12.7 Dynamics, Chemistry, and Preservation of Organic Matter in Soils

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12.7.1 Soil Organic Matter and Soil Functions

The soil is the largest active terrestrial reservoir in the global carbon cycle (see **Chapter 10.10**). At the same time, soil organic matter (SOM), which spans a continuum from fresh detritus to highly processed, mineral-associated organic matter (OM), is the foundation of sustainable terrestrial ecosystems. The estimates of the organic C stocks in 0–100 cm depth in the world's soils range from 1220 Pg (1 Pg = 1015 g; Sombroek et al., 1993) to about 1550 Pg (Batjes, 1996; Eswaran et al., 1993; Jobbágy and Jackson, 2000). Recent studies suggest that the soil C pool may be even greater and could account for 2000 Pg (Janzen, 2005). These higher values may be mainly due to additional recent estimations of the C pool stored in boreal soils under permafrost conditions (Tarnocai et al., 2009; Zimov et al., 2006). The residence time of stable fractions of SOC can be 41 000 years (von Lützow et al., 2006), making it a much more stable sink than living plant biomass.

The C enters the soil via root and litter deposition. It varies depending on plant species and growth, thus providing a vast range of different organic molecules entering the soil as precursors of OM formation (see **Section 12.7.2** for details). These compounds may either be mineralized; mineralization being the process that transforms the organic molecule to CO_2 and mineral forms of N, P, and S (see **Chapter 10.16**). Alternatively, these compounds are only partly mineralized and new microbial structures are synthesized, both summarized as transformation of SOM. If new products that are not common in living plants or microorganisms occur, we talk of a humification of organic compounds in soil. All, mineralization, transformation, and mineralization, alter the chemical composition of SOM (see **Section 12.7.3** for details). The underlying rates determine the turnover of SOM in soil, with some compounds degrading faster (labile C pools) while other being protected from potential rapid decay (stable C pools; see **Section 12.7.4** for details). Frequently, it is analytically difficult to differentiate between compounds of different stability; hence, biomarker and stable isotope techniques are applied as tools for elucidating both the origin and residence time of specific SOM components (see **Section 12.7.5** for details). In general, the residence time of a given compound is lower if it is either not bioaccessible or not bioavailable for decay, that is, when stabilization processes delay its rapid decomposition (see **Section 12.7.6** for details). Whereas the major proportion of SOM is mineralized within months, stabilized SOM fractions may reside in soil at timescales of decades to several millennia (Sollins et al., 1996; Trumbore, 2009; von Lützow et al., 2006). All these processes contribute to the soil C cycle (**Figure 1**). It is an open cycle, with feedback mechanisms to the atmosphere, hydrosphere, and lithosphere. It is important for all, plant growth, climate regulation, weathering, and soil formation as well as soil fertility.

One of the most fundamental functions of SOM is the provision of metabolic energy, which drives soil biological processes. In essence, it is the transformation of carbon by plant, micro-, and macrobiological processes that provides energy and results in the establishment of a cycle that connects above- and belowground energy transformations. A high SOC pool is necessary to guarantee basic soil functions, such as providing high agronomic yields of crops and pastures by providing sufficient available water capacity, maintaining plants' nutrient supplies, restoring soil structure (Carter, 2002; Roose and Barthes, 2001), and minimizing risks of soil erosion.

It is well established that SOM is essential for a number of physical (soil structure, porosity, color, and water holding capacity (WHC)), chemical (cation exchange capacity (CEC) and buffering), and biological (habitat and nutrient source) soil functions (**Table 1**).

SOM is essential for maintaining soil structure and aggregate stability. Soil structure is the result of individual soil particles clumping or binding together in peds or aggregates, which in turn is also defining the arrangement of soil pores between them. Soil structure has a major influence on water and air movement, biological activity, root growth, and seedling emergence. The addition of SOM can not only reduce bulk density and increase WHC but also increases soil aggregate stability. High levels of SOM in mineral soils are associated with high aggregate stability and large aggregate size.

Soil physical functioning is strongly related to the capacity of soil to store and supply water and air for plant growth and at the same time providing a habitat for a vast range of microorganisms. Soil structure is also strongly interconnected with the soils ability to retain water. The ability of soil to retain water is termed WHC. Specifically, the amount of plant-available water in relation to air-filled porosity at field capacity is often used to assess soil physical fertility. With an increase in SOC content, there is increased aggregation and decreased bulk density, which is associated with higher soil pore space and often also with the pore space that provides plant-available water.

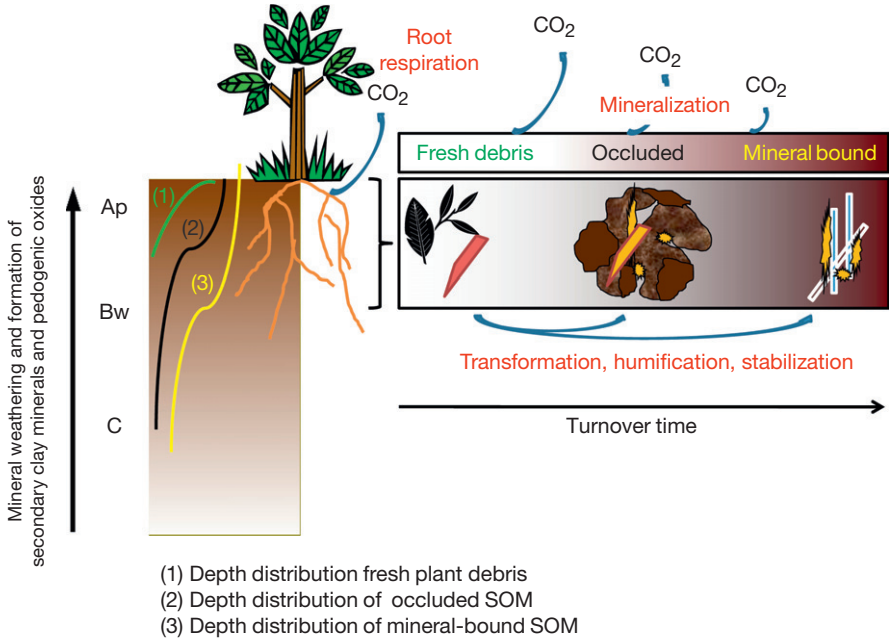


Figure 1 The continuum of soil organic matter (SOM) in the soil C cycle.

Table 1 Role of raising soil organic matter contents for different soil properties

Physical effects	*Chemical effects*	*Biological effects*	*Negative side effects*
+ Aggregation and aggregate stability	+ C sequestration	+ Energy and carbon source for microorganisms	+ Greenhouse gas emissions
+ Erosion resistance	+ Storage of N, P, S	+ Heterotrophic nutrient supply	+ Uncontrolled release of nitrate to the groundwater
+ Decompaction	+ Cation exchange capacity	+ Regulation of food webs and antagonistic potentials against plant diseases	+ Hydrophobicity and thus reduced WHC
+ Aeration and porosity	+ Buffer capacity		
+ Infiltration[a]	+ Sorption and immobilization of pollutants		
+ Water storage[a]			
+ Soil warming			

[a]Due to increased porosity.

The dark brown or black color of SOM is relevant for the thermal properties of bare soils, that is, most agricultural soils. A dark surface horizon contributes to soil warming and thus promotes biological processes, such as germination.

SOM has a high capacity and strength of bonding with most metals and organic compounds present in the soil solution. The CEC is the capacity of a soil to bind cations in an exchangeable form and is determined by the negative charge present in a mass of soil. A high CEC is favorable as it contributes to a soil's capacity to retain plant nutrients, such as K^+, Ca^{2+}, or Mg^{2+}. The negative charge of soils can be present as permanent charge derived from isomorphic substitution in phyllosilicate clay minerals and variable charge, which depends on soil pH. Variable charge in soils is provided also by clay minerals, but mainly by acid functional groups of OM, mainly carboxylic acids, but to a lower extent also phenolic acids. Although organic matter is a major contributor to variable charge of most soils, it is of specific importance in soils low in clay minerals with exchange capacity, that is, highly weathered kaolinite-dominated tropical soils or sandy soils in general. As a large proportion of decomposed and thus oxidized organic matter with high CEC is associated with the clay fraction, most of the CEC is located in the fine fraction of soils.

CEC and pH are closely related to the buffering capacity of a soil, its resistance to changes in pH when an acid or base is added. A high buffering capacity is associated with high CEC. At high CEC, more acidity is neutralized to affect a given increase in the percentage of base saturation (base saturation = sum of exchangeable bases/buffered CEC). SOM acts as a buffer over a wide range of soil pH values, due to the presence of a number of different functional groups in SOM, such as carboxylic, phenolic, acidic alcoholic, amine, amide, and others.

SOM also provides sportive capacity for many other natural and anthropogenic metals (such as Cu and Cd) and organic components (pesticides, polycyclic aromatic hydrocarbons (PAHs), and other organic pollutants) found in the soil solution. SOM is considered the primary sorbent for nonionic

organic compounds in almost all soils, except soil with very low OM contents. High sorption affinities have been demonstrated for PAHs, and soot, char, and other carbonaceous particles are strongly sorbing forms of SOM.

It is important to keep in mind that biological processes in turn influence both soil chemical and soil structural properties as they greatly affect soil structure and soil redox reactions. In soils, a highly complex trophic food chain used energy provided by OM and results in the establishment of a cycle that connects above- and belowground energy and C transformations. These processes in turn influence the formation of increasingly complex and stable OM, accompanied with the loss of CO_2 to the atmosphere via respiration. Thus, the basic carbon and energy source for heterotrophic production is the carbon input from net primary production (NPP) and SOM accumulates as long as NPP exceeds respiration. The amount of SOM stored in a soil reflects the balance between C added in equilibrium with decomposition and leaching.

Tillage generally decreases SOM due to erosion and disruption of the physical, biochemical, and chemical mechanisms of SOM stabilization, but SOM can generally reaccumulate after the cessation of cultivation. Historically, terrestrial C pools have declined significantly due to land use changes and in particular due to deforestation, that is, the conversion of forest environments to agricultural land (Jandl et al., 2007). Hence, the amount of C stored in soil greatly varies with management, though mainly in the surface A horizons. Noteworthy, the major part of SOM is stored in the subsurface, for example, below 30 cm soil depth. More than 70% of total SOM can be found in subsoils, and this portion varies with different type of soils (e.g., Batjes, 1996; Guo et al., 2006). In part, this is due to different chemical and physical interactions of SOM with the weathering products of different parent materials; that is, relating SOM dynamics to the genesis of different soil types is currently an emerging research topic (see **Section 12.7.6** for details). It therewith also affects the provision of other nutrients that are either part of SOM (N, P, and S) or associated to it (mainly inorganic cations, such as Ca, Mg, K, and trace metals). SOM contains most of the N in soils, as well as large proportions of the S and P. Although we focus here on SOM, it should be kept in mind that N, P, and S are mainly bound in the OM of soils. Thus, the cycling of these compounds in soils is strongly related to the C cycle.

Organic N incorporated into SOM represents a major reservoir of N on the Earth's surface. The biochemical N derived from plant or animal residues is thought to be extensively altered, forming more stable compounds in soils, but the type of changes in chemical speciation, their timing, and mechanisms are not clear (Gärdenäs et al., 2011). More than 95% of the total N in soils occurs in the form of organic N compounds (Bremner, 1965). Most of the inorganic forms of N are susceptible to the immediate loss from the soil in the form of dissolved NO^{3-} or gaseous N_2O or NH_3. Only NH^{4+} is reversibly adsorbed to clay minerals or fixed between mineral lattices of vermiculite, illite, and montmorillonite (Stevenson, 1994). Thus, especially in the subsoil, substantial proportions of N may occur in the form of NH^{4+} adsorbed or fixed in clay minerals.

Organic phosphorus (P) is also a major component of total soil P (Magid et al., 1996). P occurs in soils in inorganic and organic forms and is cycled between these forms via mineralization and sorption/desorption processes. From 15% to 80% of the phosphorus in soils occurs in organic forms, the exact amount being dependent upon the nature of the soil and its composition. Higher percentages of organic P occur in peats and forest soils.

Total soil S significantly correlates with soil organic C and total N, suggesting that S is an integral part of SOM (Biederbeck, 1978). In soils, S occurs in inorganic and organic forms and is cycled between these forms via mobilization, mineralization, immobilization, oxidation, and reduction processes. Organic S is the main S fraction in soils, contributing up to 95% or even 98% of total soil S in surface soils and as much as 99% in subsurface soils (Scherer, 2009).

12.7.2 Input and Quantity of SOM

12.7.2.1 Amount of OM in Soils

The organic C contents and stocks differ widely depending on soil type. Routine soil surveys collect C stock data down to a depth of 1 m, and scientists studying the composition and mechanisms of stabilization of SOM have mainly focused on the A horizon with the highest SOM concentrations. There is no a critical level nor a saturation level for SOC content, but an optimum range of SOC concentration of 2–3% in the root zone covering a wide spectrum of soils (Lal, 2010), with SOC contents decreasing further down in the soil profile in most soil types. OM stored in subsoil horizons below the A horizon has received increasing interest in recent years as high proportions of total C stored within the soil profile may be found in subsoil horizons despite low OM concentrations (Batjes, 1996; Jobbágy and Jackson, 2000; Rumpel and Kögel-Knabner, 2011). **Table 2** gives an overview of the organic carbon (OC) and ON contents in major soils, based on the world survey by Batjes (1996), although these data do not account for the recently higher estimates of total soil OC of 2000 Pg (Janzen, 2005). The proportion of SOM stored in the first meter of the world soils below 30 cm depth ranges between 63% and 46%, except for Podzoluvisols, where 30% of OC is stored below the first 30 cm. A recent study suggests that in the northern circumpolar permafrost region, at least 61% of the total soil C is stored below 30 cm depth (Tarnocai et al., 2009). Therefore, subsoil C may be even more important in terms of source or sink for CO_2 than topsoil C. Another property of subsoil C is its high radiocarbon age, which suggests that a high proportion of this C is stable at longer timescales (e.g., Paul et al., 1997; Scharpenseel et al., 1989).

The source of the organic N incorporated into SOM is biochemical N from plant and animal residues (predominantly proteinaceous substances), which undergo a complex series of transformations, mediated by microbial and abiotic processes, ultimately resulting in the stabilization of the nonmineralized N fraction in soils. The concentration of total N in topsoils varies widely, depending on the OC content, ranging from 1 to 2 g kg^{-1} in agricultural topsoils. Higher concentrations are reported for grassland and forest soils.

When the turnover time of N in the soil is calculated with respect to the input of dead plant materials, the mean residence time (MRT) of nitrogen in soils is about 50 years (Schlesinger,

Table 2 Mean organic carbon contents for four depth intervals by FAO–UNESCO soil units

Soil unit	*0–30 cm*			*0–50 cm*			*0–100 cm*			*0–200 cm*		
	Mean	*CV*	n	*Mean*	*CV*	n	*Mean*	*CV*	n	*Mean*	*CV*	n
Acrisols	5.1	83	309	6.7	84	302	9.4	82	269	10.4	113	56
Cambisols	5.0	91	531	6.9	82	481	9.6	77	332	15.7	92	36
Chernozems	6.0	60	64	8.6	56	61	12.5	60	44	19.6	18	6
Podzoluvisols	5.6	65	9	5.9	52	7	7.3	43	7	7.8	31	3
Rendzinas	13.3	114	19	–	–	0	–	–	0	–	–	0
Ferralsols	5.7	60	256	17.6	61	251	10.7	63	228	16.9	61	79
Gleysols	7.7	109	243	9.7	100	211	13.1	109	142	19.9.	212	14
Phaeozems	7.7	53	202	10.5	48	194	14.6	47	147	21.6	54	15
Lithosols	3.6	128	4	–	–	0	–	–	0	–	–	0
Fluvisols	3.8	114	300	5.6	122	278	9.3	136	200	16.1	172	18
Kastanozems	5.4	52	22	7.5	55	19	9.6	50	8	–	–	0
Luvisols	3.1	100	604	4.3	85	555	6.5	78	377	9.9	56	42
Greyzems	10.8	49	4	13.6	53	4	19.7	53	3	23.3	87	2
Nitosols	4.1	85	77	5.6	80	74	8.4	72	67	11.3	47	20
Histosols	28.3.	47	42	46.4	47	42	77.6	47	34	218	31	4
Podzols	13.6	101	82	17.3	92	75	24.2	94	43	59.1	60	6
Arenosols	1.3	108	262	1.9	93	237	3.1	77	166	5.5	58	14
Regosols	3.1	122	86	4.0	114	66	5.0	133	42	7.0	48	9
Solonetz	3.2	92	59	4.2	78	53	6.2	83	39	5.1	31	4
Andosols	11.4	69	160	16.5	65	154	25.4	69	120	31.0	52	13
Rankers	15.9	153	6	–	–	0	–	–	0	–	–	0
Vertisols	4.5	87	267	6.7	71	254	11.1	58	205	19.1	46	29
Planosols	3.9	99	54	5.2	86	48	7.7	56	28	16.9	66	4
Xerosols	2.0	64	113	2.8	61	103	4.8	53	73	8.7	53	8
Yermosols	1.3	121	44	1.8	93	37	3.0	44	24	6.6	12	3
Solonchaks	1.8	73	63	2.6	67	59	4.2	67	42	5.7	97	3

Data are in kg m^{-2} and extracted from Batjes (1996).

1991). In comparison, for the total pool of OC in soils, a MRT of about 26 years (Schlesinger, 1991) or 40 years (Oades, 1988) was estimated. This indicates that N, mostly in the form of organic N, is conserved in soils. Evaluating these numbers, one has to bear in mind that the MRT of organic material in soil varies over several orders of magnitude between the surface litter and the various humus fractions.

Concentrations of total P in topsoils range between 100 and 900 mg kg^{-1} (Stevenson, 1994). The continued application of P fertilizers and manures in amounts in excess of plant requirements leads to an accumulation of P in topsoils under agriculture. Organically bound P constitutes often more than 50% of the total P but may range from as low as 15–20 to more than 80–90% (Stevenson and Cole, 1999; Tate, 1985). The MRT of organic P in soils is estimated between 350 and 2000 years (Paul and Clark, 1996).

The major S-containing input materials to soils are proteins. They also constitute up to 30% of the organic S in soils. In the last years, S has become a major limiting factor for plant production. Major reasons are the reduction of sulfur dioxide emission from power plants and various industrial sources and low S fertilization in agricultural soils.

12.7.2.2 Plant and Microbial Input to SOM

The amount and composition of the OM entering the soil through plant and microbial residues are given in the overview by Kögel-Knabner (2002), which is updated here with recent developments and data.

12.7.2.2.1 Aboveground input

Forest litter consists mainly of foliage or coniferous needles. Branches, bark, and fruits, in comparison, represent only 21% in cool-temperate climates (Jensen, 1974) and 20–40% in coniferous forests (Millar, 1974) of the total aboveground litterfall. The contribution of herbaceous vegetation to total litterfall amounts to less than 5% in forests of the temperate zones. Meentemeyer et al. (1982) estimated that the proportions of foliage in total aboveground litterfall in coniferous forests were to be 200–600 g dry mass m^{-2} $year^{-1}$. Similar orders of magnitude apply also for the aboveground litter input in deciduous forest. Litterfall in coniferous forests (e.g., in spruce stands) is not bound to a defined season. In general, the average amount of total aboveground litter input in forests increases with decreasing latitude and increasing productivity from the boreal coniferous forests (100–400 g dry mass m^{-2} $year^{-1}$) to the tropics (600–1200 g dry mass m^{-2} $year^{-1}$) (Waring and Schlesinger, 1985).

In natural forests, woody debris is not removed and thus comprises an important component of the total OM input (Harmon et al., 1986; Preston et al., 1998). In contrast, in highly managed forests, most of the woody debris and the logs are removed and the litter input is shifted in composition from woody to nonwoody materials.

Less information is available on the OM input for arable and grassland ecosystems. Input varies depending on the

amount and type of crop residues and fertilizer applications. Typical values for farmyard manure input in different European long-term agroecosystem experiments range between 100 and 360 g C m^{-2} $year^{-1}$ (Körschens et al., 1998). Values are much higher if the crop residues returned to the soil and the belowground C are also estimated.

12.7.2.2.2 Belowground input

A considerable proportion of the organic material becomes incorporated into the soil as belowground input, that is, as root litter and rhizodeposition.

