mass:charge ratio. Second, the volatilization of different types of pyrolysis fragments varies (e.g., in Py-FIMS volatilization decreases with increasing polarity of the fragments). As a result, differences in signal intensities at various m/z values within any one soil sample do not necessarily correlate with contents of the parent molecules present in the original sample. It is appropriate, however, to utilize variations in a given m/z signal intensity to infer difference in structural chemistry across a series of soil samples run under a constant set of analytical conditions.

Various on- and offline derivatization processes have been developed to reduce differences in the volatilization of the various pyrolysis products. Derivatization Py-MS techniques utilizing tetramethylammonium hydroxide (TMAH) convert hydroxyl and carboxyl groups into their equivalent methyl ethers and methyl esters, respectively. Pyrolysis methylation with TMAH enabled detection of aliphatic C_2–C_{39} monocarboxylic acid methyl esters, C_4–C_{30} dicarboxylic acid dimethyl esters, benzenecarboxylic acid methyl esters and a range of other methylated compounds (Schulten and Leinweber, 1996) The incorporation of a gas chromatograph between the pyrolysis chamber and the mass spectrometer can further aid in the separation of similar pyrolysis fragments prior to detection and analysis by the mass spectrometer.

Fourier Transform Infrared Spectroscopy (FTIR)

In its application to studies of the chemical structure of soil organic C, the absorption of infrared radiation of different frequencies can be used to determine the type of the atoms to which C is bound as well as the nature of the bond. Detailed identification of chemical structure is possible for pure simple organic molecules, but the dominance of signals derived from mineral components limits the application of FTIR spectroscopy to the study of soil organic C in mineral soils. Even after extraction of organic materials from soils, the complex and heterogeneous nature of the organic C results in spectra exhibiting absorption bands spanning wide ranges of frequency with few well-resolved peaks. However, comparisons of spectra obtained before and after various chemical degradation or derivation treatments (e.g., carbohydrate hydrolysis and methylation or acetylation) can yield useful information. The use of difference spectra (spectrum of an untreated sample minus that of a pretreated sample) can provide insight into chemical structures. An example of the difference spectrum associated with the removal of organic C from a soil is given in Fig 2.4c and can be used to provide

an approximation of the chemical nature of the organic materials removed in the pretreatment, provided that a significant alteration of the soil mineral components has not occurred.

Infrared spectra contain a vast amount of information pertaining to chemical structure. The problem experienced to date has been how to get at the information and utilize it in a meaningful manner. The use of multivariate statistics such as partial least squares (PLS) allows those portions of an FTIR spectrum that are correlated to other measurements (e.g., total sugar concentration as identified by H_2SO_4 hydrolysis and subsequent colorimetric determination) to be identified across a range of soil samples. Once such relationships have been identified, the content of the required parameter of interest can be estimated with a known degree of precision using FTIR in conjunction with the predictive equations. The rapid nature of modern infrared analyses (several min./sample) when utilized in this manner, would facilitate the acquisition of data without the need for utilizing laborious routine procedures. Skjemstad et al. (1997) have presented the results of such an evaluation in which a strong correlation ($r^2 = 0.977$) was found between aromatic C content as measured by solid-state CPMAS ^{13}C NMR and that generated using PLS procedures in conjunction with FTIR. Given that the typical time required to acquire a solid-state ^{13}C NMR spectrum for a mineral soil is 6–24 h, an enormous potential exists to utilize FTIR data to facilitate an assessment of the chemical nature of soil organic C, provided that enough ^{13}C NMR data exists to complete an appropriate calibration procedure.

2.5.2 Dissolved Organic Carbon

Dissolved organic C (DOC) is a small but important and dynamic fraction of soil organic C. Its importance relates largely to its mobility, both within the soil and from the soil into groundwater or surface water bodies. From a biological point of view, it provides a mobile source of energy and the nutrients associated with it can make an important contribution to nutrient availability and cycling. From a chemical point of view it behaves as a reactive component of the soil solution, and facilitates transport of other materials. A detailed review of information on DOC in soils was recently completed by Herbert and Bertsch (1995).

The term dissolved refers to materials in solution that do not settle out under the influence of gravity. The smaller and more polar an organic molecule, the more likely that it will stay in aqueous solution. Whether or not a particular organic molecule is dissolved depends on the water content of the soil, and the nature of the surfaces and other solutes. At the larger, less polar end of the range, the boundaries between dissolved, colloidal and particulate organic matter are not definite. The definitions are usually made operationally. For example, DOC is usually defined as organic C that has passed through a particular suction cup or filter or that occurs in the supernatant after centrifuging a soil suspension at a given relative centrifugal force for a given period. These operational parameters should be clearly stated in discussions of DOC in soil, and it is important to note that processes such as adsorption onto or clogging of filters or suction cups may significantly influence the nature and amount of material obtained (Grossman and Udluft, 1991). In this chapter, DOC has been defined as that which passes through a 0.45 μm filter.

2.5.2.1 Isolation and Measurement

Before measurement or characterization, DOC must be extracted from the soil. The means of extraction determine the amount and nature of the material extracted (Herbert and Bertsch, 1995). While extraction at or near the water content of interest is desirable, such a procedure may result in very small volumes being collected. At high soil water potential (more negative and drier), extraction becomes impractical, but at low soil water potential (less negative and near saturation), sufficient volumes are often easily obtained. In the field, DOC has been extracted by the use of tension or zero-

tension porous cups or plates, or by wick lysimeters (Grossman and Udluft, 1991). In the laboratory, DOC can be extracted by forcing solution out of the soil through a porous membrane using vacuum or centrifugal force or by leaching repacked columns or undisturbed cores (Dunnivant et al., 1992). For convenience, many studies have used extracts made by shaking soil with water or dilute salt solutions, followed by separation of the solution by centrifugation or filtration. Material extracted by alkaline solutions has also been used to represent DOC. However, this practice is likely to be inappropriate, because materials dissolved by alkali differ from those found dissolved in soil solution (Novak and Bertsch, 1991).

Once a soil extract has been obtained, DOC contents are estimated by oxidizing the dissolved organic C to CO_2, and then measuring the amount of CO_2 produced or oxidant consumed. A common technique that appears satisfactory in most cases is oxidation by persulfate and UV radiation followed by detection of the CO_2 evolved by IR absorbance or other techniques. Techniques that measure the amount of oxidant consumed face similar problems as those discussed in Section 2.3 for the analysis of soil organic C contents. The yellow to brown color of DOC has resulted in the use of absorbance in the visible or UV range to quantify DOC concentrations. Absorbance is simple and convenient and readily lends itself to continual monitoring and logging. However, it should be kept in mind that it is not a direct measure of concentration, as different organic materials differ widely in their absorption properties.

2.5.2.2 Gains, Losses and Amounts

DOC enters the soil as leachate from vegetation and litter, and is generated within the soil through the processes of excretion from organisms and desorption or dissolution from the solid phase. It is lost through biological uptake, extracellular mineralization, sorption, precipitation and as leachate into surface water courses or groundwater. The concentration of DOC is governed by all these processes, and typically ranges from 5–50 mg L^{-1} in surface and litter horizons, and from 0.5–5 mg L^{-1} or less in B and C horizons (McDowell and Likens, 1988).

Plant roots and microorganisms excrete a large variety of soluble organic materials. For example, in anaerobic soils, organic acids (mostly low molecular weight fatty acids) are major byproducts of decomposition. Uptake of organic molecules by roots has been documented, but this removal mechanism is probably of minor importance.