In a global review of root distributions, grasses had the shallowest root profiles, trees were intermediate, and shrubs had the deepest profiles (Jackson et al., 1996). Specific allocation patterns through vegetation types were also found to govern vertical SOC distribution (Jobbágy and Jackson, 2000). Generally, grassland and steppe soils receive a higher proportion of the total carbon input as root litter in comparison to forest ecosystems under similar climatic conditions. The importance of roots for soil C sequestration is underlined by the fact that they have a high potential to be stabilized in soil (Rasse et al., 2006b). On a global average, approximately 30%, 50%, and 75% of the total root biomass occurs in the top 10, 20, and 40 cm of soil (Jackson et al., 1996). Maximum rooting depth depends on the plant species, but may be much deeper than is commonly estimated (Canadell et al., 1996; Richter and Markewitz, 1995). In forest soils, the contribution of root litter to the input of OM in the forest floor in cool-temperate climates varies between 20% and 50%, depending on the tree species and the life-form (evergreen or deciduous; Vogt et al., 1986).

Despite their importance as a subsoil C source, root C flux to soil is poorly understood mainly due to uncertainties associated with the measurement of total root C input, in particular from root exudation and root cell sloughing. Root litter production can be estimated from root turnover. Root turnover can be measured directly using observation of roots from birth to disappearance with microrhizotrons (Kleja et al., 2008). However, minirhizotrons are only able to estimate the most dynamic roots (<1 mm) and not roots with larger diameter (>1 mm) for which isotope techniques as ^{14}C and ^{13}C may be more suitable (Majdi and Andersson, 2005). Depending on the method, the longevity of roots was found in the order of 1–18 years (Gaudinski et al., 2001; Kleja et al., 2008). Annual turnover was 53% for grassland fine roots, 55% for wetland fine roots, and 56% for forest fine roots (Gill and Jackson, 2000).

Rhizodeposition, that is, all OC released by living roots, accounts for a substantial input of OM in soils. Most of the exudates are rapidly consumed by soil microorganisms and thus are fed into the SOM transformation system. With the use of different labeling techniques, it is possible to quantify the amount of OM translocated into the soil belowground (Brüggemann et al., 2011; Elfstrand et al., 2008). The total input of OM in rice cropping systems in the Philippines and Nepal, consisting of aquatic photosynthetic biomass, rice root biomass, root exudates, and fine root turnover, ranged between 0.30 and 0.48 g C m^{-2} $year^{-1}$ (Bronson et al., 1998). Mean belowground input of C in a long-term experiment with cereals, rape crops, and fodder beet was between 30 and 50 g C m^{-2} $year^{-1}$ (Gerzabek et al., 1997).

OM may be translocated in the subsoil as dissolved organic matter (DOM), particulate OM, via bioturbation, and transport of clay-bound OM in certain soil types (lessive). The sharp decrease of dissolved organic carbon (DOC) concentrations with depth of mineral soil is due to the strong retention in the mineral soil by adsorption. The process of DOC movement and retention within the mineral soil was found to be responsible from 19% to 50% of the total carbon stock in forest soils and for 9% in a prairie soil (Kalbitz and Kaiser, 2008; Sanderman and Amundson, 2008). Using the microrhizontron technique, root C input in the mineral soil was estimated 73–78 g C m^{-2} $year^{-1}$ for a northern hardwood forest (Kleja et al., 2008). At this site, DOC input ranged between 11% and 26% of the total carbon input. However, considering root litter and DOC decomposition rates, the authors estimated DOC and roots equally important for SOM buildup in soil.

Physical carbon transport down the soil profile as colloidal Fe/Al-humus complexes is an important process increasing SOM of volcanic subsoils (Osher et al., 2003). In Alisols, Luvisols, Acrisols, and Lixisols (FAO taxonomy), SOM input into subsoils may occur as organomineral complexes. Particulate OM such as black carbon (BC) seems to migrate easily into deeper soil horizons (Dai et al., 2005; Rumpel et al., 2009) and could constitute an important input of chemically recalcitrant C into subsoil horizons of fire-affected ecosystems (e.g., Mueller and Kögel-Knabner, 2009).

Migration of particles can be enhanced by bioturbation. Earthworms, termites, ants, arthropods, and tree roots are efficient in burying soil while forming voids in the form of burrows, nests, chambers, galleries, and root channels (Lavelle et al., 1997). Bioturbation affects directly as well as indirectly inputs of SOC in subsoils (Wilkinson et al., 2009). Direct inputs include litter sequestration into nests, termitaria, borrows, etc., and bioturbator waste disposal in form of dead tissues. Indirect inputs of SOC into subsoils may occur by infilling of biogenic pits with litter, redistribution of SOC, and subsurface mixing and burial. Biologically mediated soil burial rates range between 1 and 2 m My^{-1}. In soils under agricultural use, the vertical mixing of the soil by tillage also incorporates OM into the mineral soil and affects the thickness of the topsoil OM-rich plow horizon.

12.7.2.3 Plant Compound Classes

Plant tissues can be divided into various compound classes, including storage and other materials that are intracellular (proteins, starch, and chlorophyll) as well as structural components that occur in membranes, extracellular (cutin and lipids), or as cell wall constituents (cellulose and hemicelluloses) (Kögel-Knabner, 2002). The storage materials of plants are easily degradable and thus are important carbon and energy sources for microorganisms. The major organic compounds of plant litter are polysaccharides and lignin. According to Millar (1974), spruce needles are composed of 20% cellulose and lignin, 12% polyoses, 1–5% protein, and 1–6% ash. Leaf litter contains 8–14% ash, 10–19% hemicelluloses, 10–22% cellulose, 5–8% lignin, and 2–15% raw protein (Williams and Gray, 1974). Data from different analyses for

arable crop residues showed a high variability for lignin and cellulose contents (Rahn et al., 1999). Only 50–60% of the total OM of plant litter is accounted for by chemical degradative techniques (Kögel et al., 1988).

12.7.2.3.1 Cellulose

Cellulose is the most abundant biopolymer, as it comprises the major structural component of the cell walls of lower and higher plants. We find high cellulose contents in stalks and stems and in other woody parts of plants. Cellulose is also a component of the cell walls of algae and fungi, whereas it is only seldom found in bacteria (De Leeuw and Largeau, 1993; Peberdy, 1990).

Cellulose is a linear polymer glucan and is composed of glucose units (>10 000), which are linked by β-(1–4)-glycosidic bonds. The regular arrangement of the hydroxyl groups along the cellulose chain leads to the formation of H-bridges and therefore to a fibrillar structure with crystalline properties.

12.7.2.3.2 Noncellulosic polysaccharides

The noncellulosic polysaccharides of the plant cell walls are often summarized as hemicelluloses or polyoses. Noncellulosic polysaccharides differ from cellulose in their composition of sugar units (mainly pentoses, hexoses, hexuronic acids, and desoxyhexoses), side chains, and branching. Hemicelluloses are a group of polysaccharides of different composition, which consist of cellulose-like sugar units bound together with glycosidic linkages, but are more or less strongly branched and have a lower degree of polymerization than cellulose. Xylans are a widespread hemicellulose group, consisting of (1–4)-glycosidic units of β-D-xylose. They comprise 5–30% of the polysaccharides in woody tissues. Mannans are composed of a chain of (1–4)-glycosidic-linked β-D-mannose, which are partly supplemented with side chains of α-D-galactose (bound by (1–6)-glycosidic bonds). Glucomannans with a glucose–mannose ratio of 1:2 are mainly found in deciduous trees. Galactans are water-soluble, highly branched polysaccharides composed of (1-3/6)-glycosidic-bound β-D-galactose. Similar heterogeneous noncellulosic polysaccharides are found not only in plants but also in bacteria, fungi, and algae.

12.7.2.3.3 Lignin

Lignin is a high molecular, three-dimensional macromolecule consisting of phenyl propane units. Lignin fills out the cell walls, which consist predominantly of linear polysaccharidic membranes, providing structural rigidity. Lignin is an important element of the cell walls of vascular plants, ferns, and club mosses. Together with hemicellulose, lignin is found in the primary wall, in the secondary wall, and in the middle lamella of the voids of the cellulose microfibrils. After the polysaccharides, lignin is the most abundant biopolymer in nature and a large contributor to the residues of the terrestrial biomass.

Figure 2 shows the model of spruce lignin as described by Adler (1977), which contains all essential structural elements. The primary building units of lignin (monolignols) are the cinnamyl alcohols, coniferyl alcohol, sinapyl alcohol, and *p*-coumaryl alcohol, using the conventional terminology of the carbon atoms (deviating from the IUPAC terminology). The monomers react through the so-called dehydrogenative polymerization to a three-dimensional macromolecule, which contains a multitude of C–C and ether-linked compounds. The arylglycerol-β-arylether (β-O-4) linkage dominates by far, followed by biphenyl (5–5) and phenylcoumaran (β-5) linkages. Figure 2 also covers the most frequent types of bonds and their structure in gymnosperm and angiosperm lignin. Most of the linkages in lignin molecules are not hydrolyzable.

Lignin in gymnosperms, angiosperms, and grasses is classified based on differences in monolignol composition. The lignin of gymnosperms is composed almost exclusively of guaiacyl propane monomers, which are derived from coniferyl alcohol. Angiosperm lignin contains approximately equal proportions of guaiacyl propane units and syringyl propane units, derived from sinapyl alcohol. Lignin of grasses is composed of about equal proportions of guaiacyl propane, syringyl propane, and *p*-hydroxyphenyl propane units. Additionally, around 5–10% *p*-coumaric acid and ferulic acid, which are predominantly esterified to the terminal hydroxyl groups of the propyl side chains, are found in lignin. The proportions of coniferyl, sinapyl, and *p*-coumaryl alcohol amount to 94:1:5 in spruce lignin, 56:40:4 in beech lignin (Fengel and Wegener, 1984), and 1:1:1 in grass lignin. Nimz (1974) was the first to develop a structural model for angiosperm lignin using European beech as an example. In these models, the ultrastructure of lignin is considered to be heterogeneous and formed by random polymerization.

12.7.2.3.4 Tannins and other polyphenols

Tannins are defined as polyphenols that occur in higher plants. They precipitate proteins in aqueous solutions and therefore act as tanning substances (Haslam, 1981). Besides tannic substances, plants contain a multitude of other secondary phenolic substances. Tannic substances are distinguished in two groups, the condensed tannin (CT) or nonhydrolyzable tannin (also termed proanthocyanidine) and the hydrolyzable tannins (HT) (Haslam, 1981).

The CT are polyphenols from polyhydroxy-flavan-3-ol units, which are linked mostly through C—C bonds between C-4 and C-8 and sporadically between C-4 and C-6 and, therefore, not acid- or base-hydrolyzable.

HT have two basic units, namely, sugar (mostly D-glucose or similar polyoles) and phenolic acids. They are a heterogeneous group of macromolecules, which can be differentiated into gallotannin and ellagitannin. Gallotannins have a central sugar unit, which is esterified with several molecules of gallic acid (Figure 3). Ellagic acid is the basic phenolic unit of ellagitannins. Tannins are quantitatively important components of various plant parts. They occur in various organs of higher plants, especially in dicotyledones.

12.7.2.3.5 Lipids

Lipids are organic substances that are insoluble in water but extractable with nonpolar solvents, for example, chloroform, hexane, ether, or benzene (Dinel et al., 1990). Lipids are a heterogeneous group of substances that occur both in plants and in microorganisms. They comprise among others hydrocarbons (*n*-alkanes, branched alkanes, olefins, and cyclic alkanes), ketones (monoketones and ß-diketones), primary and secondary alcohols (alcandiols), free fatty acids, wax esters (primary alcohol esters and triesters), and terpenoids

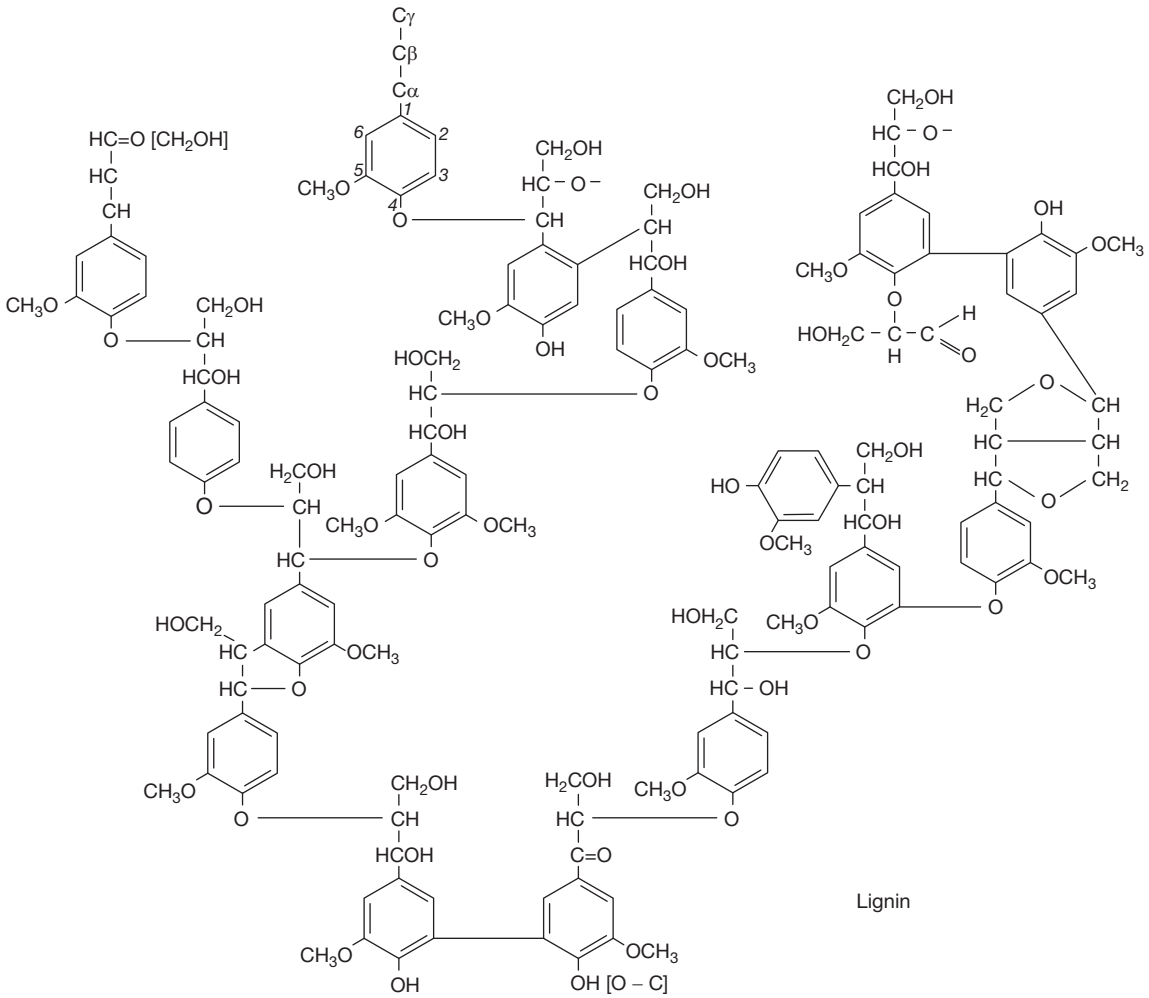


Figure 2 Model of lignin according to Adler (1977), including the conventional ring and side-chain carbon denominations (differing from the IUPAC nomenclature) and the major types of bonds.

(Dinel et al., 1990). The surface lipids of plants are comprised of a number of different structural groups. They cover the surface of leaves and needles with a thin layer as a component of the plant cuticle. The lipids in soil originate from plants as well as microorganisms, whereas soil animals only play a minor role. **Figure 4** shows the most important components of the soil lipids, which are already found as components of plant lipids.

12.7.2.3.6 Cutin and suberin

Cutin and suberin are polyesters that occur in vascular plants. Cutin composes the macromolecular frame of the plant cuticle in which the low molecular waxes and fats are embedded. Together, they form the cuticle. The cuticle covers the epidermis and protects the surface of plants against desiccation by the atmosphere. In contrast, suberin is a cell wall component of cork cells, which compose the periderm layer of surficial as well as subterranean parts of woody plants. The content of suberin is particularly high in bark and in plant roots.

The cutin polymer is composed of di- and trihydroxy and epoxy fatty acids with a C_{16} and C_{18} chain length (**Figure 5**). In the C_{16} group, dihydroxypalmitinic acid dominates, and in the C_{18} group, oleic acid and hydroxyoleic acid dominate. These are mainly linked by ester bonds and some ether bonds (Kolattukudy, 1981). Suberin is composed of aliphatic and aromatic components. In contrast to cutin, it contains monomers with a higher chain length of C_{20}–C_{30}, in particular 1-alcanols, fatty acids, ω-hydroxy fatty acids, and especially α,ω-dioic acids with a C_{16} or C_{18} chain length. In addition, suberin contains phenolic acids, especially hydroxycinnamic acids. Whereas it was supposed for a long time that the aliphatic and aromatic units are linked by ester bonds in one macromolecule, recent research indicates that there are distinct aromatic and aliphatic domains (Bernards and Lewis, 1998). The cuticle of some plants, for example, *Agave americana*, contains a nonhydrolyzable biopolymer, which consists of polymethylene chains in addition to the hydrolyzable polyester material.

12.7.2.3.7 N-, S-, and P-containing compounds

Between 2% and 15% of the plant dry mass is assigned to N-containing compounds (Haider and Schäffer, 2009). Nitrogen is a component of three very important biological macromolecular structures, that is, proteins/polypeptides,

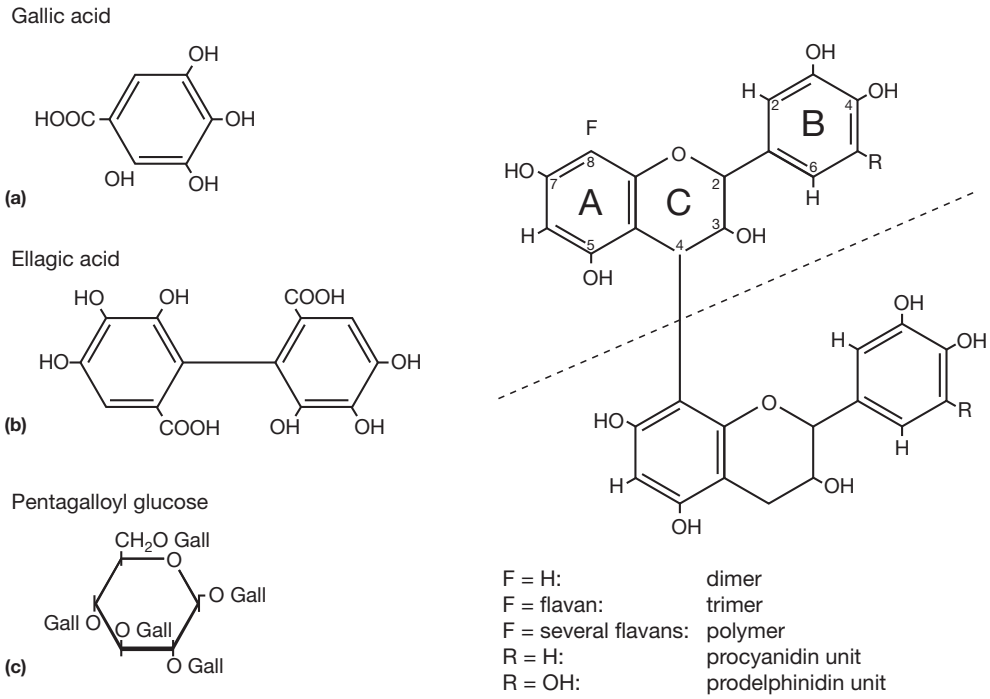


Figure 3 Structure of hydrolyzable and nonhydrolyzable tannins. GALL, gallic acid. Reproduced from Kögel-Knabner I (2002) The macromolecular organic composition of plant and microbial residues as inputs to soil organic matter. *Soil Biology Biochemistry* 34: 139–162, with permission from Elsevier.

DNA (deoxyribonucleic acid), and RNA (ribonucleic acid). Minor biological sources of organic N are smaller molecules, such as porphyrins (mainly chlorophyll and hemoglobin). The nucleotides forming DNA and RNA are composed of a phosphate, sugar, and heterocyclic N-containing base unit, that is, the purine units adenine and guanine and the pyrimidine units uracil, cytosine, and thymine. A substantial input of organic N in soils occurs via rhizodeposition (Whipps, 1990). Root exudates containing N are mainly amino acids and amides, but nucleotides and flavonones are also reported (Hütsch et al., 2002; Kuzyakov et al., 2003; Uren, 2001). Proteins also form the main S-containing materials that enter soils, with the amino acids cystine, cysteine, and methionine.

Inositol phosphates are synthesized mainly by plants, but small amounts are also reported to be found in bacteria and fungi (Turner et al., 2002). Inositol phosphates are esters of hexahydroxy cyclohexane. In plants, inositol hexaphosphates are mainly found in storage organs in the form of Ca or Mg salts, called phytin. In addition to inositol hexaphosphate, other inositols only partly esterified with phosphates are found in plants and soil. The membranes of all living organisms contain a phospholipid bilayer. The phospholipids are mostly derivatives of glycerin with phosphodiester structures, sometimes also phosphomonoesters. In the phosphodiester structures, the phosphate group is bound to amino alcohols, such as choline (lecithin), 2 aminoethanol, or L-serine. Phospholipids in soils are mainly of microbial origin and are predominantly phosphatidylcholines, followed by phosphatidylethanolamines (Stevenson and Cole, 1999). In archaea, which also play a role in soils, ether-linked lipids are found. Microbial inputs are dominated by nucleic acids with 60% of total P and phospholipids, accounting for 5–30% of the microbial and fungal input, and even more in plant input to soils.

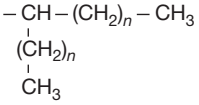
12.7.2.3.8 Specific components of fungi and bacteria

As in the cell walls of plants, the cell walls of fungi consist mainly of homo- and heteropolysaccharides (Kögel-Knabner, 2002). Cell walls of some fungi also contain relatively high proportions of proteins. Lipids and melanins are quantitatively minor components of fungal cell walls. The basic unit of the cell walls of fungi and also the exoskeleton of insects is chitin. Chitin is composed of *N*-acetyl-D-glucosamine in β-(1–4)-glycosidic bonds. Fungi but also some bacteria synthesize various melanins, which occur as components of the cell walls, incorporated either in the structure of the cell wall or as its outermost layer (Butler and Day, 1998). Melanin pigments contain protein, carbohydrates, lipids, and a polymeric core that consists of various types of phenolic, indolic, quinone, hydroquinone, and semiquinone monomers. Melanins absorb visible light in the entire wavelength spectrum and are therefore black- to brown-colored.

Bacterial cell walls are composed of a peptidoglycan (murein), which contains carbohydrate as well as amino acid elements (Kögel-Knabner, 2002). The carbohydrate backbone of murein is composed of *N*-acetylglucosamine and *N*-acetylmuramic acid. Whereas glucosamine is also found in insects and fungi, muramic acid is only found in bacteria. In addition to the 20 major amino acids of proteins, bacterial cell walls also contain a series of unusual amino acids, linked in a two-dimensional structure, which provides rigidity and elasticity to the bacterial cell wall. Cell walls of Gram-positive bacteria contain approximately 20–40 murein layers, whereas the

n-alkanes $CH_3-(CH_2)_n-CH_3$

branched alkanes



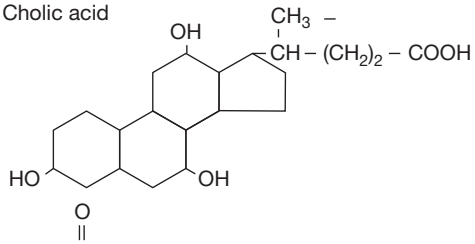
n-alkenes $CH_3-(CH_2)_n-CH=CH-(CH_2)_n-CH_3$

n-fatty acids $CH_3-(CH_2)_n-COOH$

n-alcohols $CH_3-(CH_2)_n-CH_2OH$

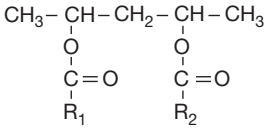
Di-alcohols $CH_3-CHOH-(CH_2)_n-CH_2OH$

Sterines Cholic acid

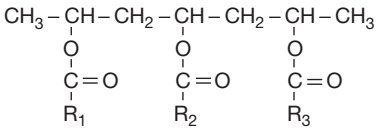


Monoester

Diester



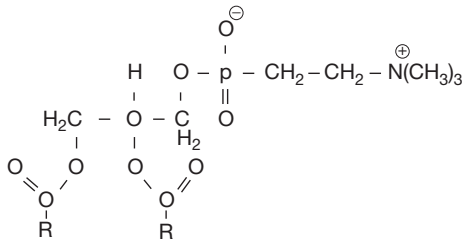
Triester



Major types of lipids founds in plant, algae, bacteria, and fungi

(a)

Phospholipid fatty acids (PLFAs)

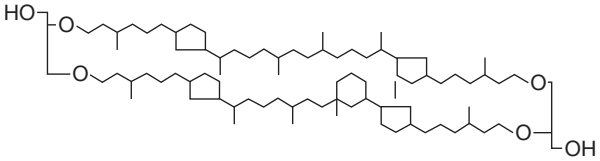


R = fatty acids that are used for microbial fingerprints

(b)

Glycerol dialkyl glycerol tetraethers (GDGTs), based on 2,3-dialkyl-*sn*-glycerol backbones

Crenarchaeol
m/z 1292



Specific membrane lipids from bacteria (PLFAs) and archaea (GDGTs)

(C)

Figure 4 Major types of lipids found in plants and microorganisms. Modified from Kögel-Knabner I (2002) The macromolecular organic composition of plant and microbial residues as inputs to soil organic matter. *Soil Biology Biochemistry* 34: 139–162, with permission from Elsevier.

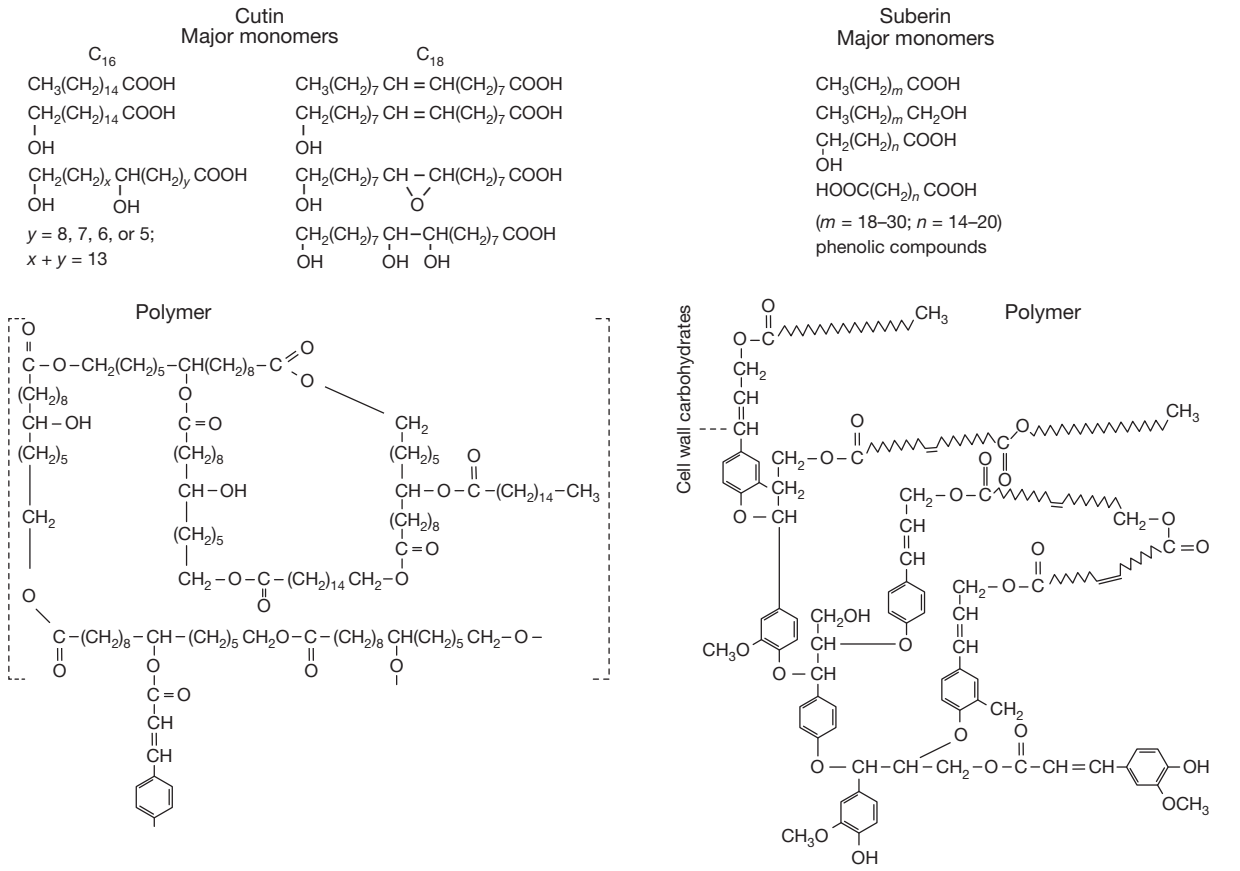


Figure 5 Major components and their structural associations in cutin and suberin. Reproduced from Kögel-Knabner I (2002) The macromolecular organic composition of plant and microbial residues as inputs to soil organic matter. *Soil Biology Biochemistry* 34: 139–162, with permission from Elsevier.

cell walls of Gram-negative bacteria are composed of fewer, even possibly only one murein layer. Therefore, murein amounts to approximately 50% of the dry weight of the Gram-positive but only 10% of the dry weight of the cell wall of Gram-negative bacteria. Whereas glucosamine is also found in insects and fungi, muramic acid, and diaminopimelic acid are only, and galactosamine to a large extent found in bacteria (Stevenson, 1994). A number of algae and bacteria have been reported to contain substantial amounts of insoluble, non-hydrolyzable aliphatic biomacromolecules, termed algaenan and bacteran. They derive from condensation of complex lipids and are located in the cell wall (Largeau and De Leeuw, 1995).

Between 50% and 60% of the bacterial biomass can be assigned to N-containing compounds (Haider and Schäffer, 2009), polymers of amino acids, amino sugars, and DNA and RNA. The ratio of protein to RNA is around 5 and the ratio protein/DNA about 2. The relatively high content of N-containing biomolecules is responsible for the low C/N ratio of 5–8 of bacterial biomass (Paul and Clark, 1996). Fungi contain approximately 14–52% N-containing compounds.

Teichoic acids are acidic mucopolysaccharides in the cell wall of Gram-positive bacteria with a phosphodiester structure. They frequently consist of repeating units of glycerol or ribitol and are connected by phosphate esters (De Leeuw and Largeau, 1993).

The domain Archaea is a third line evolutionary descent, different to Bacteria and Eukarya. They were first discovered in various extreme environments, for example, hot springs, hydrothermal vents, solfataras, salt, and soda lakes. With modern molecular techniques, archaea have been found in many normal habitats among others also in soils (Chaban et al., 2006). It has become clear that archaea have been underestimated with respect to the role they play in the C and N cycle of many ecosystems, and especially also in soils.

In recent years, the specific lipid components of membranes of bacteria (phospholipid fatty acids, PFLAs) and archaea (glycerol dialkyl glycerol tetraethers, GDGTs) have gained major interest, because they can be used as fingerprints for the composition of the microbial community in soils (see **Section 12.7.5**). Examples for the structure of these components are given in **Figure 4**. The lipids of these organism are now known to contain many unique and characteristic polar lipids, based on 2,3-dialkyl-*sn*-glycerol backbones, that is, the stereochemistry is the opposite of that found in the two other primary kingdoms, Bacteria (eubacteria) and Eukarya (eukaryotes). As most of the archaea from soils have not been cultivated, their overall composition and contribution to SOM cannot be assessed at present.

12.7.2.4 Charcoal

Apart from biological processes, fires may also significantly affect the properties and fate of SOM. The incomplete

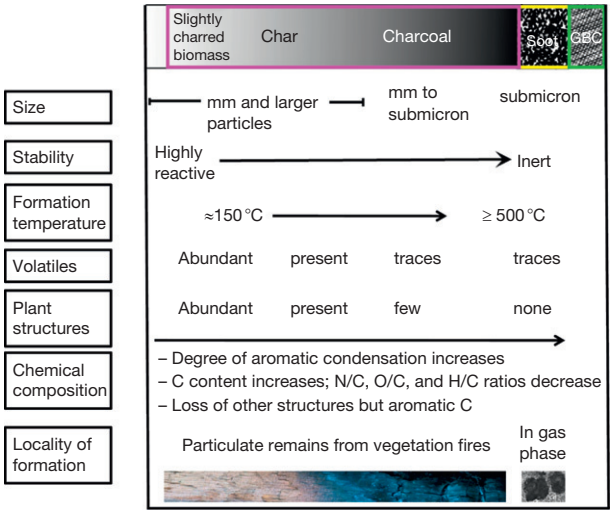


Figure 6 Black carbon: properties and conditions of formation (based on data from Brodowski et al., 2005a; Hammes et al., 2007; Hedges et al., 2000; Keiluweit et al., 2010; Masiello, 2004; Schmidt and Noack, 2000).

combustion of organic materials leaves behind a continuum of differently condensed aromatic structures (charred biomass, char, and charcoal; **Figure 6**), commonly assigned as black carbon (BC). In addition, soot-BC is formed via condensation from the gas phase (particle size 30–40 nm). It possesses a lower microporosity and higher degree of aromatic condensation than char-BC and thus exhibits a greater stability in the environment (Elmquist et al., 2006; Masiello, 2004). Besides, also coalified materials like lignite or bituminous coal show in parts structures similar to BC from burning events (Hammes et al., 2007; Laskov et al., 2002). Particularly in areas close to open cast mining, a significant part of the SOM may thus not solely originate from plant debris and fire events but from airborne pollution. Such 'foreign' C may comprise up to 50% of total C in the surface soil (Rethemeyer et al., 2007) and interferes, thus, also with common methods used for assessing the age and turnover time of total SOM.

The global BC production has been estimated to range from 40 to 600 Tg $year^{-1}$ (Schmidt and Noack, 2000). More than 80% of the BC produced is deposited on soils (Kuhlbusch and Crutzen, 1995), from where it may be slowly incorporated into the soil matrix, for example, by burying animals (Eckmeier et al., 2007). Both the chemical recalcitrance and interactions of the BC structures with minerals then protect them from rapid degradation (Brodowski et al., 2005b, 2006). Once produced, BC can thus reside in soils and sediments for a few hundred to several 10 000 years (e.g., Flessa et al., 2008; Goldberg, 1985; Masiello and Druffel, 1998).

12.7.3 Composition and Transformation of Organic Matter in Soils

12.7.3.1 Bulk SOM Composition

Above- and belowground plant residues, root deposits, microbial residues, and their transformation products all contribute to the formation of the OM in soils (Kögel-Knabner, 2002; Rasse et al., 2005). Thus, in contrast to sediments, each soil horizon represents a mixture of these materials in different stages of degradation (see **Chapter 10.7**). Therefore, also the solid-state ^{13}C NMR spectra of bulk soils are essentially mixtures form the different materials present in soils (see **Chapter 15.11**). The review of Mahieu et al. (1999) shows that ^{13}C NMR spectra from bulk soils are remarkably similar, dominated by signals from O/N-alkyl C (45%), followed by alkyl (25%) and aromatic C (20%) and carboxyl and amide C (10%). This is in part due to the fact that the SOM in topsoils is dominated by high proportions of plant residues with a relatively uniform composition. **Figure 7** gives examples of the bulk SOM composition found in different soils as estimated in solid-state ^{13}C NMR spectra. The major signals are found at chemical shifts of 30, 56, 72, 105, 119, 130, 150, and 175 ppm (Kögel-Knabner, 1997). **Figure 7** also shows that spectra can be considerably improved by destroying the mineral phase, especially iron oxides containing paramagnetic iron, and at the same time concentrating the OC. The general composition of bulk soil organic C and N is given in **Table 3**.

Signals in the O/N-alkyl C region (45–110 ppm), with the most prominent resonance at 72 ppm, represent C2, C3, and C5 carbon atoms of polysaccharides. The signal at 105 ppm is assigned to the anomeric C1 carbon of cellulose and hemicellulose. The signals usually occur with shoulders around 65 and 80–90 ppm, and often only assigned to polysaccharides, but also include a contribution from lignin side-chain C and proteins. The broad resonances between 30 and 55 ppm reveal the presence of proteins or peptides. For a detailed assignment of molecular components of litter and SOM to the ^{13}C NMR spectra, consider Kögel-Knabner, 1993 and Nelson and Baldock (2005).

The O/N-Alkyl-C structures often account for 30–60% of the total OC in mineral soils. However, since plant-derived celluloses and hemicelluloses can be almost completely decomposed in soils, a number of studies have shown that polysaccharides of microbial origin accumulate during biodegradation of SOM in the mineral soil, as, for example, indicated by analysis of individual carbohydrates after hydrolysis or pyrolysis (Guggenberger et al., 1994; Murayama, 1984; see also **Section 12.7.5**). Besides, we thus also find a significant amount of amino sugars, which are of exclusively microbial origin. Their contribution to the total polysaccharides in soils increases during decomposition (see **Section 12.7.5** for a detailed description of amino sugars as biomarkers). In a study making use of the natural isotope difference of C_3 and C_4 plants, Derrien et al. (2006) found a mean age for the carbohydrate fraction of a cultivated soil between 60 and 100 years. They attributed this relatively old age for typically biodegradable compounds to a protection in the inorganic matrix or to the continuous recycling of the carbon atoms of OM, including the sugar molecules themselves, by the soil microbes. Thus, the mean age of carbon in soil sugars might be as great as or even greater than the mean age of bulk SOM (Gleixner et al., 1999, 2002), and their contribution to the slow turnover pool of SOM may exceed that of lignin (Amelung et al., 2008; Dignac et al., 2005; Schmidt et al., 2011). Also, when SOM decomposition proceeds with depth or when the soil is fertilized, it has been illustrated that with increasing depletion of SOC, the OC-normalized contents of polysaccharides hardly changed, whereas the contents of lignin phenols were significantly lower (Amelung et al., 1997; Kiem and Kögel-Knabner, 2003; see also **Table 4**). Kiem and Kögel-Knabner (2003) therefore concluded that the two

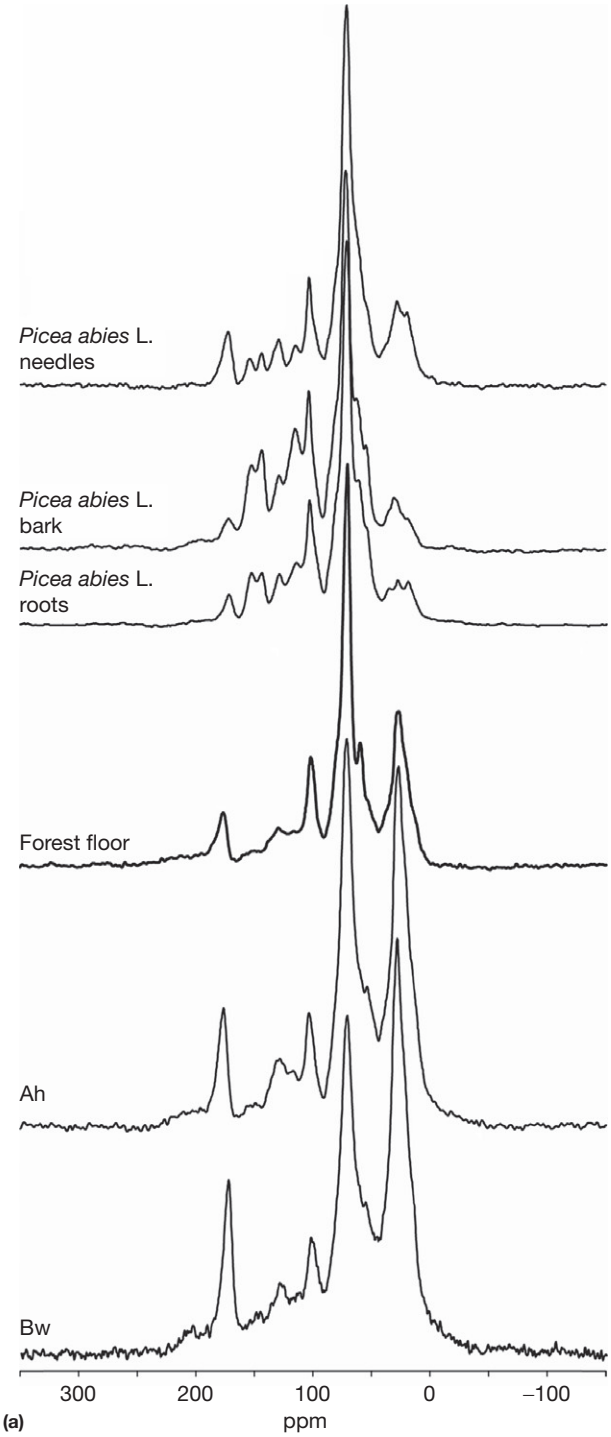


Figure 7 Bulk SOM composition found in different soils as estimated in solid-state ^{13}C NMR spectra. (a) Pine litter, forest floor, and mineral soil (spectra with permission from John Wiley & Sons from Spielvogel S, Prietzel J, and Kögel-Knabner I (2006) Soil organic matter changes in a spruce ecosystem 25 years after disturbance. *Soil Science Society of America Journal* 70: 2130–2145; Spielvogel S, Prietzel J, and Kögel-Knabner I (2008) Soil organic matter stabilization in acidic forest soils is preferential and soil type specific. *European Journal of Soil Science* 59: 674–692).