Microbial uptake, decomposition, and mineralization are the major mechanisms determining the concentration and nature of DOC. The amount of DOC in soil has been correlated with soil respiration and denitrification potential (Burford and Bremner, 1975; Davidson et al., 1987). From this, it is sometimes inferred that DOC is the active fraction of SOM, or that it is the pool turning over most rapidly. However, equating DOC with the active pool is only a very rough approximation. Although many organic substrates (e.g., cellulose) are solubilized by enzymes prior to mineralization, the flux of readily mineralized substrates through the DOC pool is not necessarily reflected in the size of the pool, because the concentration of readily available materials such as monosaccharides, simple organic acids, or amino acids is kept very low due to their rapid assimilation or mineralization. Nevertheless, the concentration of readily mineralizable DOC may be temporarily higher in some situations, such as where roots are active or where fresh organic residues have been added (Nelson et al., 1994). The proportion of DOC that is mineralized in short-term incubation studies generally varies between 3 and 40% (Boyer and Groffman, 1996; Nelson et al., 1994), and varies with the soil depth from which it was extracted (Nelson et al., 1994). DOC, as a whole, may not be any more easily mineralized than particulate or adsorbed fractions. Some DOC appears to be biologically recalcitrant (Zsolnay and Steindl, 1991), with the reasons not being well understood. While physical entrainment

may protect particulate organic matter from microbial attack, it is doubtful as a stabilization mechanism for DOC which can diffuse towards organisms (Adu and Oades, 1978).

The processes of adsorption/desorption and dissolution/precipitation are governed by the nature and concentration of the DOC and other solutes, pH, and the nature of the solid phase materials. Sorption occurs on many soil materials through a variety of mechanisms (Oades, 1989). It is greatest at low pH (Jardine et al., 1989), and large or hydrophobic molecules are preferentially adsorbed compared to small or hydrophilic molecules (Dunnivant et al., 1992; Kaiser et al., 1996). In soils with high surface area or high clay content, concentrations of DOC are kept low by adsorption of organic molecules onto mineral surfaces (Nelson et al., 1993). Where multivalent cations, such as Fe or Al in acid soils and Ca in neutral to alkaline soils, are abundant DOC concentrations are kept low because organic complexes of multivalent cations do not ionize readily and are of relatively low solubility. Ong and Bisque (1968) showed that the flocculating effect of cations on DOC was proportional to the sixth power of their valence. Multivalent cations may also form bridges between dissolved organic molecules and mineral particles, thereby taking the organic molecules out of solution (Nelson and Oades, 1998). In water-saturated sediments, DOC concentrations can be high due to dissolution of Fe and Al complexes (Thurman, 1985), and this is probably also the case in waterlogged soils. In soils with low surface area or in soils with a high proportion of monovalent cations, a higher proportion of organic C tends to be dissolved (Nelson and Oades, 1998). Seasonal factors such as temperature and moisture and management factors such as acidification, tillage and application of fertilizer, lime, or manure all influence the amount and nature of DOC in soils (Herbert and Bertsch, 1995). In a leaching environment, DOC that is not retained in the soil by adsorption or precipitation mechanisms is lost to groundwater or surface water (Nelson et al., 1993), where it has a significant influence on water chemistry. Preferential flow through macropores can greatly enhance transport through the soil and loss to water bodies (Jardine et al., 1990).

2.5.2.3 Chemical Structure

The chemical structure of soil DOC is complex and varied. Molecular weight ranges from a few hundred to hundreds of thousands (Homann and Grigal, 1992). Conventional wet chemical molecular techniques can typically identify about 50% of the structures in DOC; the rest remains unidentifiable. Easily identified structures include carbohydrates, hydrocarbons, polyphenolic compounds, and amino, aliphatic and aromatic acids (Stevenson, 1994). Complex material that is not easily identified is commonly referred to as humic substances, most of which can be classified as fulvic acid because it remains dissolved at low pH.

Due to the complexity of DOC, samples are frequently fractionated, either as a characterization or preparative technique for other characterization methods. One of the most widely used fractionation techniques involves sorption on nonionic and ion exchange resins (Herbert and Bertsch, 1995). These and related techniques yield fractions termed hydrophilic and hydrophobic acids, bases and neutrals. DOC has also been fractionated on the basis of molecular size, using gel permeation chromatography or ultrafiltration (Herbert and Bertsch, 1995). Materials in DOC fractions are still complex, and it is not always clear to what extent materials are lost, gained or altered during the fractionation process.

Important characteristics of DOC include its acidity, chemical structure, and sorption behavior. Titratable acidity, largely due to low molecular weight organic acids, varies from 6 to 15 $mol_c\ kg^{-1}$ C (Herbert et al., 1993). Examination by ^{13}C NMR spectroscopy has shown that DOC consists of carbohydrate, aromatic, aliphatic and carbonyl structures (Novak and Bertsch, 1991). In litter and surface horizons, DOC contains a high proportion of aliphatic material and hydrophobic acids, whereas, in deeper horizons, it is less aliphatic and dominated by hydrophilic acids (Easthouse et al., 1992).

2.5.3 Particulate Organic Matter

Particulate organic C (POC) is defined as the C found in fragments or organic debris with a recognizable cellular structure. POC may be derived from any source, but is usually dominated by pieces of plant structures. In the following discussion, POC found in Histosols and on the mineral soil surface (litter) will be dealt with separately from that found within the mineral matrix.

2.5.3.1 POC in Histosols and Forest Litter Layers

Histosols and forest litter layers present a simple system in which to characterize the chemistry of POC and the chemical changes associated with POC decomposition. The absence of mineral particles facilitates a selective chemical characterization of POC, and reduces the biological stabilization of labile organic C via adsorption onto mineral surfaces or physical entrapment within aggregations of mineral particles. In these highly organic materials, decomposition and chemical transformation processes are controlled by the composition of the plant residues and the changes imparted by the decomposer community.

The chemical composition of organic C contained in Histosols has been examined by numerous researchers using ^{13}C NMR. Using rubbed fiber (see Lévesque et al., 1980 for a definition) as an indicator of extent of decomposition, positive correlations were obtained with the contents of alkyl and aromatic C and negative correlations were obtained with the contents of O-alkyl C (Hammond et al., 1985). Cultivating Histosol surface layers induced an increase in alkyl C and reductions in O-alkyl and aromatic C, relative to the uncultivated Histosol (Preston et al., 1987). The reduction in aromatic C presumably resulted from the presence of a more oxidizing environment in the cultivated soil, and an enhanced activity of aerobic lignin degrading fungi. Preston et al. (1989b) and Nordén et al. (1992) examined the chemical changes associated with decomposition of peat by performing ^{13}C NMR analyses on particle size fractions. Nordén et al. (1992) observed a progressive loss of identifiable plant structures and an accumulation of alkyl C and loss of O-alkyl C as particle size decreased. Similar results were obtained by Preston et al. (1989b), but a loss of aromatic C was also noted, and the magnitude of the chemical changes observed across the particle size fractions increased as the overall extent of decomposition exhibited by the Histosols increased.