(Continued)

compounds differed in their contribution to the refractory C pool: the polysaccharide contribution to the refractory C pool is comparable to the labile C pool, whereas lignin is quantitatively less important within the refractory OC than within labile OC pools.

After the polysaccharides, the second most dominant part of SOM is alkyl-C structures. They produce NMR signals at 0–45 ppm. The signal at 30 ppm originates from methylenic C in long-chain aliphatic compounds of varying origin, such as fatty acids, lipids, cutin acids, and other probably not yet

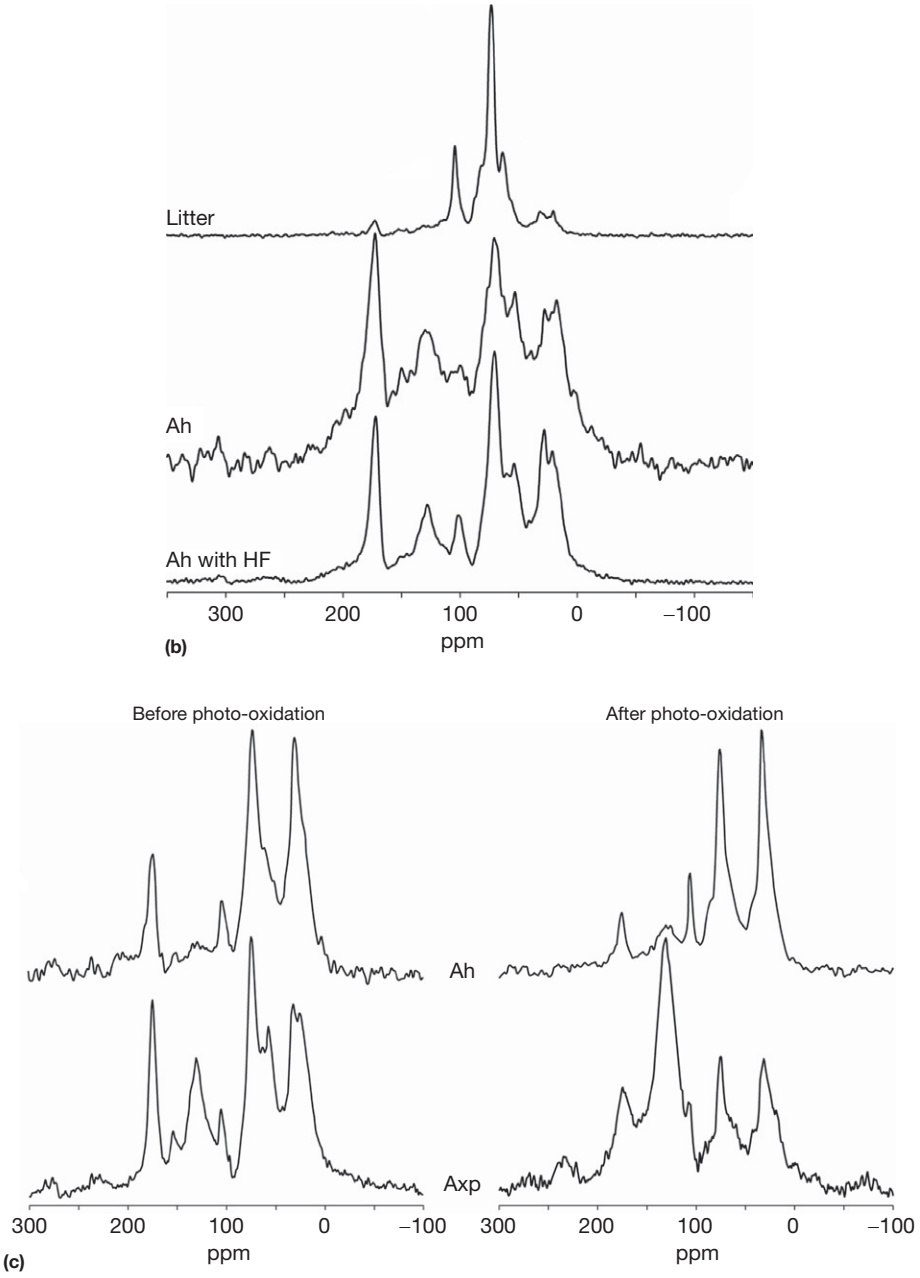


Figure 7 (b) Grassland soil from the Inner Mongolia steppe (unpublished); (c) A horizon from a Chernozem rich in charred OM (below) and a Haplic Alisol (above) with no/low contribution of charred OM. Reproduced from Schmidt MWI, Skjemstad JO, Gehrt E, and Kögel-Knabner I (1999) Charred organic carbon in German chernozemic soils. *European Journal of Soil Science* 50: 351–365, with permission.

identified aliphatic biopolymers. It correlates with the signal at 175 ppm in the carboxyl-C region (160–200 ppm), which is derived from carboxyl and amide groups in various compounds. Hence, alkyl C mainly comprises a mixture of extractable and bound lipids and in total comprises 10–30% to total soil OC in mineral soils, with about 5–10% originating from extractable lipids (**Table 3**). As far as we know, they are of both plant and microbial origin. Ester-linked macromolecules such as cutin and/or suberin may be released by base hydrolysis. These compounds usually account for an additional 10–15% of carbon in A horizons but may be very important with regard to carbon storage in subsoils (Nierop et al., 2003). The remaining part of alkyl C comprises aliphatic compounds, which are not released by conventional base hydrolysis (Kögel-Knabner et al., 1992; Rumpel et al., 2005). The nature of these compounds is still not well known.

The signal intensity in the aryl C region (110–160 ppm) represents aromatic carbon derived from lignin, tannins, and

Table 3 Typical composition of bulk soil organic C and N as estimated from NMR (first column) and biomarker analyses (second column)

SOM components as identified by ^{13}C and ^{15}N NMR	*Identified component*	*% contribution to total plant biomass C*	*% SOC in mineral topsoil*	*% SON in mineral topsoil*	*References (choice)*
Alkyl C		10–20	15–25		Preston et al. (1998)
	Lipids, steroids		5–10	–	Dinel et al. (1990)
	Cutin/suberin		10–15	–	Kögel-Knabner et al. (1992), Kögel-Knabner and Hatcher (1989)
O/N-Alkyl C		55	30–60		Kögel et al. (1988), Kögel-Knabner et al. (1988)
	Neutral sugars	40–50	20–45	–	Cheshire (1985), Amelung et al. (1997)
	Amino acids	10	<10%	30–60%	Stevenson (1994), Amelung et al. (2006)
	Amino sugars	–	<4%	3–10	Bremner (1958), Stevenson (1994), Greenfield (2001), Roth et al. (2011)
Aromatic C		10–20	10–30		
	Lignin		5–15[a]	–	Amelung et al. (1997), Amelung et al. (1999a,b,c), Kögel et al. (1988)
	Black C	0	4–35	<10%[b]	Masiello (2004), Rodionov et al. (2010)
	Tannins, polyphenols	<5	<2[c]	–	Maie et al. (2003)
Carboxylic C		5	5–15	–	
	Uronic acids[d]		3–6	–	Amelung et al. (1999a,b,c)
	Fatty acids[d]		<5%	–	Dinel et al. (1990)

[a]Estimated from the sum of lignin-derived phenols, and based on the yields from Klason lignin of woody tissues (Kögel et al., 1988).
[b]Estimated on the basis of usually wide C/N ratios of BC particles; only grass char may exhibit narrow C/N rations (Hilscher and Knicker, 2011). Yet, this char is of low stability and contributes less to total SOM that does more stable BC in other soils.
[c]Yields for extracted polyphenols from soils are very low, probably due to strong adsorption (Halvorson et al., 2011).
[d]Total contribution to SOM.

Table 4 Amounts of total OC, polysaccharide C, and VSC lignin from contrasting treatments of long-term agroecosystem experiments. The contribution of polysaccharides and lignin to the refractory carbon pool of arable soils was investigated in C-depleted (long-term bare fallow) and conventionally managed plots of long-term agroecosystem experiments

	Fertilized plots	*C-depleted plots*
Residual amounts of total OC (%)	100	52 ± 8
Residual amounts of polysaccharide C (%)	100	54 ± 10
GM/AX ratio	0.89 ± 0.09	1.13 ± 0.18**
Residual amounts of VSC lignin C (%)	100	18 ± 6
Ac/Al_V	0.23 ± 0.06	0.38 ± 0.12*

*, ** Difference of the managements significant at the 0.05 and 0.01 probability level, respectively.
Data presented are mean values from eight different long-term experiments in central Europe and are given residual amounts as a five of the fertilized/conventionally managed plots. Data extracted from Kiem and Kögel-Knabner (2003).

charcoal. In total, mineral soils contain between 10% and 20% aromatic carbon. The signals at 56, 119, 130, and 150 ppm are assigned to methoxyl C, protonated aromatic C, C-substituted aromatic C, and phenolic C, respectively, in lignin. It seems that the aromatic C is mainly derived from plant origin, and it seems that there is very little microbial contribution to aromatic compounds in soils, except for soils containing BC from repeated burning. If the signal intensity is high at 130 ppm for C-substituted aromatic C and not associated with the corresponding signal intensities for the other lignin components, this is an indication for the presence of charred material (BC). It may be very stable in soil and sediments and reside in the environment for millennia (Masiello and Druffel, 1998).

The BC usually constitutes between 4% and 35% of soil OC (Masiello, 2004; Rodionov et al., 2010). In extreme cases, a BC content of up to 45% of the whole soil organic C has been proposed for some Chernozemic soils in Germany (Schmidt et al., 1999); in Australia, where wildfires are common, BC might even account for up to 60% of the total noncarbonate C (Skjemstad et al., 1996, 1999). A high charcoal content is often associated with low lignin contents measured after CuO oxidation (Schmid et al., 2001), as lignin seems to be altered by

vegetation fires (Certini et al., 2011). In soils of highly industrialized areas of Germany, the atmospheric deposition of combusted particles and coal dust from coal processing industries contributed up to 80% of the total soil OC (Rumpel et al., 1998; Schmidt et al., 2000). On the other hand, charred organic C contents are very small or nondetectable in temperate forest soils, which were not subjected to regular burning (Schöning et al., 2005; Skjemstad et al., 1997), and can even be small in forest soils that burn rather often, due to complete reburning of charcoal to ash (Czimczik et al., 2005).

The properties of BC vary largely but nonlinearly with formation temperature. While few endothermic reactions may start around 100 °C, differential scanning calorimetry suggests that exothermic reactions start around 150 °C with the depolymerization of lignin (Yang et al., 2007). When heating proceeds, carbohydrates are rapidly decomposed, volatiles disappear, and so-called transition chars characterize the BC continuum of char and charred SOM (**Figure 6**; Keiluweit et al., 2010). At around 400 °C heating temperature, sharp rises in aromaticity have been detected due to condensation reactions that become typical for the amorphous structures at this charring (charcoal) stage. At even elevated temperatures (>500–600 °C), heterocyclic C is lost, and O/C and H/C ratios drop below 0.2 and 0.8, respectively. Finally, the volatiles are refixed, and turbostratic crystallites are being increasingly embedded into the amorphous structure (soot) or prevail in graphitizied carbon black (GBC; **Figure 6**; see also Keiluweit et al., 2010). At these later stages, plant remains are no longer detectable. If protein-containing plant residues undergo burning, the resulting charred material contains a considerable amount of 'black nitrogen,' which may contribute to the refractory soil organic nitrogen pool (Gärdenäs et al., 2011).

With a typical C/N ratio in mineral soils between 8 and 12, about 10% of the organic C, on the average, is connected to N. The major part of the organic nitrogen is bound in amide-N functional groups, most probably as part of proteinaceous material (Knicker, 2004). Plant proteins undergo rapid biodegradation when entering the soil, that is, similar to polysaccharides, microbial biosynthesis likely contributes to a major fraction of protein C and N in soil. Nevertheless, hydrolysis with 6 N HCl usually releases less than 50–60% of this total N (Amelung et al., 1996; Stevenson, 1994). Therefore, at least some of the organic nitrogen in soil samples, identified as amide-N, must be present in a form protected from microbial degradation and resistant to drastic chemical treatment. This resistance may explain to some degree the difficulties in identifying such structures with common wet chemical degradative methods.

Cheshire et al. (1999) used ^{15}N NMR spectroscopy to follow the incorporation of labeled ^{15}N fertilizer during the decomposition of wheat straw. They found that the organic N after incubation was mainly present in fungal tissue, and only to a small extent in bacterial tissue. Together with the data on microbial biomass and microbial biomarkers (ergosterol and glucosamine), this led to the conclusion that fungi are predominantly involved in the immobilization of N during straw decomposition in soils. Most of the N in SOM thus seems to originate from stabilization of microbial residues and products. There is growing evidence that a large part of the stable OM in soils is composed of microbially and faunally derived compounds. Microbial residues in soils contain components specific for microorganisms, such as murein, chitin, and certain lipids. And all these compounds have been shown to accumulate in soils.

Microbial proteins are considered to be better able to bind to mineral surfaces, as well more likely to arrive at these surfaces, than are residues of vascular plants, thus producing a particularly stably bound, N-rich inner layer of organic material associated with the fine fraction of soils (Kleber et al., 2007). In line with this concept, N-containing materials together with polysaccharides are preferentially stabilized in the very early phases of soil formation (Dümig et al., 2012). Thus, the ^{15}N CP NMR spectra from many soils show only one major signal, which is attributed to N in amide structures (**Figure 8**). However, a detailed study by Smernik and Baldock (2005) showed that nonprotonated heterocyclic N is insensitive to ^{15}N NMR under conventional conditions in soil clay fractions and may be often underestimated. Heterocyclic N is detected with other techniques, such as XANES or analytical pyrolysis, although it has also been discussed whether the products might be an artifact of the analytical procedure.

12.7.3.2 Organic Matter in Subsoils

In recent years, it has become clear that it is necessary to also consider the OM in subsoils. Although up to 2/3 of total soil organic C may be found in subsoils, until now, little information is available for OC composition in the subsoil, except for rather C-rich soil horizons, such as spodic B horizons, which have been extensively studied (Rumpel and Kögel-Knabner, 2011). The elemental and isotopic evidence suggests that SOM in subsoils is more microbially processed than topsoil OM and most probably has a higher proportion of microbial-derived compounds. Enrichment of microbial-derived amino sugars in subsoil horizons was found by Liang and Balser (2008) who stated that "microbial residues are refractory and that they contribute to terrestrial carbon sequestration." Further evidence for the importance of microbial over plant-derived carbon in subsoil horizons was obtained from the analysis of noncellulosic neutral carbohydrates. Microbial-derived sugars associated with the mineral phase were found to be positively correlated to the ^{14}C activity of the bulk sample, suggesting that these easily degradable substances are effectively stabilized by mineral interactions (Rumpel et al., 2010). Microbial sugars in the clay fraction of subsoil horizons were found to be associated with poorly crystalline Fe oxides but this was not the case for plant-derived lignin (Spielvogel et al., 2008).

Generally, the SOM content and its C/N ratio are decreasing rapidly below the A horizon. Low C/N ratios have been attributed to highly processed SOM. In most subsoils, C/N ratio is approaching that of microbes (Wallander et al., 2003). In subsoils, which are generally characterized by a very low OM content, high nitrogen content may be related to the presence of mineral nitrogen sorbed to clay surfaces. Mineral nitrogen was found to contribute to about 20% to the total nitrogen of deep soil horizons, and even when subtracted, C/N ratios of most soils are decreasing with depth (Jenkinson et al., 2008;

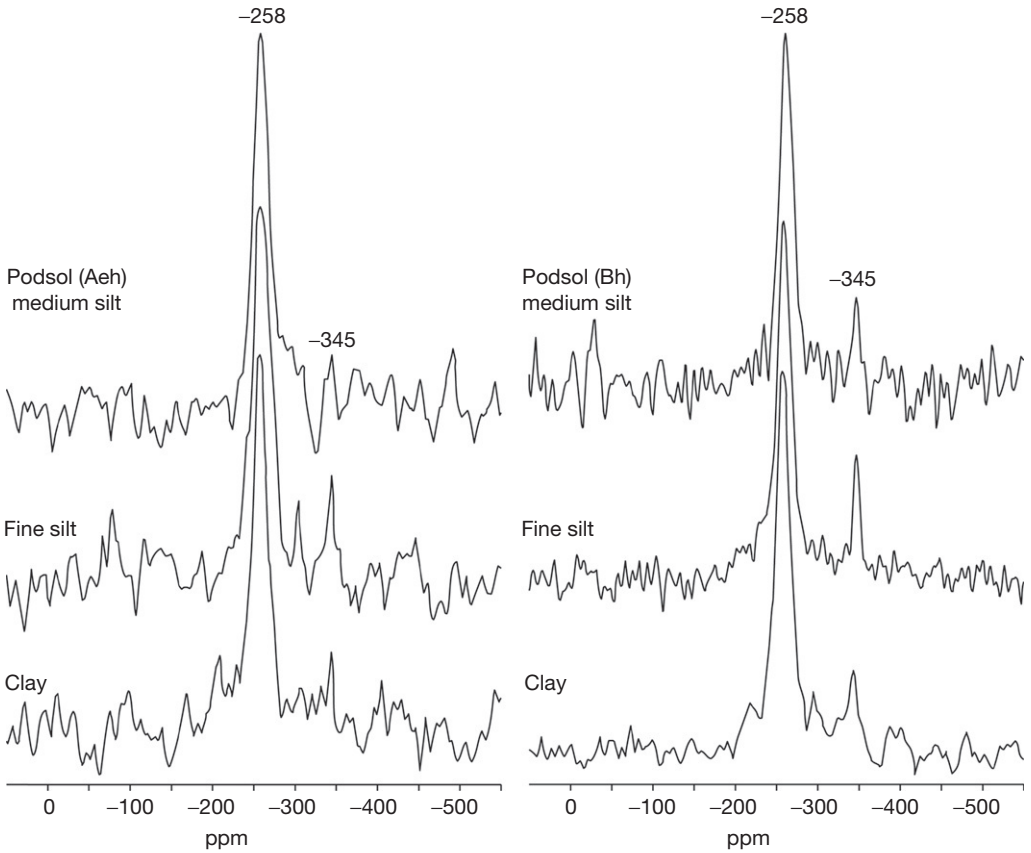


Figure 8 Solid-state ^{15}N NMR spectra from fine fractions of podzol A and B horizons. Reproduced from Knicker H, Schmidt MWI, and Kögel-Knabner I (2000) Nature of organic nitrogen in fine particle size separates of sandy soils of highly industrialized areas as revealed by NMR spectroscopy. *Soil Biology Biochemistry* 32: 241–252, with permission from Elsevier.

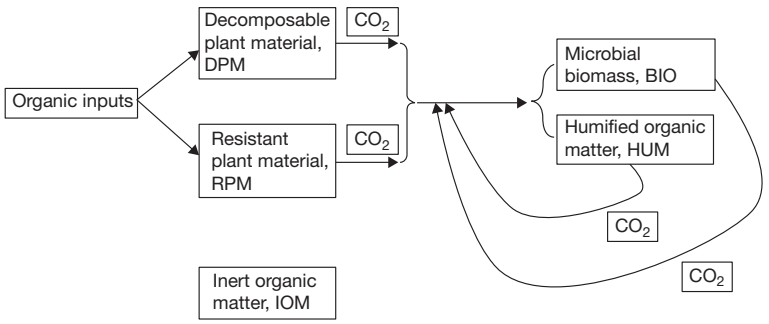


Figure 9 The RothC carbon turnover model. Reproduced from Coleman K and Jenkinson DS (1999) *ROTHC-26.3. A Model for the Turnover of Carbon in Soil. Model Description and Users Guide*. Harpenden, Herts: IACR Rothamsted, with permission.

Krull and Skjemstad, 2003). An increase in C/N with depth in some soils may be explained by the presence of charred material (Dümig et al., 2009).

12.7.4 Turnover of SOM

12.7.4.1 Pools and Models

Turnover models of SOM are necessary for a quantitative understanding of C dynamics in soils and serve to predict the SOM content under different scenarios (Smith et al., 2002). Widely used soil carbon models, such as CASA, IBIS-2, CENTURY, and Rothamsted (Jenkinson, 1990; Parton et al., 1994), treat SOM as consisting of discrete pools of different turnover times. The current models subdivide 'active' or 'labile' pools by assigning different decomposition rate constants to organic input materials (McGill, 1996). **Figure 9** shows the widely used RothC model. There is consensus in the literature that the active pool is composed of fresh plant residues, root exudates, decomposer feces, and faunal and microbial residues (Smith and Paul, 1990). Due to its short turnover times of 1–5 years, the microbial biomass is considered to be a major part of the active or

labile pool, (e.g., CENTURY model by Parton et al., 1987). The 'intermediate' or 'slow' OM pool is typically assumed to turn over on decadal timescales, while 'passive' or 'inert' OM is defined as such organic materials whose turnover happens on centennial and millennial timescales and is largely unaffected by management or disturbance. In contrast to other models (e.g., CENTURY), RothC relies on a completely inert pool of OC in addition to the slow or passive pool. The formation of intermediate and passive pools in the models is treated as a selective preservation of recalcitrant substances and basically relies on the assumption that the stable fractions are the leftovers from mineralization of plant residues. This also applies to cohort models with variable rate constants describing the decreasing substrate quality during decomposition (Agren and Bosatta, 1996; Janssen, 1984). In some models, soil texture controls the selective rate constants as static input parameter (Jenkinson, 1990; Parton et al., 1987; Verberne et al., 1990). The analytical identification of the pools has challenged researchers ever since because of intrinsic difficulties.

12.7.4.2 Assessing Mean Residence Times on the Bases of C Isotopic Composition

Turnover rates k may be determined by different methods: (a) decomposition studies, (b) *natural labeling* of OM using stable ^{13}C tracers, (c) *in situ labeling* of OM with 'bomb' ^{14}C, and (d) the ^{14}C-dating technique. Decomposition studies (a) of litter mostly quantify the short-term decomposition and consequently the turnover of the active pool being highly dependent on residue quality (selective preservation due to recalcitrance; Jenkinson, 1971; Ladd et al., 1983; Swift et al., 1979) (see **Chapters 12.5** and **15.20**). Carbon has three naturally occurring isotopes (^{12}C, ^{13}C, and ^{14}C). Two of these, ^{12}C and ^{13}C, are stable C isotopes, whereas ^{14}C is radioactive. Their natural abundances are ~98.89% for ^{12}C, 1.11% for ^{13}C (Boutton, 1996), and finally $<10^{-10}$% for ^{14}C (Goh, 1991) of the total carbon present in the environment. Changes in the abundance of either the stable $\delta^{13}C$ isotope composition or the natural $\Delta^{14}C$ radiocarbon abundance by modern C frequently indicates an exchange of the inherent soil C by other C sources and may thus provide a clue for assessing the mean residence time (MRT) of soil C. Carbon isotope techniques (b) using stable ^{13}C tracers in chronosequences of human-induced land use changes (e.g., C3 plants to C4 plants) are used by *natural labeling* of OM to study the turnover dominated by relatively recent inputs over timescales ranging from a few years to several hundreds of years (Balesdent et al., 1987; Bernoux et al., 1998; Six and Jastrow, 2002). If series of archived samples (over few decades or longer) are available, one can calculate the rate loss of the native and crop-derived OM by exponential kinetics. The method is useful to evaluate if a fractionation procedure can separate young and old OM. Atmospheric testing of thermonuclear weapons in the 1950s and 1960s caused an *in situ labeling* of OM with 'bomb' ^{14}C (Goh, 1991) that can be used to differentiate pools with different turnover rates, (c) ranging from seasonal to millennial timescales (O'Brien and Stout, 1978; Scharpenseel et al., 1989; Trumbore, 1993). This method also requires a series of archived samples. The ^{14}C-dating technique (d) follows a different strategy. The transformation of ^{14}C with a half-life of 5570 years in plants into soil OM is used to date OM fractions in a time frame of 200–40 000 years. Samples with an age less than 200 years are designated as modern (Goh, 1991).

12.7.4.2.1 $\delta^{13}C$ abundance measurements as a tool for turnover assessment

When the ^{13}C concentration is at or near natural abundance levels, the $\delta^{13}C$ notation is generally used (eqn [[1]), whereas for samples being highly enriched in ^{13}C, changes in isotopic abundance are frequently expressed in percent of total C atoms:

$$\delta^{13}C(‰) = (^{13}C/^{12}C_{sample} - ^{13}C/^{12}C_{standard})/(^{13}C/^{12}C_{standard}) \times 1000 \quad [1]$$

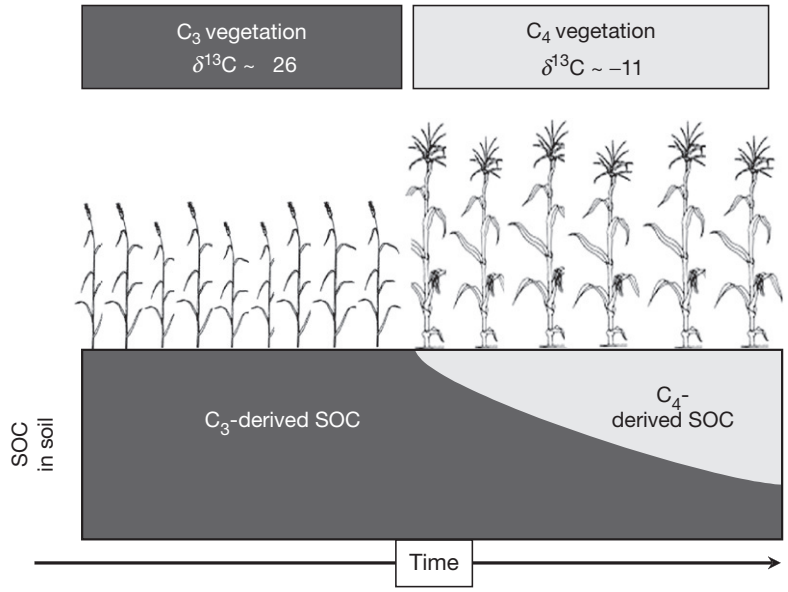
with $\delta^{13}C$ is the parts per thousand, or per mill (‰) difference between the ^{13}C content of the sample and the standard Vienna Pee Dee Belemnite, with a natural ^{13}C abundance of 0.00112372. When the ^{13}C label is high, the δ notion is not needed and a useful index is the atom % excess, which is the enrichment level of a sample relative to the background or baseline level prior to the tracer administration.

In most biological systems, heavier isotopes are discriminated (sometimes referred to as fractionated) compared to their lighter counterparts because of kinetic and thermodynamic processes. Therefore, for example, the CO_2 emitted in soil respiration contains relatively more ^{12}C and less ^{13}C than the soil it originated from (Bol et al., 2003). The summation of biological, chemical, and physical fractionation processes in soil is that natural $^{13}C/^{12}C$ isotope ratios ($\delta^{13}C$) uniquely record and integrate information relating to the types of sources that formed SOM (e.g., Dungait et al., 2010; Kuzyakov and Bol, 2006), rates of SOM formation (Amelung et al., 2008; Balesdent et al., 1987), or paleoenvironmental conditions that prevailed when the SOM was formed (e.g., Boutton et al., 1998; Croft and Pye, 2003; Lichtfouse, 2000).

It is possible to manipulate the natural $\delta^{13}C$ range by both artificial labeling experiments and natural isotope labeling (e.g., induced by cropping a C4 plant on a C3 soil), which is of great benefit to trace the mechanisms of SOM transformation and turnover (reviews: Amelung et al., 2008; Balesdent and Mariotti, 1986; Glaser, 2005).

The natural abundance ^{13}C labeling tracer approach in soil studies is based on the physiological differences during the photosynthetic fixation of CO_2 between C3 and C4 plants, which lead to plants with distinct $\delta^{13}C$ values (**Figure 10**). As C3 plants discriminate ^{13}C more than C4 plants do, their $\delta^{13}C$ values usually range from ~−32‰ to −22‰ (mean −27‰), whereas those with a C4 pathway range from −17‰ to −9‰ (mean −13‰) (Boutton et al., 1998). Whenever vegetation changes from C4 to C3 plants or vice versa, the ^{13}C input into SOM changes and the MRT of bulk SOM or individual SOM fractions can be evaluated.

An example of artificial natural abundance labeling techniques is the so-called free-air CO_2 enrichment (FACE) method. This is done in field-scale based experiments that artificially increase atmospheric CO_2 to 100–240 ppm above the current ambient values (~380 ppm) without directly altering any of the other environmental conditions. The additional



SOC fraction	SOC (g C kg^{-1})	Maize-derived C (%)	Turnover time* (years)
Total SOC	13.0	35.7	54
Mineral-associated SOC (Heavy fraction, >2 g cm^{-3})	11.3	31.4	63
Free particulate organic matter (fPOM, free light fraction, <1.6 g cm^{-3})	0.5	64.8	22
Particulate organic matter occluded in aggregates (oPOM, occluded light fraction, 1.6–2.0 g cm^{-3})	1.1	38.3	49

* Mean apparent SOC turnover time. Calculation is based on the assumptions that the fractions are homogeneous and can be described with a single-pool model.

Figure 10 Apparent turnover time of total SOC and SOC in density fractions. Calculations are based on data from John et al. (2005) on changes of the δ^{13}C values in a Stagnic Luvisol derived from loess 24 years after changes of C_3 vegetation (wheat) to C_4 vegetation (maize); translated from Blume et al. (2010).

CO_2 supplied from artificial sources is generally different in the δ^{13}C value (generally −25‰ to −70‰) compared to that present in air (∼− 8‰) and by this changing the overall (atmospheric + artificial) CO_2 δ^{13}C value. Plants present in FACE experiments thus become ^{13}C labeled when compared to plants growing under ambient conditions, and so is the SOM labeled when produced from the FACE plants.

The calculations currently used are similar to those used for natural isotope labeling outlined in the succeeding text. The fractional input (F^*) of C from the new ^{13}C natural source into the existing soil C pool (or constituents) can be estimated using a linear mixing model as follows:

$$F_{new} = (\delta_{final} - \delta_{initial})/(\delta_{source} - \delta_{initial}) \quad [2]$$

with F_{new} being the proportion of new C present in the soil for all labeling approaches, δ_{source} being the δ^{13}C or atom % ^{13}C of the source C applied to the soil, and δ_{final} and $\delta_{initial}$ are the final and initial δ^{13}C or atom % ^{13}C of the soil C pool at the beginning and end of the experimental period.

There are different mathematical approaches to interpret the kinetics of new C incorporation into the bulk soil or in the isolated fraction (Bernoux et al., 1998). The simplest option assumes that SOM consists of a homogeneous C reservoir, that is, a single pool, that decomposes exponentially:

$$C_{old}(t) = C_{(t=0)} \exp\{-kt\} \quad [3]$$

with $C_{old}/C_{(t=0)} = 1/F_{new}$, t = time since isotope label was introduced, and k = rate constant. For a single homogeneous C pool, the MRT of the former C then corresponds to the inverse of the rate constant, that is,

$$MRT_{single\ pool} = 1/k = -t(\ln(1 - F_{new})) \quad [4]$$

An alternative considers two reservoirs of SOC, fast and slow cycling. The loss from each of these pools is again described with exponential kinetics, and a set of parameters rules the way that fresh input is divided among the two pools (with a split factor s) and/or transferred from between them (transfer rate tr). The 2-pool model approaches are usually recommended for describing the fate of biomarkers in soil, and introducing a transfer rate between pools is obligatory for modeling the turnover of microbial-derived C pools, because the latter are formed only after a delay, that is, after

the ^{13}C input into a labile plant-derived C pool is in a second step consumed by soil microorganisms (Derrien and Amelung, 2011). As outlined by Derrien and Amelung (2011), the equivalent MRT of the ^{13}C atoms in soil is then composed of the MRT of both C pools, that is, for a parallel pool approach (plant input split into labile and stable C inputs):

$$MRT_{equivalent,\,parallel} = s \times MRT_1 + (1 - s) \times MRT_2 \quad [5]$$

and for a successive pool approach (isotope labeled transferred)

$$MRT_{equivalent,\,parallel} = MRT_1 + tr. \times MRT_2 \quad [6]$$

High costs of CO_2 supplied from cylinders or gas tanks to enhance atmospheric CO_2 limit long-term FACE experiments to laboratory approaches (e.g., Bull et al., 2000; Evershed et al., 2006), to small field experiments (e.g., Leake et al., 2006), and, particularly, to fairly short periods of time (i.e., weeks to months; only very few FACE studies extend to a few years). As a result, FACE studies hardly discover the potential heterogeneity of SOM transformation at field scale (e.g., Bornemann et al., 2010), and they generally only completely label those components of the soil with ^{13}C, which have a relatively high turnover rate. The MRT used in this sense is synonymous to 'turnover time.'

12.7.4.2.2 $\Delta^{14}C$ abundance measurements as a tool for turnover assessment

Radiocarbon (^{14}C) is continuously produced by cosmic radiation in the atmosphere. A dynamic equilibrium between production, decay, and uptake in other reservoirs of the global carbon cycle, such as biosphere, oceans, soils, and sediments, leads to more or less globally constant ^{14}C concentrations in the atmosphere and in the reservoirs directly in exchange with the atmosphere. If the exchange is small compared to the size of the reservoir, like in the deep ocean, the radioactive decay of ^{14}C with a half-life of 5730 years leads to reduced ^{14}C concentrations in this reservoir. If exchange stops totally, due to the death of the organism or the sealing off of the material, for example, in the soil column, the decreasing ^{14}C concentration due to decay indicates the time elapsed since the exchange stopped. The ^{14}C content of macrofossils like seeds, leaves, stems, and shells in an ancient paddy soil thus reflects their time of growth (and death), while that of various organic molecules and fractions may, in addition, indicate their degree of continuing exchange with the atmosphere.

The rapid increase in atmospheric $^{14}CO_2$ concentrations beginning in the 1950s, as a consequence of surface thermonuclear weapons testing, followed by a slow decline in atmospheric $^{14}CO_2$ as radiocarbon became incorporated in the biosphere, has provided a means to assess the age of relatively recently formed organic material (Trumbore, 2009). This so-called bomb carbon caused an in situ labeling of OM with ^{14}C (Goh, 1991) that can be used to differentiate pools with different turnover rates, ranging from seasonal to millennial timescales (O'Brien and Stout, 1978; Scharpenseel et al., 1989; Trumbore, 1993). A major constraint of this technique is that it requires a series of archived samples. If such samples are available, radiocarbon measurements in samples taken from the same place before and after the thermonuclear bomb tests provide a stringent test of any model for the turnover of OC in soil (Jenkinson et al., 2008). The method also allows to follow the incorporation of bomb carbon to the subsoil and shows that subsoil OC contains a significant proportion of reactive OC (Baisden and Parfitt, 2007).

The turnover times (or related MRT) of soil constituents estimated using $\delta^{13}C$ natural abundance tracer techniques can be compared to those obtained by radiocarbon (^{14}C) dating (Boutton et al., 1998; Krull et al., 2005). The estimated turnover times of $\delta^{13}C$ natural abundance tracer techniques are based on OM changes, which occurred after the vegetation shift over the decadal to century scale, whereas ^{14}C dating evaluates the residence time of C in all pools (even the very slow or inert compartment with turnover times of >100–1000s years). Therefore, the turnover times using the former method are generally lower than those obtained by ^{14}C dating. On the other hand, recent inputs of C from fossil energy sources add C, which is free of ^{14}C (e.g., Brodowski et al., 2007; Rethemeyer et al., 2004a; Rumpel et al., 2003). If this C is incorporated into the global soil C cycle, all bulk turnover times assessed via radiocarbon dating might be too long.

Note that in all cases, the $\delta^{13}C$ and $\Delta^{14}C$ labeling approaches trace the fate of a given cohort of C atoms – they can be recycled several times before being lost from the system. A long MRT does therefore not necessarily imply that the C is ecologically inactive and not frequently used by soil microorganisms. With the recent advent of new analytical tools, the compound-specific tracings of $\delta^{13}C$ abundances are now increasingly being employed to obtain a separate MRT for plant and for soil microbial cell wall constituents (reviews: e.g., Amelung et al., 2008; Glaser, 2005). In the former case, the MRT of the atoms is likely identical with the MRT of the whole cell wall biomarker, whereas in the case of microbial products, the true residence time of the whole molecule may be substantially shorter than the residence time of its C atoms, because of frequent microbial recycling and resynthesis.

12.7.4.2.3 Turnover of OC in topsoils and subsoils

The use of both ^{13}C and ^{14}C methods for turnover studies in subsoils is complicated by the complexity of pedogenetic transformation and translocation processes that form the subsoil horizons (Rumpel and Kögel-Knabner, 2011). Generally, the stable isotope ratios $\delta^{13}C$ are increasing with depth and degree of decomposition in soils without vegetation change (Balesdent and Balabane, 1996; Balesdent et al., 1993; Nadelhoffer and Frey, 1988). There are several factors reported to be responsible for a ^{13}C enrichment of subsoil SOM. The increasing atmospheric $^{13}CO_2$ due to fossil fuel burning (the so-called Suess effect) may account for a 1.5‰ increase since 1800 (Leavitt and Long, 1988). It may also be ascribed to a preferential stabilization of ^{13}C-enriched compounds, such as polysaccharides and amino acids, and the preferential decomposition of ^{13}C-depleted compounds, such as lipids and lignin. In some cases, mainly under C4 grassland, a decrease of $\delta^{13}C$ with depth was recorded (Dümig et al., 2008; Gill and Burke, 1999; Martin et al., 1990; Volkoff and Cerri, 1987). This may be explained by the accumulation of ^{13}C-depleted charred material, as C4 grasslands are prone to disturbance by fire. Isotopic fractionation during microbial respiration was also considered to be another mechanism

leading to ^{13}C enrichment. Van Dam et al. (1997) reported ^{13}C enrichment of 3‰ due to microbial respiration. Recently, it was suggested that this mechanism does not contribute to ^{13}C enrichment of SOM with increasing depth (Boström et al., 2007). Instead, Boström et al. (2007) hypothesized that the increase of $\delta^{13}C$ of OM as well as the ^{13}C enrichment of respired CO_2 with soil depth is caused by an increasing contribution of microbial-derived carbon.

The radiocarbon age of SOM is usually increasing with soil depth, and carbon present in the subsoil horizons is characterized by a low ^{14}C activity (Eusterhues et al., 2003; Krull and Skjemstad, 2003; Paul et al., 1997; Scharpenseel et al., 1989). In a comprehensive study by Scharpenseel et al. (1989), the radiocarbon age in 1 m depth of different soil types exceeded 1000 years. The reasons for the increase of the ^{14}C age of SOM with depth are not completely understood (Trumbore, 2009). High ^{14}C age of SOM may indicate that stabilized carbon compounds with long residence times are found in subsoil horizons at higher concentrations. However, recycling of old, stabilized SOM in subsoils through microbial biomass may also lead to old ^{14}C age of chemically labile, newly synthesized carbon compounds (Rethemeyer et al., 2005). Thus, old ^{14}C ages of subsoil OM may also be observed as a result of continuous microbial recycling of labile material (Gleixner et al., 2002).

For SOM in subsoils, it must additionally be considered that the ^{14}C activity may be influenced by the contribution of substrate inherent geogenic carbon, which is usually carbon dead (= older than 50 000 years). This may be the case for soils developed from sedimentary parent substrates, such as loess. The small amounts of carbon associated with loess deposits represent a small proportion of SOC in surface horizons, but could be significant at depth (Helfrich et al., 2007; Paul et al., 2001). Therefore, the very old radiocarbon age of some soils may simply be due to dilution of geogenic (rock-derived) dead carbon with younger SOM. However, even for SOM in soils developed from parent substrate free of geogenic C (e.g., granite), radiocarbon ages of several thousand years have been reported (e.g., Eusterhues et al., 2003). Further indication for low turnover of subsoil carbon was derived from stable carbon isotope analysis on sites, where a C3 vegetation was replaced by a C4 vegetation. At a site, where a forest dominated by C3 vegetation was replaced by corn (C4 species) monoculture in the United States, incorporation of C4 carbon reached 4–15% in 50–100 cm depth after 30 years (Collins et al., 1999). This corresponds to MRTs of 100–700 years. In an agricultural soil in France, 10 years of continuous corn after wheat monoculture resulted in 10%, 5%, and 2% corn derived SOC at 15, 50, and 100 cm depth, respectively (Rasse et al., 2006a).

12.7.5 Origin and Turnover of Specific Components in Soils

In principle, the biogeochemical cycling of SOM may affect the whole range of its biomolecules (compare **Section 12.7.3**; composition and transformation of SOM). Yet, several compound classes of SOM like carbohydrates or aliphatic C may have multiple sources, that is, the mere monitoring of compositional changes of SOM hardly informs about the key players involved in its formation and transformation. However, it is possible to trace biomarkers. A biomarker is an organic compound with a defined structure indicative of its producer. It may represent a larger group of molecules in living or dead organism cells. Hence, there are biomarkers that characterize living soil biomass and thus the structural diversity of the living soil microbial community. Other biomarkers rather point to the organic residues of plants, microorganisms, animals, or coals in soil. Origin and turnover of different biomarkers have been reviewed in detail by, for example, Amelung et al. (2008), the **Section 12.7.5.1** is a summary thereof, compiled with examples on the fate of these biomarkers in soil.