Assessments of the chemical changes induced by decomposition in forest soils typically include a characterization of the different litter layers encountered in progressing from the fresh litter located at the top of the forest floor through to the well-humified materials located at the top of the upper mineral soil horizon. ^{13}C NMR data collected for a range of German forest soils exhibiting examples of the mull, moder, and mor humus forms showed an increase in alkyl C and a decrease in O-alkyl C contents with depth for all soils (Zech et al., 1992). Changes in aromatic C content were less consistent, but in general, they tended to decrease with increasing extent of decomposition. Baldock and Hatcher (unpublished data, see Baldock et al., 1997) observed a similar pattern of alkyl and O-alkyl C contents in litter layers found under red pine and tamarack plantations, but aromatic C content tended to increase with extent of decomposition. Variations in the aromatic C content with increasing extent of decomposition content are suspected to arise from differences in the activity of lignin degrading fungi. An assessment of the possible mechanisms accounting for an accumulation of alkyl C in forest litter layers is presented in Section 2.5.4.2.

In studies where depth profiles are used to assess the chemical changes associated with decomposition, it is assumed that the composition of the original plant residues deposited on the soil surface has not changed as the litter layers have developed. Where significant differences in the vegetative source of organic C exist, variations in the chemical composition of litter and humified organic C are possible. Krosshavn et al. (1992) observed differences in the chemical composition of organic C found in peats and forest litters derived from different types of vegetation. For samples

exhibiting a similar degree of decomposition and organic C content, the greatest differences in chemical composition were noted between peat and forest organic C; however, differences between forest types were also noted. Thus, when characterizing the changes in chemical composition induced by decomposition in different deposits of terrestrial organic C, care must be taken to ensure that differences in vegetative background are not confounded in the analysis.

2.5.3.2 Particulate Organic Materials Found Within the Mineral Soil Matrix

POC found within mineral soils is usually dominated by plant-derived materials, but can also contain fungal hyphae, spores, pollen grains, and faunal skeletons, as demonstrated by microscopic examinations (Waters and Oades, 1991; Oades and Waters, 1991). This fraction of soil organic C serves as a source of both energy and nutrients for soil organisms, and as a source of nutrients for plants. POC fills an intermediate position between fresh undecomposed plant materials and the more decomposed humus fraction. POC has been separated from the mineral matrix by two main methods: (1) sieving of dispersed soil samples to yield a macroorganic fraction, and (2) collection of dispersed soil materials which float on a heavy liquid to yield a light fraction (Gregorich and Janzen, 1996). A discussion of the methodologies used to separate the macroorganic and light fractions from soil is given in Gregorich and Ellert (1993). Although both POC fractions are dominated by plant residues, the nature of the materials collected in each fraction may differ. In fractions collected on the basis of particle size, humified organic materials bound strongly to large inorganic particles and organic debris coated with mineral particles will be retained on the sieves and included in the macroorganic fraction. In the light fractions, such organo-mineral complexes may have a density higher than that of the fractionating solution and will not be included in the light fraction.

A prerequisite for the collection of either type of POC fraction is a dispersion of the soil, preferably using physical processes which minimize alterations to the chemical composition and particle size distribution of organic fragments. Ultrasonic dispersion is now utilized widely to accomplish this task; despite the potential for a fragmentation of the organic particles and a redistribution of organic materials within the soil with this method (Elliott and Cambardella, 1991; Cambardella and Elliott, 1993). The amount of organic C which accumulates in the macroorganic and light fractions is a function of the intensity of dispersion and the nature of the dispersing medium. Golchin et al. (1994a) observed a loss of light fraction C (< 1.6 Mg m^{-3}) with increasing duration of ultrasonic dispersion, when the dispersion was accomplished in water. The procedure which maximized the extraction of light fraction C involved an initial removal of a free light fraction by gentle end-over-end shaking of soil in the heavy liquid, followed by an extraction of the POC occluded within mineral particle associations by using a 300 s ultrasonic treatment in the heavy liquid.

The lower size limit of the macroorganic fraction varies between investigations, but usually corresponds to the lower size limit of the sand fraction, 20 μm for the ISSS and 50 μm for the American particle size classification systems. Solid-state ^{13}C NMR was used by Oades et al. (1987, 1988) and Baldock et al. (1992) to determine the chemical composition of the organic materials associated with various particle size fractions after ultrasonic dispersion and fractionation by sieving and sedimentation. A density separation was applied to the macroorganic fractions to concentrate the organic C and allow acquisition of acceptable ^{13}C NMR spectra. The chemical composition of the largest macroorganic particles (250–2000 μm or 53–2000 μm) resembled that of plant materials. The reduction of macroorganic particle size to 20–53 μm, induced via an increase in the extent of decomposition, was associated with a loss of O-alkyl C and an accumulation of aromatic and alkyl C. Similar results were obtained by Skjemstad et al. (1993) for four additional Australian soils. The changes in chemical composition noted by Baldock et al. (1992) were consistent with a preferential utilization of carbohydrate structures by soil microorganisms and a preservation of lignin and aliphatic

structures during decomposition. In progressing into the finer fractions, where the dominant form of organic C would be microbial metabolic products and humified materials adsorbed onto mineral surfaces, aromatic C contents decreased and alkyl C contents increased significantly. The increased alkyl C content could not be explained by a selective preservation of plant-derived alkyl C alone, and it was postulated that a contribution was made from microbial alkyl C synthesized as a metabolic product of decomposition processes. These observations led to the development of a simplified model which describes the oxidative decomposition of POC fragments in mineral soils (Baldock et al., 1992). The model is consistent with a biopolymer degradation model proposed by Hatcher and Spiker (1988) for the genesis of humic substances.

The separation of light fractions from soils utilizes the difference in particle density between organic and mineral particles. Organic particles generally have a density of ≤ 1.0 Mg m^{-3} while that of mineral particles is > 2.0 Mg m^{-3}. Most studies, where light fractions have been isolated, have used heavy liquid densities ranging from 1.5 – 2.0 Mg m^{-3}; however, liquids with densities as low as 1.0 Mg m^{-3} have been used for the isolation of light fractions from soils having a low mineral particle density, such as Andisols (Golchin et al., 1997b). Studies on soil aggregation have suggested that many soil aggregates have cores of organic particles (Waters and Oades, 1991) and that macroaggregates form around particles of plant residues (Beare et al., 1994a; Buyanovsky et al., 1994; Golchin et al., 1998). As a result, two forms of light fraction POC exist in soils: (1) free POC without significant association with mineral particles, and (2) occluded POC strongly associated with mineral particles or buried within soil aggregates. The extent to which a soil is disrupted will, therefore, dictate the amount of free and occluded light fraction released and measured, particularly in highly aggregated fine-textured soils. The chemical composition of free and occluded light fractions was examined by ^{13}C NMR for five different soil types (Golchin et al., 1994a). Relative to the free light fractions, which had a chemical composition similar to that of the plant materials deposited on the soil, the occluded light fraction always showed decreased contents of O-alkyl C and increased contents of alkyl C. A significant increase in aromatic C was observed for two of the five soils when progressing from the free to occluded light fractions and only minor changes in the carbonyl C region were detected. This result indicated that the free and occluded POM in soils are chemically distinct, and that the occluded fraction exhibits a chemical structure consistent with a more highly decomposed POC fraction. This work was extended to examine the nature of the organic materials associated with the occluded light fraction in more detail by fractionating it into four density classes: < 1.6, 1.6–1.8, 1.8–2.0, and > 2.0 Mg m^{-3} (Golchin et al., 1994b). Again, different chemical compositions were observed for the different classes of occluded organic C. Progressing from the 1.8–2.0 to 1.6–1.8 to < 1.6 Mg m^{-3} occluded fractions, chemical changes were again consistent with an enhanced extent of decomposition. Microscopic examination of these occluded fractions indicated that the < 1.6 and 1.6–1.8 Mg m^{-3} fractions existed as fragments of plant debris exhibiting characteristics associated with extensive decomposition (e.g., the presence of lignin coils and large pores). The 1.8–2.0 Mg m^{-3} fraction was found to exist as only slightly decomposed plant fragments strongly bound to and buried within a mineral matrix. The chemical composition of organic C contained in the > 2.0 Mg m^{-3} fraction did not resemble that of plant fragments, and was considered representative of microbial residues and humified organic materials of plant origin adsorbed onto mineral surfaces. These results were summarized by Golchin et al. (1994b) in a model linking the chemical composition of the light fraction POC to decomposition and aggregation. The model was supported by subsequent work examining the organic C turnover rates for the various free and occluded POC light fractions (Golchin et al., 1995) and then was extended by Golchin et al. (1998)

In addition to the contributions of decomposed plant residues to soil POC fractions, evidence of significant contributions to POC fractions from charcoal or charred residues in some soils has been

presented (Skjemstad et al., 1996b). After treating soil silt fractions (< 53 μm) with an ultraviolet photo-oxidation process capable of oxidizing most of the biologically derived organic components found in soils (for a description of the method, see Skjemstad et al., 1993), the residual organic materials of three soils showed a particulate morphology and a chemical composition consistent with charcoal. The large broad aromatic C peak observed in ^{13}C NMR spectra acquired for the ultraviolet photo-oxidized and HF-treated samples was similar to that found for chars produced by heating cellulose to > 400 °C (Shafizadeh, 1984), and for thermally degraded cork (Pascoal Neto et al., 1995). The significant enhancements noted in the aromatic region of ^{13}C NMR spectra acquired using a Bloch decay pulse sequence, relative to the standard cross-polarization pulse sequence, were also consistent with the highly condensed/nonprotonated aromatic C typically found in charcoal and charred plant residues. Skjemstad et al. (1996) calculated charcoal C contents of 3.2, 3.4, and 8.3 mg charcoal C g^{-1} soil which accounted for up to approximately 30% of the total organic C found in the soils. Golchin et al. (1997a,b) examined the nature of the POM fraction in a series of Andisols, in which the length of time since annual burning of grassland had ceased, differed. UV photo-oxidation was unsuccessful in identifying a residual charcoal component within the POC fractions because of the presence of inorganic cementing agents which are not removed by the photo-oxidation procedure. However, data acquired from the PSRE and Bloch decay NMR techniques indicated that, relative to the site where annual burning had not been practiced, annual burning of grasses led to the presence of a charcoal-like fraction as evidenced by the following characteristics: (1) nonlignin highly aromatic C separated physically from undecomposed plant residue like C and (2) the presence of condensed and proton deficient aromatic C (Golchin, 1997a). Subsequent density fractionation of these Andisols, followed by application of PSRE and Bloch decay NMR experiments (Golchin et al., 1997b), showed that charcoal was distributed throughout the 1.0–2.0 Mg m^{-3} fractions. However, the charcoal accounted for a greater proportion of the organic C in the < 1.6 and 1.6–1.8 Mg m^{-3} occluded POC fractions of all sites, even those without a recent history of burning.

The presence of significant quantities of nonlabile charcoal in soils will have significant implications for studies of POC composition and dynamics. The aromatic portion of soil fractions, after accounting for lignin and lignin like structures (e.g., tannins), is typically considered to be derived from humic substances. Using estimates of lignin and tannin contents based on ^{13}C NMR data, Skjemstad et al. (1996) demonstrated that much, if not all, of the aromatic C remaining, after accounting for lignin and tannin structures, could be accounted for by their estimates of charcoal C, and that extracted humic acid fractions had chemical structures consistent with charcoal. Models of POC dynamics typically utilize total organic C measurements to quantify the size of POC pools. The presence of even small quantities of inert charcoal C in POC fractions could significantly alter estimates of turnover times and radiocarbon ages associated with the fraction of soil POC not derived from charcoal or charred plant materials.

2.5.4 Soil Humus

Soil humus refers to the amorphous organic materials remaining in soils after extraction of the water-soluble fraction and exclusion of particulate organic materials (Fig. 2.3). Humus consists of a mixture of humic substances and nonhumic biomolecules. In alkaline and neutral soils, humus dominates the soil organic fraction because of the rapid decomposition of plant residues by soil fauna and microorganisms. In acidic soils, plant fragments make a larger contribution to the soil organic fraction; however, humus still represents an important fraction and can contribute significantly to soil processes (e.g., podzolization and mineral dissolution). Although recent evidence questions the importance and validity of the classical humic fractions (Section 2.5.1.1), it is not yet possible to simply dispel their importance in soils and a discussion of their chemical properties is required.

2.5.4.1 Humic Substances

The component fractions of soil humic substances, humin, humic acid and fulvic acid, exhibit a continuum of several chemical characteristics (Fig. 2.3). Since the differentiation of the three humic fractions is based simply on their solubility in alkaline and acid solutions, fractionation procedures are method dependent. Quantitative, reproducible fractionation can only be achieved by strict adherence to a given methodology. Changes in methodology (e.g., the type and concentration of solute in the extractant) can significantly alter the partitioning of soil humus C into these fractions and the chemical characteristics observed for each fraction (Hayes et al., 1975). A standard extraction methodology exists (Swift, 1996) and well-characterized reference and standard humic substances are available from the International Humic Substances Society.

The ability to extract and de-ash soil humic and fulvic acids facilitated the acquisition of detailed data pertaining to their chemical composition and physical properties. Much less information has been collected for soil humin fractions; however, the introduction of spectroscopic methods capable of *in situ* analysis has enhanced our understanding of the composition of soil humin (Saiz-Jimenez et al., 1979; Preston and Newman, 1992). Average chemical formulae for humic and fulvic acids as suggested by Steelink (1985) are $C_{10}H_{12}O_5N$ and $C_{12}H_{12}O_9N$, respectively. Humic acids contain more C and N but less O than fulvic acids. Stevenson (1994) and Swift (1996) have provided detailed compilations of the chemical methods used to quantify the content of functional groups, the degradative methods used to identify structural components, and the physical methods used to measure properties such as molecular weight and particle size. Data collected by Schnitzer (1977) on the functional group content of humic and fulvic acids extracted from soils found in different climatic zones showed significant variations. Solid-state ^{13}C NMR analyses of humic acids and fulvic acid fractions from several soil types also revealed structural differences (Malcolm, 1990).

Detailed reviews of the chemical composition and structure and physical properties of humic substances can be found in Oades (1989), Hayes et al. (1989), Stevenson (1994), and Beyer (1996). On the basis of the information presented in these reviews, the chemical and physical properties of soil humic substances can be summarized as follows: (1) aromatic rings are a significant component and multiple substitution with carboxyl, hydroxyl, carbonyl and alkyl groups exists; (2) significant quantities of C1-C20 alkyl C chains either unsubstituted or substituted with O-containing functional groups are present, with smaller chain lengths predominating; (3) aromatic and alkyl groups are bound together principally by C-C bonds and ether linkages to form the backbone structure of the humic molecules; (4) the aromatic alkyl backbone structure is random and is not characterized by a regular sequence of aromatic and alkyl groups; (5) simple and polymeric proteinaceous and carbohydrate groups may be bound to the aromatic alkyl backbone or physically associated with humic surfaces; and (6)molecular weights vary from 10^3 to in excess of 10^6 and the molecules exist in random coils, which are more tightly cross-linked and coiled in the center. An attempt to combine these characteristics has led to the generation of chemical models representative of an average structure for humic materials such as that presented by Schulten and Schnitzer (1993) for humic acid.