Biomarker analyses help to elucidate the *mechanisms* of SOM genesis and transformation, but they do not help to decipher the *rates* of SOM dynamics. For the latter purpose, it is necessary to combine biomarker analyses with the assessment of its compound-specific isotopic composition. If a biomarker is solely preserved, the isotopic composition is maintained. If it is resynthesized from other C and N sources, its isotopic composition usually changes. To identify such processes, the required experiments and subsequent calculations again involve artificial labeling (e.g., FACE studies or fertilization with ^{15}N) or isotopic shifts at natural abundance after C3/C4 vegetation change or incorporation of bomb ^{14}C (see **Section 12.7.4** for details).

12.7.5.1 Biomarkers for Plant-Derived C

Once plant litter is incorporated into soil, it loses its anatomical characteristics during degradation. Hence, the morphology is no longer of any value for inferring its origin. Biomarker analyses may help to reconstruct plant type and even the type of plant tissue it originated from and whether or not the organic material was derived from above- or belowground plant material (see **Chapter 12.15**). In any case, the preserved compound must be relatively stable in soils to detect it after a certain period of time. Useful biomarkers for plant-derived C are lignins, tannins, aliphatic compounds, and carbohydrates (**Table 5(a)**).

12.7.5.1.1 Lignins

Lignin occurs as a lignocellulose complex in vascular plants (Hedges, 1992; Otto and Simpson, 2006). Lignins are, similarly to tannins, not commonly used as an energy source for soil microorganisms and may be selectively preserved when litter decays, thus controlling its loss rates. Besides, they are synthesized by neither microorganisms nor aquatic plants, that is, once found, they indicate that plant fragments have been preserved in soil.

As intact lignin is insoluble, there is currently no analytical method available that allows for the determination of the absolute lignin content in soil. Pyrolysis field-ionization mass spectrometry can help to identify both lignin monomers and dimers in soil (e.g., Schulten and Leinweber, 1993); yet, this method requires a specific set of sophisticated scientific instruments, and it may be sensitive to catalytic oxidizing minerals. Most commonly, a method is used that releases lignin-derived phenols from reactive sites of the lignin macromolecule by alkaline CuO oxidation. The sum of vanillyl (V: vanillin, acetovanillone, and vanillic acid), syringyl (S: syringaldehyde,

Table 5 Biomarkers in soils

Major source (compound class)	*Biomarkers*	*Remark*	*References (choice)*
(a) Biomarkers for elucidating the plant origin of soil organic matter			
Lignins	Acids (ac), aldehydes (al) and ketones of the vanillyl (V), syringyl (S) and cinnamyl (Ci) structural units	• Sum V + S + Ci as marker for intact lignin • $(ac/al)_{V,S}$ ratios as markers for reactive side change oxidation • S/V and C/V ratios as markers for different plant sources • Alkylresorcinol as marker for sedges	Ertel and Hedges (1984), Avsejis et al. (2002) Goñi et al. (1998) Otto and Simpson (2005)
Tannins and other polyphenols	Condensed (CT) proanthocyanidins, and hydrolyzable (HT) gallo- and ellagitannins	• CT as markers for monocotyle gymnosperms • CT and/or HT as markers for dicotyle gymnosperms	Bate-Smith (1977), Haslam (1988) Kraus et al. (2003)
Carbohydrates	Pentoses, structural cellulose	• Ratios of arabinose + xylose to hexoses as markers for microbial carbohydrate synthesis • Cellulose content as marker for litter debris	Oades (1984) Ziegler and Zech (1991), Miltner and Zech (1998)
Lipids	*n*-Alkanes[a]	• Odd-over-even predominance $>C_{20}$ as markers for higher plant waxes	Eglinton and Hamilton (1967) Collister et al. (1994) Feng and Simpson (2007)
	n-Alkanols (primary and secondary)	• Even C_{20}–C_{34} alkanols, C_{29}-10-ol, C_{29}-diols as markers for higher and vascular plant waxes	Otto and Simpson (2005),Feng and Simpson (2007)
	n-Alkanoic acids	• Even alkanoic acids $>C_{12}$–C_{32}; even ω-hydroxy-alkanoic acids C_{20}–C_{30} as markers for higher plant waxes • Even C_{12}–C_{32} alkanoic acids and the C_{16}, C_{18} α,ω-Alkanedioic, ω-hydroxy-alkanoic acids, and di-/trihydroxy-alkanoic acids as markers for cutin and suberin	Otto and Simpson (2005) Feng and Simpson (2007), Kolattukudy (2001)
	n-Carboxylic acids	• Long-chain $>C_{20}$ as marker for various plants • $n\text{-}C_{24}/(n\text{-}C_{22} + n\text{-}C_{26})$ for differentiation of C3 and C4 crops	Wiesenberg and Schwark (2006) Wiesenberg (2004)
	Steroids	• β-sito-, stigma-, campesterol, sitosterone and derivatives as markers for plants	Bianchi (1995)
	Terpenoids	• Diterpenoids as markers for conifers • Triterpenoids as markers for angiosperms	Otto and Simpson (2005)
Lipopolysaccharides	Dicarboxylic	• Cutin, suberin as markers for root debris	Zelles (1999), Evershed et al. (2006)
(b) Biomarkers for tracing living microorganisms in soil organic matter			
Phospholipid fatty acids		• As markers for	Zelles (1999)
Ester-linked, saturated	Straight chain	• Prokaryotes and eukaryotes	Zelles (1999), Evershed et al. (2006)
	>C20	• Eukaryotes, mosses, higher plants	Zelles (1999), Evershed et al. (2006)
	Branched chain	• Gram-positive bacteria	Zelles (1999), Evershed et al. (2006)
	Iso/anteiso (e.g., *i*15:0, *i*17:0, *a*15:0)	• Gram-positive bacteria	Evershed et al. (2006)
	10Me	• Gram-negative bacteria	Kroppenstedt (1992)
	10Me17:0, 10Me18:0	• Actinomycetes	O'Leary and Wilkinson (1988)
	– 10Me16:0; *i*17:1	• Sulfate reducers	Kroppenstedt (1992), Evershed et al. (2006)
	Cyclopropyl	• Gram-negative bacteria	Ratledge and Wilkinson (1988)
		• Anaerobic gram-positive bacteria	Ratledge and Wilkinson (1988)
	16:1ω5	• Arbuscular mycorrhizal fungi	Olsson et al. (2005)

(*Continued*)

Table 5 (Continued)

Major source (compound class)	*Biomarkers*	*Remark*	*References (choice)*
Ester-linked, mono-unsaturated	ω7	• Gram-negative aerobes	Zelles (1999), Evershed et al. (2006)
	ω7	• Obligate anaerobes	Zelles (1999), Evershed et al. (2006)
	ω9	• Gram-positive bacteria: widespread	Zelles (1999), Evershed et al. (2006)
	ω8, for example, 16:1ω8c, 18:1ω8c	• Methanotrophic bacteria	Evershed et al. (2006)
		• Eukaryotes	Ratledge and Wilkinson (1988)
		• Cyanobacteria	Zelles (1999)
	20:4ω6	• Protozoae	Cavigelli et al. (1995)
	20:5ω3; 18:3ω3	• Algae	Boschker and Middelburg (2002)
	18:2ω6	• Fungi	Boschker and Middelburg (2002)
Ester-linked, hydroxylated	α	• Gram-negative bacteria	Zelles (1999), Evershed et al. (2006)
		• Actinomycetes	See above
	ω	• Fungi	See above
Non-ester-linked, unsubstituted		• Eukaryotes	Zelles (1999)
Non-ester-linked, hydroxylated	α, for example, α24:0; α26:0	• Fungal hyphae	Wells et al. (1996)
Glycerol dialkyl glycerol tetraether lipids (GDGTs)		• . . . as markers for both living and possibly also dead residues of	
	Isoprenoid GDGTs	• Archaea	Schouten et al. (2007)
	Crenarchaeol	• Crenarchaeota	Sinninghe Damsté et al. (2002)
	Branched GDGTs	• Bacteria	Schouten et al. (2007)
Steroids	Ergosterol	• As markers for fungi	Clemmensen et al. (2006)
Nucleotides	Adenosine-tri- (ATP), -di- (ADP), -mono-phosphate (AMP)	• Traces living microbial biomass (calculation of energy status)	Dyckmans et al. (2003), Atkinson and Walton (1967)
(c) Biomarkers for microbial residues in soil organic matter			
Neutral sugars (hexoses)	Galactose, mannose, fucose, rhamnose	• Mainly microorganisms	Oades (1984), Murayama (1984)
Acidic sugars	Galacturonic acid, glucuronic acid	• Extracellular bacterial gums, mucilage	Cheshire (1979), Amelung et al. (1999b)
Lipids	Alkanols C_{16}–C_{18}, *n*-alkanoic acids C_{14}–C_{18}, iso-alkanoic acids C_{16}, C_{18}	• Microbial contribution to lipid pattern by bacteria and fungi (relative to odd numbers)	Otto and Simpson (2005), Feng and Simpson (2007)
Lipopolysaccharides	Ester- and ether-linked plasmalogens	• Anaerobic bacteria	Harwood and Russell (1984), Zelles (1999)
Terpenoids			
Biohopanoids	Bacteriohopanepolyols (e.g., bacteriohopanetetrol, aminobacteriohopanetriol)	• Bacteria	Shunthirasingham and Simpson (2006)
Geohopanoids	Hopanoic acids, hopanols, C_{30} hopenes, hopanoidal aldehydes and ketones	• Hopanoid degradation	Innes et al. (1997)
Amino sugars	Glucosamine	• Fungal chitin (excess to muramic acid attributed to fungi)	Parsons (1981), Chantigny et al. (1997), Amelung et al. (2008)
	Muramic acid	• Bacterial peptidoglycane	Parsons (1981), Amelung et al. (2008)
	Galactosamine	• Bacterial capsular and extra-cellular polysaccharides; some bacterial cell walls (GluN/GalN ratio indicates shift of bacterial to fungal-residues)	Sharon (1965), Kögel and Bochter (1985)
		• Small amounts in some fungi (e.g., myxomycetes)	Sharon (1965), Herrera (1992)

(*Continued*)

Table 5 (Continued)

Major source (compound class)	*Biomarkers*	*Remark*	*References (choice)*
Amino acids			
Nonprotein amino acids	β-Alanine	• Organic matter decomposition (produced from aspartic acid)	Cowie and Hedges (1994), Dauwe and Middelburg (1998)
	γ-Aminobutyric acid	• Organic matter decomposition (produced from glutamic acid)	Cowie and Hedges (1994), Dauwe and Middelburg (1998)
Enantiomers	D-Alanine, D-glutamic acid	• Peptidoglycane as markers for bacterial cell walls	Schleifer and Kandler (1972), Amelung (2003)
Glomalin-related soil proteins (GRSP)	Glomalin	• Arbuscular mycorrhizal fungi (AMF) (+ other heat-stable proteins co-extracted)	Purin and Rillig (2007), Preger et al. (2007)

[a]For *n*-alkanes or *n*-carboxylic acids, there are many different ratios used in the literature to differentiate between different sources such as C3 or C4 vegetation (not further discussed here).

Modified from Amelung W, Brodowski S, Sandhage-Hofmann A, and Bol R (2008) Combining biomarker with stable isotope analyses for assessing the transformation and turnover of soil organic matter. *Advances in Agronomy* 100: 155–250.

acetosyringaldehyde, and syringic acid), and cinnamyl (Ci: *p*-coumaryl, ferulic acid) phenolic CuO oxidation products (VSC) then serves as relative measure of the total lignin concentration in plants, sediments (Hedges and Mann, 1979; Otto and Simpson, 2005), and soils (Kögel, 1986). As angiosperm and gymnosperm woods and grasses comprise different abundances of V, S, and Ci units, plant source assignment may be achieved by calculating S/V and Ci/V ratios (Goñi et al., 1998; Hedges and Ertel, 1982; Hedges and Mann, 1979). A lignin phenol vegetation index was introduced by Tareq et al. (2004) with distinct values for gymnosperm and angiosperm woods and needles.

During litter decomposition, the mass ratios of acids to aldehydes of the vanillyl $(ac/al)_V$ and of syringyl structural units $(ac/al)_S$ increase with an increasing degree of lignin oxidation (Amelung et al., 1999a; Lobe et al., 2002; Meentemeyer, 1978). Selective loss of syringyl units are reflected by decreasing S/V ratios (e.g., Ertel and Hedges, 1984; Kögel, 1986; Zech et al., 1996); hence, the composition of lignin-derived phenols also informs about the degree of degree of lignin oxidation.

12.7.5.1.2 Tannins

In leaves, bark, and needles, the tannin concentration may reach 40 wt% and hence can even exceed the proportion of lignin present (Benner et al., 1990; Kuiters, 1990; Matthews et al., 1997; see also **Section 12.7.2**). In soil, tannins may inhibit microorganisms (Kraus et al., 2003). Besides, tannins have the ability to precipitate proteins (Bate-Smith and Swain, 1962), which might be the primary effect of tannins on biogeochemical nutrient cycling (Kraus et al., 2003). There are two major classes of higher plant tannins: the CT (proanthocyanidins) and the HT (gallotannins and ellagitannins; Kraus et al., 2003), both with large structural diversity (Okuda et al., 1995; Porter, 1992). While gymnosperms and monocots contain only CT, dicots can produce either CT or HT or a mixture thereof (Bate-Smith, 1977; Haslam, 1988). However, the analysis of tannins is difficult, and sophisticated detection techniques such as MALDI-TOF MS (Behrens et al., 2003) are needed to trace them in soil. As these methods have not yet been combined with compound-specific stable isotope assessment, the turnover of tannins in soil is still uncertain.

12.7.5.1.3 Aliphatic compounds

According to Nierop (1998), the plant-derived aliphatic compounds can be divided into three classes: (i) (extractable) lipids, (ii) the biopolyesters cutin and suberin, and (iii) nonhydrolyzable biopolymers, such as cutan and suberan (Tegelaar et al., 1989).

The most easily detectable components of the extractable lipid (i) fraction are *n*-alkanes. They are typical for epicuticular waxes produced by vascular plants, which generally comprise complex mixtures of different aliphatic compounds (Baker, 1982; Bianchi, 1995; Kolattukudy and Espelie, 1989; Otto and Simpson, 2005; Tulloch, 1976). However, exact source assignment is difficult, since also fossil fuels (e.g., Bi et al., 2005), microorganisms (Schnitzer et al., 1986), and decomposition processes from other aliphatic precursors contribute to their origin (Lichtfouse, 1998; Lichtfouse and Eglinton, 1995). As a broad generalization, cuticle waxes of terrestrial plants contain predominantly long-chain *n*-alkanes ($>C_{20}$; Collister et al., 1994), while short-chain *n*-alkanes ($<C_{20}$) are common in all algae, fungi, bacteria, and plants (Bourbonnière et al., 1997; Collister et al., 1994; Dinel et al., 1990).

The ester-bound biopolymers cutin and suberin (ii) are preserved better in soils (Bull et al., 2000; Nierop and Verstraten, 2004; Nierop et al., 2003). The cuticle of all aerial parts (leaves, fruits, flowers, and seeds) of higher plants contain cutin, waxes, and sometimes cutan. Suberin is an important component of all protective and wound-healing layers of all other plant parts, including bark, woody stems, and underground parts (Nierop and Verstraten, 2004). Cutin is mainly composed of *n*-alkanoic acids and C_{16} and C_{18} ω-hydroxyalkanoic acids (Kolattukudy, 2001), while suberin is made of an aliphatic polyester and a polyphenolic domain (Bernards and Razem, 2001) and ω-hydroxyalkanoic acids with chain lengths $\geq C_{20}$. Additionally, α,ω-alkanedioic acids with predominant chain lengths of C_{16}–C_{24} are only present tissue containing suberin but not in tissue containing cutin (Kolattukudy, 2001).

The presence of ω-hydroxyalkanoic acids with chain lengths of $\geq C_{16}$ is characteristic for the suberin of Pinaceae (Matzke and Riederer, 1991; Nierop, 2001). Hence, ω-hydroxyalkanoic acids and the ratio of the di- and trihydroxyalkanoic acids (cutin) and α,ω-alkanedioic acids (suberin) may be used to differentiate between above- and belowground plant-derived debris in soil (Nierop and Verstraten, 2004).

The (iii) plant-derived cutan and suberan are thought to be the most resistant aliphatic fractions and, thus, to account for the relative enrichment of aliphatic compounds during SOM degradation (Augris et al., 1998; de Leeuw and Largeau, 1993; Tegelaar et al., 1989). They are not hydrolyzable, that is, they are currently not yet assessable using biomarker analyses, but they may contribute to the production of alkanes, alkenes, and methyketones in pyrolysis gas chromatography/mass spectrometry measurements (Nierop, 1998).

Other specific plant biomarkers are triterpenoids of the oleanane, ursane, and lupane type, which are specific for angiosperms (Baker, 1982; Bianchi, 1995; Otto and Simoneit, 2001; Tulloch, 1976). Friedelin, α-amyrenone, β-amyrenone, and lupenone are frequent constituents of tree barks, or could have been formed by oxidation of the corresponding 3-alcohols, ubiquitous found in green plants (Corbet et al., 1980). In contrast, diterpenoid acids of the abietane, pimarane, and isopimarane classes occur in conifers (Hegnauer, 1992; Karrer et al., 1977; Otto and Wilde, 2001). Hopanoids also belong to the class of triterpenoids but are used as biomarkers for bacterial residues and discussed later. Yet, terpenoids have rarely been used for elucidating the fate of SOM (Otto and Simpson, 2005).

The acyclic isoprenoids norpristane, pristane, and phytane are commonly derived from the phytol side chain of chlorophyll (Rontani and Volkman, 2003). The ratios of the acyclic isoprenoids pristane and phytane to the *n*-alkanes *n*-C_{17} and *n*-C_{18} (i.e., pristane/*n*-C_{17} and phytane/*n*-C_{18}) are frequently used in petroleum and environmental geochemistry for estimating and monitoring biodegradation patterns (McIntyre et al., 2007), but they have had little relevance for elucidating the fate of natural SOM.

12.7.5.1.4 Carbohydrates

Plant celluloses and hemicelluloses comprise a major source of plant C input to soils (see **Section 12.7.2**). However, when used as energy and carbon source for the soil microbial community, they may be rapidly converted and new microbe-derived carbohydrates are formed. Cellulosic polysaccharides can only be hydrolyzed by very strong acid, such as cold concentrated H_2SO_4, that is, their identification is possible after other noncellulosic polysaccharides are removed using hot 4 M TFA (Amelung et al., 1996), 2.5 M H_2SO_4 (Cheshire, 1979), or 1 M HCl (Ziegler and Zech, 1991; not suitable for subsequent monomer analyses). Fresh plant tissue comprises up to 40% cellulose C (Molloy and Speir, 1977), while SOM only comprises less than 6% of this fraction, reflecting rapid cellulose degradation during SOM genesis (Amelung et al., 1997). The source assignment of noncellulosic polysaccharides follows the observation that plant-derived sugars comprise specific pentoses (e.g., arabinose and xylose), whereas soil microorganisms primarily produce the hexoses galactose, mannose, fucose, and rhamnose (Cheshire, 1979; Murayama, 1984; Oades, 1984). According to Oades (1984), the (gal + man)/(ara + xyl) ratio is <0.5 for plants and >2 for microorganisms (see also **Table 5(a)** and **5(c)**).

12.7.5.2 Biomarkers for Living Microbial Biomass

As soon as microorganisms consume plant debris, they produce own cell wall materials, gums, and other products that become part of the SOM. Some of these compounds, particularly the phospholipid fatty acids (PLFAs) of the cell membranes, are specific for different microbial taxa but decay immediately when the organism dies. Hence, these PLFAs are suitable markers for living microbial biomass. Other markers alike are ergosterol for fungi or adenosine phosphates as energy proxy for microbial performance. In any case, neither the sum concentration of these markers nor the total amount of soil microbial biomass (e.g., estimated using substrate-induced respiration; Anderson and Domsch, 1978, or chloroform fumigation–extraction of lysed microbial cells; Murage and Voroney, 2007) usually accounts for more than 5% of total SOC, suggesting that the turnover time of living microbial biomass is rather short compared to the time involved in the genesis and accumulation of SOM.