The range in both type and content of function groups, the presence of numerous chemically different monomeric components, and the inclusion of biopolymer-like components in humic structures, suggest that a variety of different mechanisms may be involved in their genesis. The mechanisms of humic substance genesis have been reviewed (Hatcher and Spiker, 1988; Hedges, 1988; Stevenson, 1994; Shevchenko and Bailey, 1996), and there is general consensus that humic substances result from the transformation of organic plant residues. The proposed mechanisms of genesis can be placed within two contrasting categories: (1) partial biotic biopolymer degradation, where the integrity of the biopolymer is not destroyed, and the modified biopolymer forms the humic substance backbone, and (2) abiotic condensation polymerization, in which simple products of

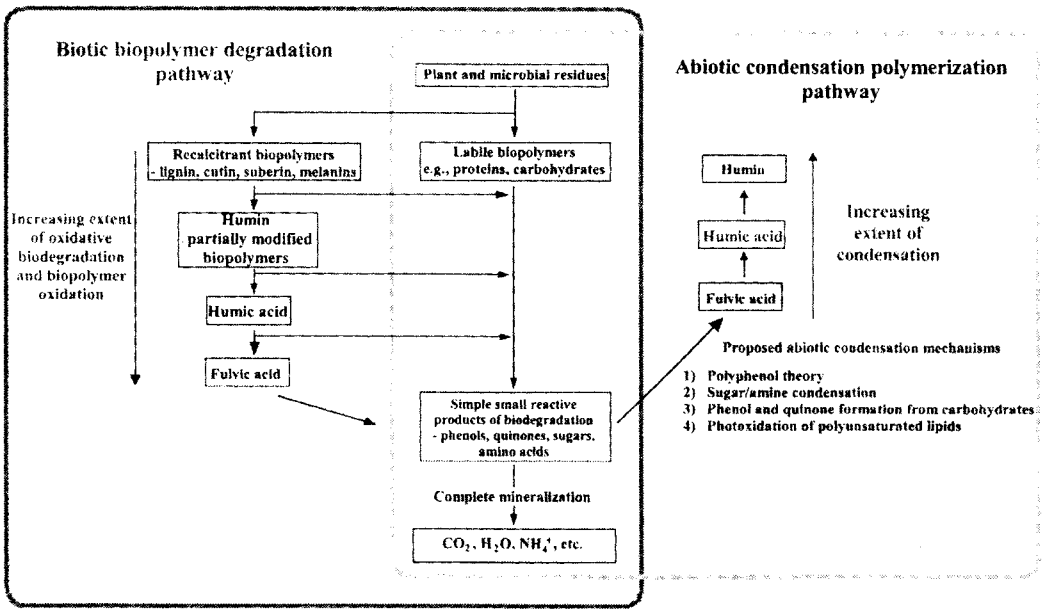


Fig. 2.5 Schematic representation of the mechanisms postulated to be involved in the genesis of soil humic substances [Based on models presented by Hedges, 1988 and Hatcher and Spiker, 1988]

biopolymer degradation repolymerize to form humic substances (Fig. 2.5). It is important to note, as suggested by Hedges (1988), that the two mechanisms of humic substance genesis are not mutually exclusive, since biopolymer degradation is prerequisite for the abiotic condensation pathway. The term abiotic is used to refer to the later steps in the pathway in which chemical reactions between simple compounds released by biotic processes condense to form the humic substances.

In the proposed biotic biopolymer degradation pathway, recalcitrant macromolecules enter the humin fraction in a partially altered state. ^{13}C NMR data have indicated the presence of lignin-like humin structures in anaerobic peats, whereas the humin fraction of aerobic soils lacks the methoxyl, aryl ether, and phenolic groups typical of lignin (Hatcher et al., 1985). Significant quantities of aliphatic C presumed to originate from plant cuticles (Nip et al., 1986b), microbial sources (Hatcher et al. 1983; Baldock et al., 1989), or the cleavage of lignin ring structures (Flaig, 1966) are also present in the soil humin fraction. As the extent of decomposition of humin molecules increases, small organic fragments are released and the content of O-containing functional groups (carbonyl and hydroxyl) increases on the residual molecule. Such increases in functional group content result in an increased extractability of the residual molecule in alkaline solution, indicative of a transition from humin to humic acid. Although similarities in chemical structure between humin and humic acids are noted, humic acids typically contain less methoxyl and more carboxyl C than humin (Hatcher et al., 1985), and pyrolysis studies indicate that the monomeric species of residual lignin structures in humic acids exhibit a more advanced stage of decomposition than those found in humin (Saiz-Jiminez et al., 1979). Further oxidative degradation fragments the humic acid molecules, and increases the content of O-bearing functional groups to produce fulvic acids and simple monomeric species. Ertel and Hedges (1984) have demonstrated that fulvic acids also contain lignin-derived structures, and that the extent of alteration was greater than that noted for humic acids. To account for the N contained in humic substances, a reaction mechanism has been proposed whereby amino groups react with modified lignin (Stevenson, 1994).

In the abiotic condensation polymerization pathway, molecular fragments released during the decomposition of precursor molecules and/or molecules released as metabolic byproducts from microorganisms polymerize via chemical reactions. As the molecular weight of the synthesized polymer increases, a progression from fulvic acid to humic acid to humin occurs. Four abiotic mechanisms have been proposed and schematic representations of the various chemical reactions are presented by Hedges (1988) and Stevenson (1994): (1) the polyphenol theory, (2) the melanoidin model (a sugar/amine condensation reaction), (3) phenol and quinone formation from carbohydrates, and (4) photo-oxidation of polyunsaturated lipids. In the polyphenol theory, monomeric phenolic species (mono-, di-, and trihydroxy phenols) are produced by the enzymatic degradation of lignin (Kirk, 1984) or synthesized by various soil microorganisms (Martin and Haider, 1971). These monomeric phenolic species are capable of forming a quinone structure in the presence of O_2 or polyphenoloxidase enzymes, which spontaneously polymerize with each other or with amines or ammonia to produce polymeric compounds. Laboratory experiments have shown quinones generated from *o*- and *p*-polyphenols condense with each other or with amino acids to form synthetic polymers with chemical structures similar to those of natural humic substances (Ertel and Hedges, 1983). In the melanoidin model, sugars and amines react to form an N-substituted glucosamine which can dehydrate, rearrange, or condense to form simple fragments (e.g., glyceraldehyde) and structurally complex brown nitrogenous polymers. Dark colored polymers can also form from carbohydrates at a similar rate in the absence of nitrogenous compounds (Popoff and Theander, 1976; Hedges, 1978). Auto-oxidative crosslinking reactions between polyunsaturated fatty acids, induced by photolysis, were postulated to be a mechanism of humic substance formation in marine environments (Harvey and Boran, 1985). Such reactions may help to explain the presence and persistence of highly crosslinked alkyl C in terrestrial systems (Kögel-Knabner et al., 1992a,b).