12.7.5.2.1 Phospholipid fatty acids

The total amount of PLFAs indicates the microbial biomass concentration (Balkwill et al., 1988; Zelles et al., 1994) and PLFA profiles reflect the fingerprint of microbial communities (Bossio and Scow, 1998). Archaea are not covered by these techniques, because archaea do not contain fatty acids in phospholipid membranes (Evershed et al., 2006; Zelles, 1999). In general, classes of PLFA are used as biomarkers for different taxonomic or functional groups of soil microorganisms (Zelles, 1999). Information on individual taxa is rarely obtained due to the lack of unique lipids for a given microbial strain. The analysis of PLFA extends the former assessment of mere methyl ester-linked fatty acid profiles (EL-FAMES; e.g., Viljoen et al., 1986). To figure out specific microbial community structures, both FAME (ester-linked (EL-FAME) and/or phospholipid-linked (PL-FAME)) analyses frequently go along with multivariate statistical approaches (Haack et al., 1994; Hamman et al., 2007; Pankhurst et al., 2001).

The straight-chain fatty acids are present in most organisms (prokaryotes and eukaryotes; Evershed et al., 2006). Some of the long-chain ester-linked saturated fatty acids ($>C_{20}$) and polyunsaturated ones are characteristic for eukaryotes, mosses, cyanobacteria, and higher plants (Evershed et al., 2006; Ratledge and Wilkinson, 1988; Zelles, 1999; **Table 5(b)**). The hyphal forms of fungi are a source of long-chain non-ester-linked OH-substituted fatty acids (Wells et al., 1996). The PLFA 18:2ω6 has been widely used to estimate the proportions of fungi in soil microbial biomass (Clemmensen et al., 2006; Högberg, 2006; Olsson et al., 2003; Zelles, 1999). The neutral lipid fatty acid 16:1ω5 is likely even specific for arbuscular mycorrhizal fungi (Olsson et al., 2003, 2005), and the PLFA 20:1ω9 has been recommended for identifying and quantifying the external hyphae of *Gigaspora rosea* (Sakamoto et al., 2004).

Many more PLFAs indicate soil bacteria, for example, *i*15:0, *a*15:0, 15:0, *i*16:0, 16:1ω7, *i*17:0, *a*17:0, *cy*-17:0, *i*18:0, 18:1ω7, and *cy*-19:0 (Frostegård and Bååth, 1996; Zelles, 1999, nomenclature correspondingly). Also β-hydroxy, cyclopropane, and branched-chain fatty acids are only produced by

bacteria and are not found in other microorganisms (Lechevalier, 1989). Gram-positive bacteria are indicated by branched-chain fatty acids (Haack et al., 1994) and the ester-linked monosaturated 16:1ω9, whereas gram-negative ones can be tracked back by specific iso/anteiso forms, monosaturated and cyclopropyl fatty acids (few of the latter though have also been detected in some anaerobic strains of gram-positive bacteria (Ratledge and Wilkinson, 1988)), and methyl branching on the tenth C atom (also typical for actinomycetes (O'Leary and Wilkinson, 1988), and sulfate reducers (Evershed et al., 2006; Kroppenstedt, 1992)). Specific markers also exist for methanotrophic bacteria (e.g., 18:1ω8c; **Table 5(b)**). Also sphingolipids, ornithine lipids, plasmalogens, and other aminolipids contain non-ester-linked PLFAs, being mainly characteristic to anaerobic bacteria (Harwood and Russell, 1984; Zelles, 1999).

12.7.5.2.2 Ergosterol and others

Ergosterol is a steroid specific for living fungi (Harwood and Russell, 1984; Ruzicka et al., 2000; Weete, 1976). To estimate the fungal biomass, ergosterol contents must be translated into fungal biomass, assuming that the latter contains on average 3 μg ergosterol mg^{-1} biomass (Clemmensen et al., 2006; Salmanowicz and Nylund, 1988). Yet, total ergosterol contents do not differentiate between different fungal taxa.

There are other chemical markers for characterizing total living microbial biomass, such as the content of adenylates (adenosine tri-, di-, and monophosphates; e.g., Bai et al., 1989; Raubuch et al., 2002; Dyckmans et al., 2003) for assessing the energetic status of soil microorganisms (Brookes et al., 1983) and thus their vulnerability to changes in environmental conditions (e.g., Ciardi et al., 1993; Formowitz et al., 2007). Similarly, quinone profiles have been used to characterize the biomass and taxonomic diversity of the soil microbial community (Katayama et al., 2001, 2002; Saitou et al., 1999).

12.7.5.2.3 Glycerol dialkyl glycerol tetraethers

None of the bacterial biomarkers mentioned so far was able to track archaea. Leininger et al. (2006), however, recently stated that crenarchaeota are the most abundant ammonia-oxidizing organisms in soil ecosystems. A novel clue to these organisms is provided from the analyses of GDGTs, which are core membrane lipids (Gattinger et al., 2003; Schouten et al., 2007). The isoprenoid GDGTs are characteristic for Archaea, with crenarchaeol being specific to the nonthermophilic *Crenarchaeota* (Leininger et al., 2006; Sinninghe Damsté et al., 2002). The structures of the methanogenic archaea are notably different from the specific bacterial isoalkane tetraethers. The branched GDGTs of possibly anaerobic soil bacteria exhibited different cyclization ratios and methylation indices, dependent on pH and temperature (Weijers et al., 2006, 2007). These differences helped developing a sea surface temperature proxy (Schouten et al., 2002) and to estimate the fluvial inputs of terrestrial OM into marine environment on the basis of a branched versus isoprenoid tetraether index (Hopmans et al., 2004), but applications to elucidating SOM dynamics are still scarce. Yet, these approaches indicate that the GDGTs likely do not solely trace living but also dead biomass of the archaea.

12.7.5.3 Biomarkers for Dead Microbial Biomass

In many cases, microbial products do not immediately disappear after cell death, but reside in soil for a limited period of time. The present biomarkers do then no longer indicate living microbial biomass, but their residues. The formation of these residues may occur within a given structural class like carbohydrates. As mentioned earlier, microorganisms synthesize hexoses, for instance, during decomposition of pentoses. Also uronic acids are common in extracellular bacterial gums (Cheshire, 1979) and have thus been suggested to reflect an enrichment of microbial products nearby soil mineral surfaces (Amelung et al., 1999b). Some lipopolysaccharides hint at residues of anaerobic bacteria (**Table 5(c)**). Besides, certain terpenoids and N-containing compounds serve as unique markers for microbial residues; they even allow, to a certain degree, to differentiate between residues from bacteria and fungi. Only rarely, these markers were assessed jointly with the simultaneous characterization of living bacteria and fungi, but when done, the general patterns correlated (Appuhn and Joergensen, 2006; Glaser et al., 2004; Kandeler et al., 2000).

12.7.5.3.1 Terpenoids

Hopanoids are amphiphilic pentacyclic triterpenoids that are essential membrane lipids by eubacteria (e.g., Farrimond et al., 2003; Rohmer et al., 1984) and have a similar function as the cholesterol in higher organisms (e.g., Talbot et al., 2007). They hint at bacterial biomass contribution in soils and sediments (Innes et al., 1997; Shunthirasingham and Simpson, 2006; Winkler et al., 2001) and include diplopterol and diploptene – the biosynthetic precursors of bacteriohopanepolyols (Rohmer et al., 1992; Talbot et al., 2003a,b; Thiel et al., 2003). While these precursors may also be present in some ferns and lichens, the C_{30} hopane skeleton linked at C_{30} to a C_5 *n*-alkyl polysubstituted chain gives a characteristic C_{35} bacteriohopane derivative (Crossman et al., 2001; Shunthirasingham and Simpson, 2006). The biohopanoids undergo a wide range of degradation processes that result in the formation of geohopanoids (**Table 5(c)**), used in paleoenvironmental studies (Farrimond et al., 2003; Shunthirasingham and Simpson, 2006).

12.7.5.3.2 Nitrogen-containing biomarkers

The analysis of amino sugars provides a clue to investigate the fate of soil C and N within residues of bacteria and fungi, because plants do not synthesize amino sugars in significant amounts (for reviews, see Amelung, 2001; Parsons, 1981). Fungal cell walls are the major source of glucosamine in soils (Appuhn and Joergensen, 2006), the contribution from invertebrates is negligible (Amelung et al., 2008; Parsons, 1981). Also bacteria contain glucosamine in their peptidoglycan cell wall, where it is linked in 1:1 proportions to *N*-acetylmuramic acid; partly it is also found in teichoic acids of the gram-positive bacteria. Hence, only the glucosamine that occurs in excess to muramic acid may be attributed to fungal sources (Amelung, 2001; Chantigny et al., 1997; Guggenberger et al., 1999). Muramic acid uniquely originates from bacterial peptidoglycan, most common in gram-positive organisms (McCarthy et al., 1998). Shifting from gram-positive to gram-negative bacteria thus theoretically limits the exact source assignment to bacteria and fungi on the basis of glucosamine-to-muramic acid ratios

(Amelung et al., 1999c; Wichern et al., 2006). Appuhn and Joergensen (2006) suggested average conversion factors of 9 to convert glucosamine to fungal C and 45 to get a measure of bacterial C from the muramic acid content.

Galactosamine is frequently occurring in capsular and extracellular polysaccharides, but also as a part of the cell walls of, for example, actinomycetes (Parsons, 1981; Sharon, 1965). Only small amounts are produced by some taxonomic classes of fungi, such as trichonomycetes and myxomycetes (Herrera, 1992; Sharon, 1965). Increasing ratios of glucosamine to galactosamine have thus also been employed to indicate a shift from bacterial- to fungal-N residues in soils (Kögel and Bochter, 1985; Sowden, 1959) and may generally support fungal/bacterial source assignment when correlating with changes in glucosamine/muramic acid ratios (e.g., Amelung et al., 2002b).

The analyses of glucosamine fail to differentiate between saprotrophs and biotrophic mycorrhizal fungi. The latter live in a symbiotic relationship with the majority of terrestrial plants (Smith and Read, 1997). The extraradical hyphae (Johnson et al., 2002; Miller and Kling, 2000) support the plants' nutrient acquisition and stress resistance (Olsson et al., 1997) and promote soil aggregation (Rillig and Mummey, 2006; Tisdall and Oades, 1982). A marker for arbuscular mycorrhizal fungal development is glomalin (Gadkar and Rillig, 2006; Johnson et al., 2004; Wright and Upadhyaya, 1996). It is extracted from soil by applying several cycles of autoclaving and quantified using a Bradford assay and immunoreactivity using the monoclonal antibody MAb32B11 (Rillig, 2004; Wright and Upadhyaya, 1996).

Individual amino acids are not specific for certain members of the soil microbial community. However, β-alanine and γ-aminobutyric acid may be produced enzymatically from aspartic and glutamic acid during SOM decomposition. Besides, several bacteria take advantage of a posttranslational racemization of certain amino acids and incorporate the D-enantiomers into their cell walls to protect it from its own proteases. Especially D-alanine and D-glutamic acid are thus suitable biomarkers for bacterial cell wall N (Amelung, 2003; Pelz et al., 1998; Schleifer and Kandler, 1972).

A formation of D-amino acids is also possible after cell death through biotic or abiotic racemization (see, e.g., book of Jollès, 1998, and articles therein). As life on earth almost exclusively uses laevorotatory amino acids (L-enantiomers) rather than D-enantiomers, the presence of peptide-bound D-amino acids other than the bacterial biomarkers mentioned earlier may indicate cell aging. Especially D-lysine has been a promising age marker in this respect when other free D-amino acids had been removed prior to analyses (Amelung, 2003). But also other D/L ratios of amino acids correlated with SOM age in sediments (Harada et al., 1996; Schroeder and Bada, 1976; Wehmiller and Hare, 1971) and palaeosoils (Mahaney and Rutter, 1989). An absolute SON dating on the basis of amino acid racemization assessment has not been achieved, so far.

12.7.5.4 Biomarkers for Off-Site Contributions to SOM

When soils are used as arable land, organic fertilization is recommended to replenish SOM losses. More recently, also biochar additions are discussed to improve soil productivity and to enhance C sequestration, based on the observation that Indian black soils in the Amazonian region (Terra Preta) likely received a significant part of their fertility from ancient additions of biochar and compost (Glaser et al., 2007; Sohi et al., 2010). In heavy industrialized areas, also coalified C from surface mining and railway emissions may contribute substantially to the soil C pool in the surface horizon (Brodowski et al., 2007; Rethemeyer et al., 2007). In any case, off-site materials are added to soils and may contribute now to SOM. To trace such inputs, steroids and bile acids are potential markers for various kinds of organic fertilizers, whereas benzene polycarboxylic acids (BPCAs) trace pyrogenic and coalified C.

12.7.5.4.1 Steroids and bile acids

In the intestinal tracts of most higher mammals, both cholesterol (an important lipid of the plasma membrane of eukaryotes; Voet and Voet, 1995) and higher molecular weight phytosterols like campesterol, sitosterol, and stigmasterol are reduced to 5β-stanols (Bull et al., 2002). Hence, cholesterol and 5β-stanoles are characteristic biomarkers for feces and animal manure (Evershed et al., 1997; Voet and Voet, 1995). Cholesterol is partly already in the gut further converted to coprostanol (5β-cholestan-3β-ol), which is then the major sterol in human feces (Bull et al., 2002; Leeming et al., 1984; Ren et al., 1996). Furthermore, 5β-campestanol and 5β-stigmastanol have a higher relative abundance in the excreta of ruminant organisms, such as cows and sheep. Analyses of stanols may thus help to elucidate the relative input of different types of fecal material (human vs. herbivore) to SOM (Evershed and Bethell, 1996; Grimalt et al., 1990; Leeming et al., 1996; Simpson et al., 1998).

Additionally, animals and humans produce bile acids, which are essential for fat digestion and cholesterol-level maintenance (Voet and Voet, 1995). They are a group of C_{24}, C_{27}, and C_{28} steroidal acids with a carboxylic acid group at the C_{23} position and a hydroxyl group on the A-ring and eventually some additional functional groups (Bull et al., 2002). Primary bile acids that form from cholesterol in the liver undergo several transformations to be converted to secondary bile acids, a small proportion of which is excreted. While in the feces of ruminant animals (bovines) mainly deoxycholic acid is found, the feces of omnivores (humans and canines) also contain significant amounts of lithocholic acid. Pigs do not produce deoxycholic acid but hyocholic acid being the distinguishing feature for human and canine (do not produce 5β-stanols) contamination. Hence, while 5β-stanols and related sterols allow for distinguishing between omnivores and ruminants, the bile acids allow additionally for differentiating between human- and porcine-derived feces (Bull et al., 2002).

12.7.5.4.2 Benzene polycarboxylic acids

Incomplete combustion results in a continuum of carbonaceous products, reaching from vapor phase condensates (soot) to charred residues (Hedges et al., 2000; Masiello, 2004; see also **Section 12.7.2.4**). The polyaromatic nature of this pyrogenic C is at least in part similar to the continuum of diagenetically coalified carbon, which is also found in soils and sediments (Brodowski et al., 2007; Dickens et al., 2004; Laskov et al., 2002). However, it is possible to oxidize the polyaromatic bone into BPCA after hot digestion with HNO_3 (Brodowski et al., 2005b; Glaser et al., 1998; Ziolkowski et al., 2011). The pattern of BPCA released is characteristic of

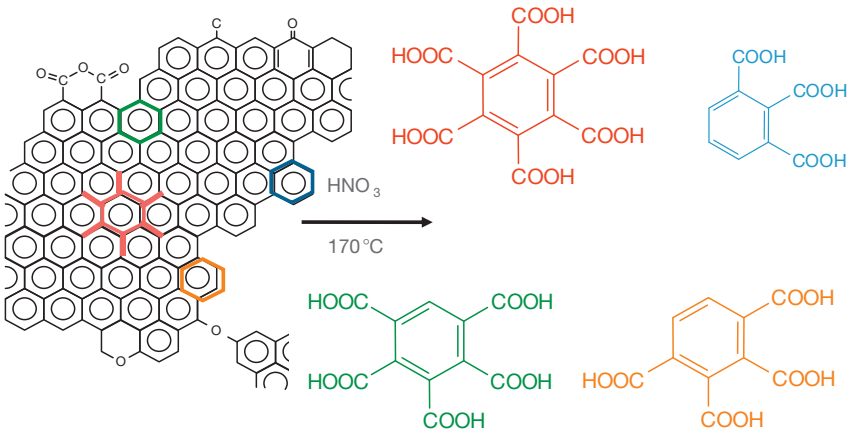


Figure 11 Structure of charcoal (modified from Goldberg ED (1985) *Black Carbon in the Environment: Properties and Distribution*, 198 pp. New York: John Wiley and Sons and Brodowski, unpublished) and benzene polycarboxylic acid degradation products.

the formation conditions of the so-called BC; the higher the degree of aromatic condensation, the more mellitic acid is formed upon BC digestion (**Figure 11**).

Noteworthy, the oxidation of BC with HNO_3 is incomplete, that is, the method relies on conversion factors of 2.27 (Glaser et al., 1998) to 4.0 (Ziolkowski et al., 2011) for estimating true BC contents. Moreover, the method recovers soot BC only incompletely (Hammes et al., 2007). For the latter fraction, however, it may be possible to isolate this pool after chemothermal oxidation of labile materials at 375 °C (CTO 375, used for sediments; Gustafsson et al., 2001; the method likely requires modification to be adapted to soils; Elmquist et al., 2006).

12.7.5.5 Examples for Applications in Soil Science

Both the contents and properties of SOM are vulnerable to land use changes. Especially when soils are plowed, aggregates are broken down, and oxidative decomposition of SOM accelerates with increased aeration and loss of physical protection. Two examples may illustrate this: (i) changes in the contents and properties of SOM with prolonged arable cropping, due to (ii) different accessibility and distribution among soil fractions.

12.7.5.5.1 Changes in biomarker signature with prolonged arable cropping

In semiarid South Africa, farmers have increasingly converted native savannah soils into cropland. Such a land conversion involves a repeated plowing of the former native grassland and the planting and harvesting of major crops, in this case mainly wheat, maize, and sunflower. With prolonged cropping, it has been hard to sustain the soil's productivity, that is, yields declined and so did the C input into the soil (**Figure 12(a)**; Lobe et al., 2001, 2005).

Since little, if any, organic fertilizers were available to replenish C losses, the stocks of SOM declined bi-exponentially (**Figure 12(a)**): after a rapid decay of SOM moieties during the first years of intensive plowing, SOC contents continued to decline, thus reflecting continued soil degradation that was not yet visible in the yields. Two processes largely explained this. Firstly, when a soil is plowed, soil aggregates are disrupted and the SOM stored therein is made accessible for decay. And indeed, monitoring the loss of C in macroaggregates largely accounts for this initial C loss, reaching steady-state equilibrium after about two decades (**Figure 12(b)**; Lobe et al., 2011). Secondly, the bare soil in-between harvest and reseeding remained prone to wind erosion. Mainly silt-associated C has been blown away, thus contributing to the slow, long-term loss of total SOC (**Figure 12(b)**; Lobe et al., 2001). As silt also contains old C and N, this loss of humus forms cannot be replaced easily, that is, SOM properties changed irreversibly upon management (Brodowski et al., 2004). Besides, with a loss of physical soil structure and silt-sized minerals, there was also no effective reformation of SOM as indicated by stable ^{13}C isotope analyses (Lobe et al., 2005).

The macroaggregates that are broken down during initial phases of soil management are known to stabilize particulate plant materials rich in lignin (Amelung et al., 1996; Golchin et al., 1994; Kölbl and Kögel-Knabner, 2004). And indeed, with the rapid loss of macroaggregates, this plant-derived C has also been rapidly lost, being reflected in a rapid decline of the total contents of VSC lignin with prolonged duration of arable cropping (**Figure 12(c)**; Lobe et al., 2002). The process is accompanied by a rapid increase in phenolic acid-to-aldehyde ratios, due to the rapid oxidative alteration of the side chains in the remaining lignin macromolecule (**Figure 12(c)**). Also C/V increased, mainly due to the increased input of cinnamyl-rich lignin from the maize species (Lobe et al., 2002; data not shown here).

When plant materials are rapidly decomposed, microorganisms may recycle part of this plant-derived C in their biomass. Hence, although the total contents of microbial biomass and residues decline, the contribution of microbial residues to the SOC remaining even tended to increase with prolonged duration of arable cropping (**Figure 12(d)**). The increased microbial transformation also left a fingerprint behind: increasing D-contents of alanine pointed to higher degree of bacterial transformation of the remaining SOM (Brodowski et al., 2004), whereas elevated ratios of glucosamine to muramic acid reflected that even more of the remaining microbial residues originated from fungi (**Figure 12(d)**; see also Amelung et al., 2002a,b; Guggenberger et al., 1999).