2.5.4.2 Nonhumic Biopolymers

Carbohydrates

The chemical structure, properties, and importance of carbohydrates in soil have been reviewed by Cheshire (1979), Oades (1989), and Stevenson (1994). Carbohydrates account for the largest fraction of soil organic C found in nonhumic biopolymers (100–250 g kg^{-1} soil organic C). They exhibit a range in molecular size from simple monosaccharides to oligosaccharides containing several monosaccharide units, to polysaccharides of high molecular weight which contain large numbers of monosaccharide units. Plants contribute directly to the soil carbohydrate fraction through the deposition of simple sugars, hemicellulose and cellulose in particulate residues and various simple sugars and polysaccharides in root exudates and mucilaginous materials. Various products of the metabolic activity of soil organisms also contribute to the soil carbohydrate fraction. These include extracellular mucilages encapsulating bacteria and fungi, cell wall structural polysaccharides (e.g., chitin) (Fig. 2.2), and intracellular polysaccharides. Relative to many other forms of soil organic C, soil carbohydrates are vulnerable to decomposition unless: (1) decomposition processes are limited by environmental conditions; (2) the carbohydrates are buried within a matrix of biochemically recalcitrant material (e.g., cellulose and/or hemicellulose buried within a lignin matrix in plant materials); or (3) the carbohydrates are biologically stabilized by adsorption onto soil mineral particles or by their physical separation from decomposer microorganisms.

In peats, forest litter layers and composts, reduced rates of decomposition and/or the preponderance of plant materials lead to a carbohydrate fraction dominated by structures of plant origin, whereas in mineral soils the carbohydrate fraction is typically dominated by microbially

derived materials. Although the carbohydrate structures presented for plant materials in Fig. 2.2 are derived from single monosaccharides, the large variety of monosaccharides found in soil and different glycosidic linkages (e.g., α, β1-4 and β1-6) gives rise to a potential for large variations in chemical structure. However, both Oades (1989) and Stevenson (1994) indicated that within any single polysaccharide molecule, it is unlikely that more than three or four different component monosaccharides can be identified.

Hydrolysis procedures result in the degradation of plant polysaccharide structures and the release of various classes of monosaccharides including neutral sugars, amino sugars, acidic sugars, methylated sugars, and sugar alcohols. The neutral sugars consist of hexoses (glucose, galactose and mannose), pentoses (arabinose and xylose), and deoxyhexoses (rhamnose and fucose) with the hexoses, particularly glucose, generally accounting for the largest component (Cheshire, 1979). Excluding glucose, polysaccharides synthesized by microorganisms are dominated by galactose, manose, rhamnose, and fucose, whereas plant polysaccharides contain appreciable contents of arabinose and xylose (Cheshire, 1979). This has led to the use of the galactose+mannose/xylose+arabinose (g+m/x+a) and rhamnose+fucose/arabinose+xylose (r+f/a+x) ratios as indices of the contribution made to the soil carbohydrate fraction by plants and microorganisms (Oades, 1984; Murayama, 1994). Values of < 0.5 for the (g+m/x+a) ratio and < 0.01 for the (r+f/a+x) ratio are indicative of carbohydrates of plant origin, while respective values of > 2.0 and > 0.40 are indicative of microbially derived carbohydrates. Guggenberger et al. (1994) used these two ratios to examine the origin of organic C associated with different particle size fractions. The changes in the two ratios across several land management treatments indicated an increased proportion of plant-derived carbohydrate with increasing particle size.

Amino sugars account for 20–60 g kg^{-1} of soil organic C. They are generally assumed to be of microbial origin. In excess of 25 different amino sugars are known to exist as products of microbial metabolism (Sharon, 1965). Monomeric amino sugars can be identified by chromatographic analysis of HCl hydrolysates. The most prevalent of the amino sugars is D-glucosamine, the monomeric component of chitin, the N-acetylglucosamine structural polymer found in fungal mycelia. Significant quantities of D-galactosamine can also be found in soils, and changes in the ratio of D-glucosamine/D-galactosamine may be indicative of the composition of the microbial decomposer community (Stevenson, 1994). The higher ratios noted by Sowden (1959) for acidic soils are consistent with the enhanced relative importance of fungi in acidic environments. Other amino sugars identified in soils include muramic acid and D-mannosamine. The dominant forms of the acidic sugars, uronic acids, are glucuronic and galacturonic acids. Measurement of the contents of these acidic sugars in soil hydrolysates is difficult because of their rapid decarboxylation which may result in losses in excess of 50%. Using a carbazole method of analysis, acidic sugars have been estimated to account for approximately 1–5% of the soil organic C; however, Greenland and Oades (1975) consider this to be a minimum value. The methylated sugars 2-O-methyl-L-rhamnose and 4-O-methyl-D-galactose and the sugar alcohols mannitol and inositol have also been identified in the hydrolysates of soils and peats (Cheshire, 1979)

The O-alkyl or (O-alkyl + di-O-alkyl) region of solid-state ^{13}C NMR spectra is often used to provide an estimate of the content of polysaccharide C in soils. Numerous studies have reported higher carbohydrate C contents based on ^{13}C NMR analysis than could be accounted for by wet chemical hydrolysis followed by quantification of monosaccharide contents of hydrolysates (Ogner, 1985; Oades et al., 1987; Preston et al., 1989a,b). For example, Oades et al. (1987) observed that in soil particle size fractions > 20 μm the content of O-alkyl C as measured by ^{13}C NMR was approximately twice that of carbohydrate C determined by acid hydrolysis and quantification of neutral, acidic, and

amino sugars. Preston et al. (1989a) found that O-alkyl C accounted for 40–50% of the signal intensity of particle size fractions of peats, a significantly greater proportion of the total organic C than was accounted for by wet chemical analysis of total carbohydrate C. Cheshire et al. (1992) proposed that the over estimation of carbohydrate C contents by ^{13}C NMR analyses resulted from the presence of secondary or pseudo polysaccharide structures which exhibited O-alkyl resonances in ^{13}C NMR, well-defined C-O vibration absorption bands in IR, and a CH_2O elemental composition. The pseudo polysaccharides differed from the normal polysaccharides in that they did not contain hydrolyzable monomeric sugars and did not yield dehydrated sugar derivatives on pyrolysis. Several organic structures proposed to account for the pseudo polysaccharide signals included highly degraded polysaccharides and melanoidins; however, any structure containing C-O bonds, including the three C atoms in lignin propanoid chains, could give rise to NMR signals within the chemical shift region typically ascribed to carbohydrate C. The three oxygenated propanoid C atoms of lignin appear over the chemical shift range of 60–90 ppm in NMR spectra (Hatcher, 1987). The use of the terms pseudo or secondary polysaccharides, therefore, appears misleading since what was really being compared was the relationship between the quantity of organic C found in C-O structures derived from many possible sources versus carbohydrate C.

Alkyl Compounds

Initial applications of solid-state ^{13}C NMR and analytical pyrolysis to the study of soil organic C and humic substances showed that significant amounts of alkyl C were present in these materials, contrary to the previous traditional beliefs of a dominance of aromatic C. Numerous solid-state ^{13}C NMR studies have shown significant increases in alkyl C content as the extent of decomposition in peats, forest litter horizons, composts and mineral soils increases (Baldock et al., 1997). The majority of research addressing the nature of soil alkyl C and the structural changes associated with decomposition processes has been carried out on forest soils. In such ecosystems, the high organic C contents of litter layers and Ah horizons, and the reduced potential for organic-mineral interactions facilitates analysis and interpretation. Extension of these results to agricultural mineral soils, especially to high clay content soils with large adsorptive capacities, should be made with caution.

Alkyl C generally accounts for 15–20% of the organic C contained in fresh litter horizons and 30–40% for the more humified litter horizons and mineral Ah horizons (Kögel-Knabner et al., 1992b). Organic materials derived from a variety of compounds contained in plant residues can contribute to the fraction of alkyl C. Soil microorganisms also synthesize alkyl structures from nonaliphatic substrate (Baldock et al., 1989; Golchin et al., 1996). Alkyl C in soil organic C consists of the following compounds (Kögel-Knabner et al., 1992a): (1) solvent extractable free and bound lipids (fatty acids, and waxes derived from plants and soil microorganisms), (2) insoluble polyesters and nonpolyesters contained in the plant cuticles and walls of cork cells in roots and bark, and (3) macromolecules synthesized by soil microorganisms.

Solvent extractable free and bound lipids account for approximately 30% of the ^{13}C NMR signal intensity in the alkyl C region observed for forest soils (Kögel-Knabner et al., 1988; Ziegler, 1989; Ziegler and Zech, 1989). The chemical nature of free and bound lipids has been discussed by Stevenson (1994). They include waxes, organic acids, steroids and terpenoids, carotenoids, porphyrins, glycerides and phospholipids. The nature of petroleum ether extractable free lipids and their relationships to the original litter materials have been examined by Almendros et al. (1996). These materials are readily metabolized by soil microorganisms in forest soils and are not considered a major contributor to the accumulation of alkyl C in humified structures (Tegelaar et al., 1989; Ziegler, 1989).

Cutin and suberin (insoluble polyesters) can also be readily decomposed by those bacteria and fungi that produce cutinase. Mammals effectively degrade cutin so that contributions to the soil via faecal deposition are minimal (Tegelaar et al., 1989). Riederer et al. (1993) measured changes in the content of cutin-derived monomers in *Fagus sylvatica* litter decomposed for 446 d. Over the first 100 d, the content of cutin monomer C, released by saponification of the residual litter, decreased proportionately faster than bulk organic C, but then decreased at a rate similar to bulk organic C over the 100–446 d period. Similar results were obtained by Ziegler and Zech (1990) and Kögel-Knabner et al. (1992b) indicating that a selective preservation of cutin structures was not responsible for the increased proportion of alkyl C noted with increasing extent of decomposition. Further, decreased concentrations of cutin and suberin were noted in progressing from litter to well-humified organic and mineral Ah horizons when concentrations were expressed per unit mass of total organic C (Kögel-Knabner et al., 1989; Riederer et al., 1993). A selective preservation of intact cutin or suberin is, therefore, not likely to contribute to the increased proportion of alkyl C observed with increasing extent of decomposition; however, microbially or chemically transformed cutin and suberin may accumulate.

Nonsaponifiable cutan and suberan (insoluble nonpolyesters) appear to be resistant to biological and chemical degradation (Tegelaar et al., 1989) and although present at low concentrations in plant residues, concentration by selective preservation could represent a mechanism for the accumulation of alkyl C in soils. Riederer and Schönherr (1988) noted that the nonpolyester fraction of *Clivia miniata* Reg. cuticle increased with ontogenetic development through a continuous transformation of polyester cutin into nonpolyester cutan. Such a reaction may be occurring via a photo-oxidative crosslinking mechanism, similar to that proposed by Harvey and Boran (1985) for the genesis of marine humic substances. Kögel-Knabner et al. (1992a,b) used a combination of selective degradation techniques and ID ^{13}C NMR to distinguish between mobile (little crosslinking) and rigid (highly crosslinked) forms of nonsaponifiable alkyl C in forest soils. Fresh forest litters contained 55–60% of their C in rigid structures and 40–45% in mobile structures. With the increasing extent of decomposition the mobile fraction was lost and the Oh and Ah nonsaponifiable alkyl C was composed almost exclusively of rigid structures. Possible mechanisms that may account for such a conversion during decomposition processes include (1) a selective preservation of rigid structures present in the initial plant residues, (2) the production of rigid metabolic products of microbial origin synthesized during decomposition, and/or (3) the conversion of mobile alkyl C to rigid alkyl C, with enhanced cross-linking being induced by chemical, physical or biological processes. In addition, rigidity as assessed by ID ^{13}C NMR may be influenced by adsorption onto mineral surfaces; however, this remains to be determined. ID ^{13}C NMR spectra acquired, for a bulk culture of intact soil microorganisms and their nonsaponifiable alkyl residues, indicated the presence of both mobile and rigid structures (Kögel-Knabner et al. 1992a). In a more detailed application of ID ^{13}C NMR to characterizing untreated intact cultures of soil microorganisms, Baldock et al. (1990b) found that 13% of fungal and 66% of bacterial alkyl C exemplified a rigid structure.

On the basis of the results obtained from forest soils, the increase in alkyl C during decomposition appears to result from an accumulation of nonsaponifiable rigid structures which may originate from selective preservation of plant and microbial residues or be produced *in situ* via biological and/or chemical transformations of existing alkyl structures. In soils with appreciable mineral surface areas, the potential exists for other forms of alkyl C (extractable free and bound lipids and cutin and suberin polyesters) to contribute through a biological stabilization imparted by adsorption onto mineral surfaces. Supporting evidence for the importance of adsorption reactions with mineral surfaces is provided by the data of Oades et al. (1987) and Baldock et al. (1992). They found significant

accumulations of alkyl C in the fine particle size fractions, with a large highly reactive surface area, for a range of mineral soils including an Alfisol, two Mollisols and two Oxisols.

Lignin

The chemical composition of lignin and its residues in soil is a function of its initial chemical structure and the extent of modification by soil organisms. Lignin is generally more resistant to biological decomposition than the other major biopolymers found in plant residues, because of its chemical structure (Fig. 2.2). The most efficient lignin degrading organisms are the group of aerobic filamentous basidiomycetes collectively referred to as white rot fungi. These organisms fragment the lignin polymer at irregular positions within both the side-chain and aromatic ring structures by the synthesis and excretion of enzymes which catalyse free radical formation (Haider, 1992; Kirk, 1987). Brown rot basidiomycetes do not fragment the lignin polymer extensively, but are capable of demethylating methoxyl groups on the guaiacyl or syringyl units to produce *o*-hydroquinonoid structures which can be easily oxidized to quinones. The quinone structures can then induce condensation reactions as discussed for the polyphenol theory. For plant litter, it is generally assumed that basidiomycetes, similar to the white rot fungi, aid in lignin decomposition after other organisms have removed the more labile components. Bacteria play a smaller role in lignin degradation, but as noted for the brown rot fungi, they can modify the nature of functional groups attached to the lignin polymer. Organisms do not gain energy or metabolites from lignin degradation (Haider, 1994), but benefit through an exposure of labile cellulose and hemicellulose buried within the lignin/polysaccharide matrix. The role of various organisms and the mechanisms of lignin degradation have been discussed recently by Shevchenko and Bailey (1996) and Hammel (1997).

The chemical state of lignin in plant residues and soils has been examined by spectroscopic and chemical degradative methods. Hatcher (1987) presented solid-state ^{13}C NMR spectra of isolated natural lignin. On the basis of this work and others, the signals from each of the various types of C contained in lignin polymers can be assigned as follows: 56 ppm = methoxyl C, 60–90 ppm = propyl side-chain O-alkyl C, 105–145 ppm = C- and H-substituted aromatic C, and 145–160 ppm = phenolic C. The chemical shift values and form of the phenolic peak can be used to provide information on the type of lignin monomers present. The aromatic C-O associated with the methoxyl group of guaiacyl units appears at 148 ppm while that of syringyl units appears at 153 ppm. Thus, softwood lignin, dominated by guaiacyl monomers would exhibit a phenolic peak at 148 ppm, hardwood lignin containing both guaiacyl and syringyl monomers exhibits two peaks at 148 and 153 ppm, and grass lignin dominated by syringyl monomers exhibits a peak at 153 ppm. On average, of the 10–11 C atoms contained in the two major lignin monomers (guaiacyl and syringyl), 2–3 are phenolic, 3–4 are C- and H-substituted aromatic, 3 are O-alkyl, and 1–2 are methoxyl. The actual values depend on the distribution of the two major monomeric species (guaiacyl and syringyl) (Fig. 2.2) and the nature of the bonds between monomeric units. Significant deviations from these values would be indicative of how the average lignin molecule was altered by decomposition processes.

In soils and peats, lignin is just one component of the decomposing residues and several signals from other types of C overlap and mask changes in the lignin structure. The propane side-chain C signals are completely hidden by the C-O C of carbohydrates, and amine C overlaps the methoxyl signals. For the methoxyl signal, however, the ID ^{13}C NMR pulse sequence can be used to differentiate between the content of methoxyl and amine C. The ID pulse sequence can also be used to determine the average amount of protonated versus nonprotonated aromatic C. Readers are referred to Hatcher (1987) for an excellent example of the application of ID to the study of lignin. Decreases in the proportions of phenolic and methoxyl C are typical of the results obtained when solid-state ^{13}C NMR has been used to characterize the chemistry of organic C in soil fractions of decreasing particle size

(Oades et al., 1987; Baldock et al., 1992; Guggenberger et al., 1995a). Such observations are consistent with the observed patterns of decomposition noted for bacteria and brown rot fungi decomposing plant residues mentioned above. Nevertheless, a degree of uncertainty exists with solid-state ^{13}C NMR data because the analysis does not indicate conclusively from which structures the various types of C were derived.

Lignin degradation is most effectively examined by procedures that quantitatively break the linkages between component monomers and measure the amount of each type of monomer. Two such methods are an alkaline CuO oxidation procedure (Hedges and Ertel, 1982) and a tetramethylammonium hydroxide (TMAH) thermochemolysis procedure (Hatcher et al., 1995). In both procedures the lignin polymer is fragmented into its component monomers, which are separated and quantified using reverse phase high performance liquid chromatography (Kögel and Bochter, 1985), gas chromatography (Hedges and Ertel, 1982; Baldock et al., 1997) or gas chromatography-mass spectrometry (Hatcher et al., 1995).

The CuO-oxidation procedure has been shown to release 25–90% of the lignin C in the form of simple phenolic monomeric structures, depending on the types of lignin monomers involved (Hedges and Ertel, 1982; Ertel and Hedges, 1984). A comparison of the lignin contents between samples can be made by summing the contents of the guaiacyl, syringyl and *p*-hydroxyphenol derivatized reaction products. The ratio of the quantity of acidic to aldehydic forms of each monomer (Ac/Al) can give an indication of the state of decomposition or structural alteration of each monomeric unit within the lignin polymer, or of the entire polymer (Ertel and Hedges, 1984; Ertel et al., 1984; Moran et al. 1991). The ratio of lignin-derived dimers/monomers present in CuO oxidation products of sedimentary lignins has also been used as a measure of the extent of fungal-induced degradation (Goni et al., 1993).

Several recent examples of the application of the CuO oxidation methodology to the study of lignin in various forms of soil organic C include work competed by deMontigny et al. (1993), Guggenberger et al. (1994a) and Amelung and Zech (1996). deMontigny et al. (1993) studied the extent of lignin alteration in nonwoody and woody forest horizons. In progressing from the surface fibric to the more humified humic layer of the nonwoody horizons, little change in the total amount of phenolic C released was noted (31–33.5 g kg^{-1} organic C); however, the guaiacyl Ac/Al ratio increased significantly from 0.43 to 1.01, suggesting that, although the lignin content did not change significantly, it became more structurally modified with increasing depth, and presumably forest floor residence time. The CuO oxidation products of lignin contained in particle size fractions (sand, silt and clay fractions) in mineral soil collected from four different ecosystems showed a decrease in lignin content and an increase in the extent of lignin alteration with decreasing particle size (Guggenberger et al., 1994). Amelung and Zech (1996) selectively removed the external 0.5 mm of soil peds and used CuO oxidation to examine the amount and state of decomposition of lignin in soil from the ped surface and ped interior. The sum of the lignin-derived phenolic compounds was significantly less for the ped surface than ped interior soil, suggesting an enhanced extent of lignin decomposition at ped surfaces. The increased Ac/Al ratios for guaiacyl and syringyl monomers and the selective loss of the more easily decomposable syringyl monomers in ped surface soil supported the hypothesis of enhanced oxidative decomposition at ped surfaces relative to ped interiors.

The TMAH thermochemolysis procedure is analogous to the CuO oxidation process except that the derivatives are methylated and ready for direct injection into a GC or GC/MS system. Hatcher et al. (1995) compared the results of the TMAH and CuO oxidation methods when performed on the samples analysed by deMontigny et al. (1993). The distribution of products obtained with both analyses was similar, as evidenced by a linear correlation between the Ac/Al ratios obtained using the two methods. However, the TMAH method provided a more sensitive indicator of the extent of decomposition because of the larger range of values obtained. The TMAH method also resulted in a

greater preservation of monomer side-chain structures than the CuO oxidation. It is, therefore, important in the TMAH analysis to include all the various derivatives containing methoxylated side chains, when estimating the amount of C contained in lignin structures from the products of the thermochemolysis reaction. The enhanced preservation of the side-chain structures may, with further research, be utilized to provide additional structural information pertaining to the lignin polymer and its alteration through decomposition. Additional studies that have utilized the TMAH procedure to examine the amount and extent of decomposition of lignin have thus far concentrated on relatively pure natural organic materials (Baldock et al., 1997; Nanny , 1997. Personnal communication) and its extension to mineral soils or mineral soil fractions has not yet occurred. Baldock et al. (1997) used the TMAH procedure in conjunction with solid-state ^{13}C NMR to examine the chemical changes associated with the decomposition of three species of wood exhibiting different stages of decomposition. The two analytical techniques were complementary, but the TMAH results showed that significant alterations to the structure of lignin could occur before significant changes in the NMR spectral intensities became apparent.

2.6 Conclusions

The diverse chemical nature of soil organic C contributes to the important role which it plays in defining the magnitude of a variety of soil properties and processes, and has made its selective chemical characterization challenging. The continual development of new technologies and new procedures or applications of existing technologies capable of studying the properties and chemical characteristics of soil organic C *in situ*, will undoubtedly further advance our understanding of this important soil component. Several research areas which offer significant potential are (1) further development and use of methods which can selectively characterize the chemical composition of SOM *in situ* and thus avoid the use of chemical extractants, (2) definition of relationships between the species composition of the decomposer community and the resultant changes in chemical structure of plant residues and soil organic materials, (3) identification and quantification of biologically significant pools of C and the importance of these pools in defining the magnitude of soil properties and processes, (4) quantification of the capacity of soils to protect organic materials from mineralization through identification and measurement of the role of soil mineral components and soil architecture, and (5) renewed application of wet chemical molecular techniques to the study and quantification of the contents of specific classes of biomolecules found in soil organic fractions, particularly in association with quantitative applications of spectroscopic techniques (solid-state ^{13}C NMR). In particular, work is required to address the problems associated with identifying the pseudo-polysaccharide and the unidentified organic N fractions.

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2.7 References

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