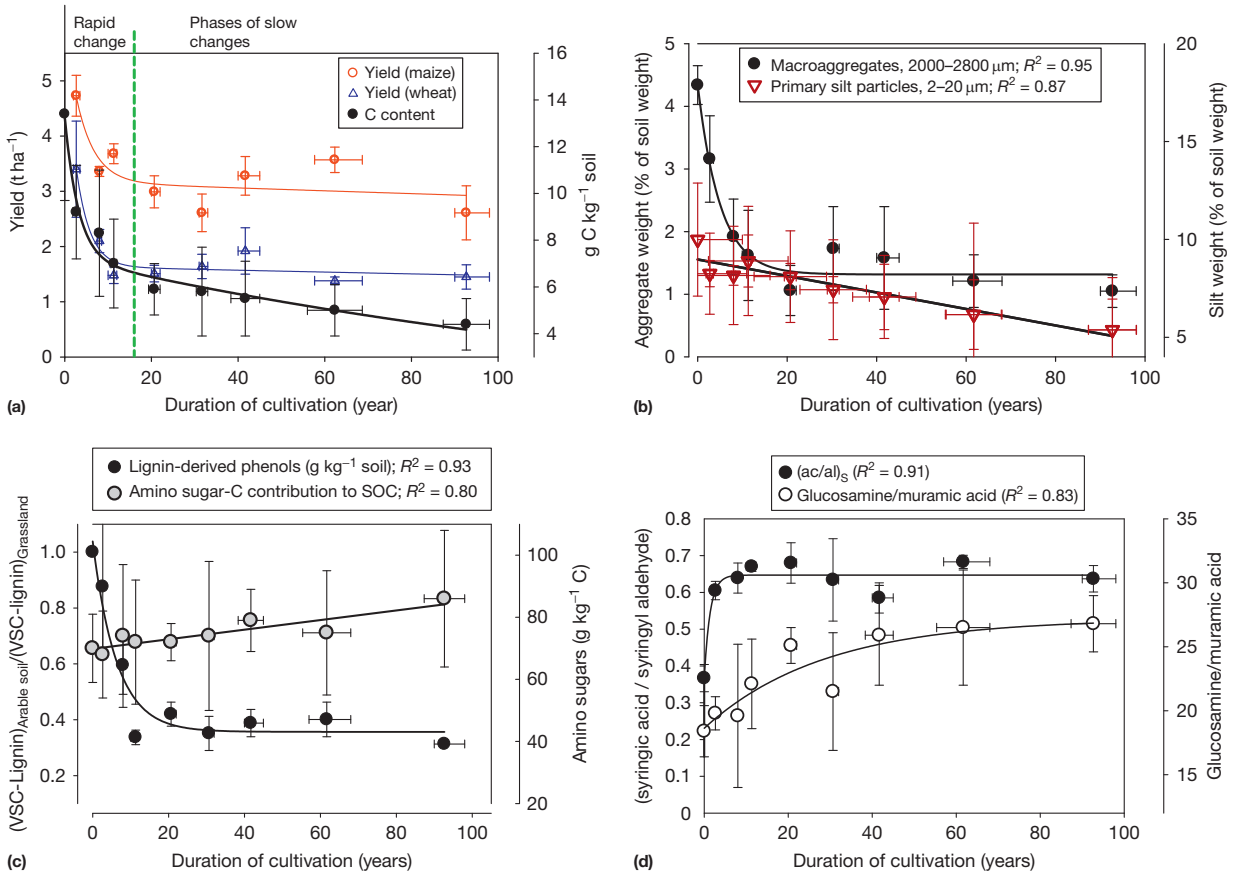


Figure 12 (a, b) Changes in soil properties and biomarker composition under prolonged arable cropping: (a) total soil organic carbon in relation to crop yield (data from Lobe et al., 2005); (b) macroaggregates and silt-associated C (data from Lobe et al., 2001, 2011). (c, d) Changes in soil properties and biomarker composition under prolonged arable cropping: (c) amino sugars and lignin-derived phenols (VSC); (d) lignin and amino sugar composition (data from Amelung et al., 2002b; Lobe et al., 2002).

12.7.5.5.2 Biomarkers in particle-size fractions

When soil structure is disturbed, different components of SOM are made available to microbial decay and turnover. To mimic the different stabilization processes of SOM, soil has been physically fractionated according to particle size, density, aggregation (size or density or combinations thereof), or by chemical methods (e.g., reviews by Christensen, 1996; von Lützow et al., 2006). Frequently, the soils are fractionated according to particle size after ultrasonic dispersion of aggregates into primary particles. The method separates coarse plant debris (little altered plant fragments; >200 or 250 µm) and fine plant debris (decomposed plant fragments, morphology is hardly maintained; >20 or 50 µm) from silt-sized particles (2–20 or 2–50 µm), from clay (<2), and fine-clay minerals (<0.2 µm). Hence, the fractionation scheme isolates a decomposition gradient of SOM: the finer the particle-size equivalent diameter, the advanced the stage of SOM alteration. This hypothesis has been supported using biomarker analyses.

Lignin as major source of plant debris exhibits its highest contents in the coarse plant materials (**Figure 13(a)**). Low acid-to-aldehyde and S/V ratios point to the low degree of lignin alteration in the coarse sand-sized SOM pools. As particle-size diameter increases, the concentration of VSC lignins declines, which is accompanied by an increased degree of side-chain alteration. In the clay fraction, the lignin signature usually resembles that of DOM, thus pointing to a solution of lignin before it was bound and stabilized by soil minerals (Guggenberger et al., 1998).

The concentration of carbohydrates is also high in the coarse-sized SOM pools, because unaltered plant debris is still rich in carbohydrate C. When SOM decomposition proceeds, these carbohydrates are degraded but also continuously replaced by microbial hexoses, which bind strongly and in preference to other SOC compounds to the oxide-rich mineral phase (**Figure 13(b)**; see also Amelung et al., 1999b; Guggenberger et al., 1994; Schwertmann et al., 2005). As a result, hexose–pentose ratios increase with decreasing equivalent diameter of the SOM fraction (**Figure 13(b)**). When solely tracing carbohydrates of microbial origin, that is, amino sugar C, it is seen more clearly that the concentrations of microbial residues increase with decreasing particle-size diameter, mainly due to the accumulation of bacterial residues rich in muramic acid (**Figure 13(c)**; see also Kandeler et al., 2000).

The SOM that is already altered by microorganisms usually has slower turnover times than that containing fresh, unaltered plant debris. As annotated earlier, the turnover rate of SOM may be estimated using stable isotope tracing of $\delta^{13}C$ values

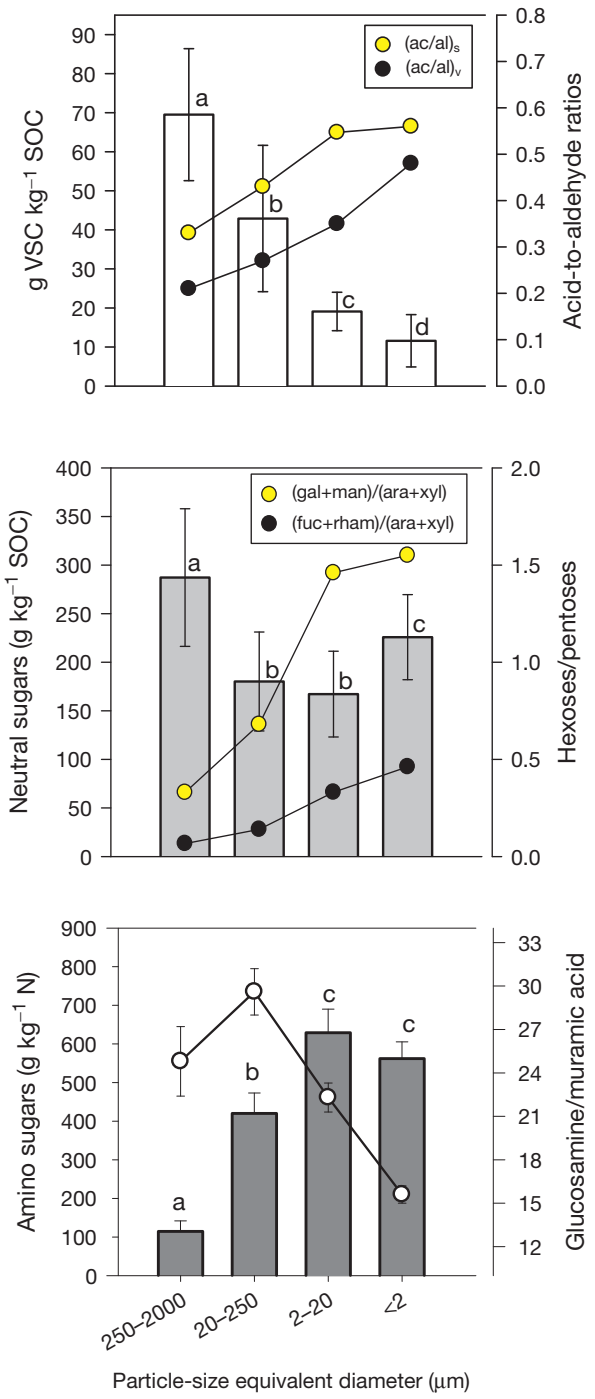


Figure 13 (a–c) Distribution of biomarkers among soil particle size fractions: (a) lignin-derived phenols (VSC) and ratio of phenolic acids to aldehydes (ac/al) of the vanillyl (v) and syringyl (s) structural units; (b) neutral sugars and ratios of the hexoses: gal, galactose; man, mannose; fuc, fucose; rham, rhamnose) to pentoses (ara, arabinose; xyl, xylose); and (c) amino sugars (data from Amelung et al., 1999a,b, 2002a,b).

after a C3/C4 vegetation change. This has also been done for physical size fractions, and the results show that the MRT of the SOM fractions increase with decreasing particle-size diameter (Balesdent et al., 1998; see also Derrien and Amelung, 2011). Hence, it is mainly the SOM of the coarse fractions, rich in lignin and plant-derived carbohydrates, that is rapidly converted and not the SOM of the fine mineral fractions that is rich in microbe-derived carbohydrate C.

12.7.5.6 Turnover Rates of Different Biomarkers

The assessment of compound-specific stable isotope ratios after artificial or natural labeling allows for ascertaining the biological source of a molecule (see **Table 5**), the paleoclimatic conditions of its formation (not considered here), and the molecule's MRT in a given sample. Technically, this aim is most commonly achieved after an initial chromatographic or thermal separation step, followed by combustion of the separated compounds to CO_2 (e.g., Barrie and Prosser, 1996; De Groot, 2004; Krummen et al., 2004; Lopez-Capel et al., 2005a, b; Wieser and Brand, 1999).

12.7.5.6.1 Biomarker-specific stable isotope analyses in artificial labeling experiments

When the C entering the soil is rapidly consumed, the process is detectable via the fast incorporation of the ^{13}C label in FACE and incubation studies. The largest of such labile C sources likely stems from root exudation. It has been estimated that plants excrete 10% to >40% of assimilated C through their roots, the different root exudates possibly selected for specific beneficial groups of microorganisms (Bergsma-Vlami et al., 2005; MacDonald et al., 2004; Nguyen, 2003; Shaw and Burns, 2003; Singh et al., 2004). Consequently, the soil–plant interface (rhizosphere) has been termed an 'oasis in the desert' from the microbial point of view (Bertin et al., 2003). As a result, the ^{13}C label from root exudates is detected within hours or days in microbial products. Paterson et al. (2007), for instance, were able to determine the specific microbial utilization of root exudates and whole rhizodeposition, using ^{13}C labeled substrate additions to incubated rhizosphere and bulk soil (podzol). Glucose and fumaric acid were utilized by a wide range of microbial populations (^{13}C enrichment in 25 and 26 PLFAs), whereas only 9 PLFAs showed the ^{13}C label from glycine degradation, mainly assigned to gram-negative bacteria. Lu et al. (2004) reported that immediately after $^{13}CO_2$ pulse labeling of rice plants, the isotopic signal was recovered in the PLFAs of rhizosphere microorganisms, suggesting a direct coupling of photosynthetic production and microbial growth. Even symbiotic organisms such as extraradical arbuscular mycorrhiza were immediately provided with the new, labeled C source (Olsson et al., 2005).

In other incubation studies, soils were amended with gases like $^{13}CO_2$, $^{13}CH_4$, and free ^{13}C-labeled monomers like ^{13}C acetate, ^{13}C urea, and dissolved ^{13}C glucose, or solids (e.g., burial of ^{13}C labeled plant tissues, ^{13}C labeled algae, or microbial cells). When combined with ^{13}C-PLFA analyses or stable isotope probing of genes, these methods helped to elucidate the activity and ecological niches of various members of the soil microbial community, like methanotrophs, actinomycetes, and many more. As a general rule, all added substrates are usually taken up within days (e.g., Petersen et al., 2004; see also above). During the vegetation period or with prolonged duration of incubation, the degree of isotopic labeling changes for the different PLFAs, suggesting that other bacterial populations evolve during rhizosphere development or that the microbial C is recycled by the soil

microbial community or both (e.g., Butler et al., 2003; Lu et al., 2004; Pelz et al., 2005). However, frequently, only few of the total PLFAs detected responded to such rapid labeling (e.g., Boschker and Middelburg, 2002; Maxfield et al., 2006; Pelz et al., 2005; Petersen et al., 2004); hence, the majority of soil microorganisms feed on older SOM. In such a case, when the soil microbial community assimilates old C, then the detected PLFA and microbial residues also appear old, although the organism is still alive.

During long-term incubation studies, it is possible to detect the ^{13}C label also in the residues of bacteria and fungi (e.g., Glaser and Gross, 2005; He et al., 2005; Miltner et al., 2005). Derrien et al. (2007) incubated a subset of soils amended with ^{13}C labeled glucose, glycine, cellulose, and wheat straw for one year. All structures were as rapidly converted as the labeled glucose, hinting at an immediate utilization of added C sources by soil microorganisms (Derrien et al., 2007). Microbially synthesized hexoses reached maximum concentrations in soil within a week, whereas a small carbohydrate fraction was stabilized (Derrien et al., 2007). The MRT increased in the order glucose (0.9 d) < cellulose (3.8 d) < labile metabolites (16 d) ≪ stabilized microbial carbohydrates (MRT ≫ 1 year; Derrien et al., 2007). The study therewith nicely confirms that in general the turnover times of added C sources are in the range of days to months when assessed under optimized laboratory conditions, hardly exceeding a few years. This is clearly different to products formed in situ like those usually traced by natural isotopic labeling in field studies with, for example, C3/C4 vegetation change, where frequent drying, nutrient limitations, low bioaccessibility, and many other factors limit the velocity at which soil C is utilized.

12.7.5.6.2 Biomarker-specific stable isotope analyses after C3/C4 vegetation change

When there are C3/C4 vegetation changes, the $\delta^{13}C$ stable isotope signature of SOM is naturally labeled in situ. The new C added to soil derives primarily from decomposed above- and belowground litter and root exudates, which may already be assimilated by soil microorganisms at the first sampling point.

Several plant-derived C structures like tannins, lignins, and certain waxes lack N and may accumulate in organic soil horizons, because they are not favorable substrate as carbon and energy source. Using compound-specific stable isotope analyses of these C structures allows to determine their residence time in soil. Work done on lignin after CuO oxidation, for example, therewith confirmed earlier work that lignin decomposition is monomer-specific, increasing in the order vanillyl (V) > syringyl (S) > cinnamyl (Ci) units (Bahri et al., 2006; Dignac et al., 2005; Heim and Schmidt, 2007). The monomer-specific MRT ranged from 7 to 33 years, which is faster than that of bulk SOM (**Figure 14**). Apparently, either other compounds than lignin were preserved for longer timescales or the CuO method only detected reactive parts of the lignin, leaving altered, nonextractable parts behind.

Other work on lignin biomarkers was based on the stable isotope analyses after SOM pyrolysis. It confirmed turnover times of plant lignins of 21–24 years (Gleixner et al., 2002). Also using stable isotope tracing of *n*-alkanes from plant waxes typically hinted at MRT in the range of a few decades (8–60 years) but not to timescales of millennia as found for bulk SOM (**Figure 14**; e.g., Cayet and Lichtfouse, 2001; Lichtfouse, 1997, 1998; Wiesenberg, 2004). In contrast to litter decomposition in organic soil layers (e.g., Meentemeyer, 1978; Parton et al., 1987), the selective preservation of certain plant-derived C structures is thus not a relevant mechanism of SOM genesis and transformation in aerobic, mineral soils (Amelung et al., 1997; 2008; Marschner et al., 2008). The stability of a certain organic molecule in soil therewith depends on environmental conditions and various kinds of organomineral interactions rather than on the chemical structure of the molecule itself (Christensen, 1996; Schmidt et al., 2011; von Lützow et al., 2006).

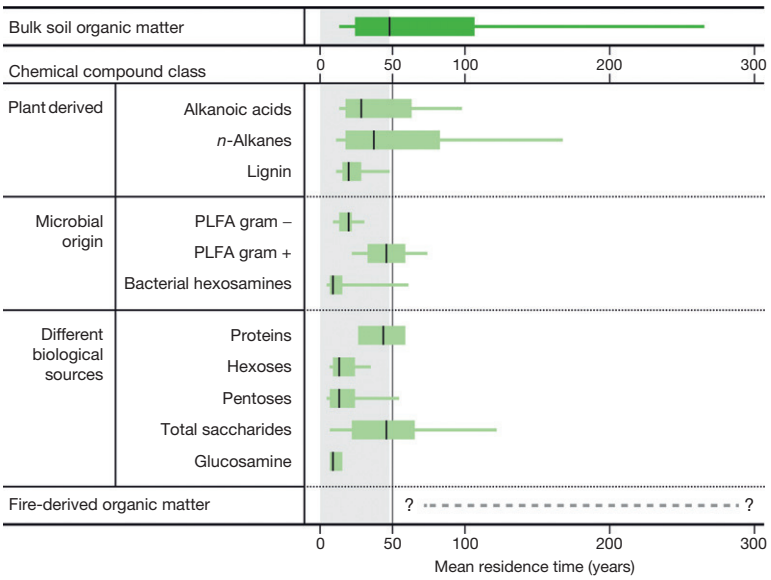


Figure 14 Mean residence time of different soil organic matter fractions (Amelung et al., 2008; redrawn from Schmidt MWI, Torn MS, Abiven S, et al. (2011) Persistence of soil organic matter as an ecosystem property. *Nature* 478: 49–56, with permission).

It is difficult to accurately identify the C3/C4 carbon source assimilated by the living microbial community, because of internal isotope fractionation during microbial synthesis. It may account, for instance, for isotopic shifts between 0 and 17 delta units within individual PLFAs, and it is usually larger for anaerobic C than for aerobic C assimilation (Abraham et al., 1998). To account for such processes, adequate controls are needed like a long-term C3 control site in addition to the plots with C4 treatments (e.g., Bol et al., 1999; Derrien et al., 2006; Dungait et al., 2010; Kramer and Gleixner, 2006). Respective studies show that even when C3/C4 vegetation changes date back for decades, soil microorganisms continue to be able to utilize C from the former vegetation, that is, this C is still available to be recycled through microbial biomass and not exclusively protected from decay. The degree to which 'old' C has been utilized by the soil microbial community has depended on soil type and has increased in the order Ferralsol (old tropical soils, rich in Fe and two-layer clay minerals like kaolinite) < Luvisol, Phaeozem (soils developed from loess, rich in three-layer clay minerals like illite, vermiculite, and smectite) < Andisol (soils formed from volcanic parent materials, rich in Al minerals like allophanes and imogolites; Burke et al., 2003; see also Amelung et al., 2008). There have been also consistent differences in the C utilization by different groups of the soil microbial community, with highest portions of freshly added SOM utilized in the order fungi ≥ Gram-negative bacteria ≥ Gram-positive bacteria (Kramer and Gleixner, 2006).

When microorganisms feed on 'older' SOM, it may easily happen that apparent long turnover times of 20 years or longer are detected for individual PLFAs. But also other microbial compounds that are formed and recycled in situ have a MRT of several years to a few decades, which is substantially longer than found in laboratory incubation experiments. The intimate contact between soil microorganisms with soil minerals therewith likely favors not only the reutilization of older C attached to minerals but likely also the stabilization of microbial C sources through interactions with Fe oxides, microaggregates, or by a capture in very fine pores (Amelung et al., 1997; Cheshire, 1979; Eusterhues et al., 2005a,b; Gleixner et al., 2002; von Lützow et al., 2007). The resulting MRT of carbohydrates is thus not lower than that of lignins (**Figure 14**), despite the chemical structure of the latter is less favorable for microbial growth. Again this finding points to the observation that the degradability of individual SOM constituents depends mainly on bioaccessibility and environmental conditions and not on the molecular structure of the chemical compound itself (Amelung et al., 2008; Marschner et al., 2008; Schmidt et al., 2011).

Because of different stabilization mechanisms, some molecules of a given compound class are readily accessible for decay, while others are not. As a result, it is mostly not correct to describe the dissipation of a biomarker with a single-pool approach as done frequently and summarized in **Figure 14**. Instead, two-pool approaches are needed, in which there is either a parallel decay from two pools of different accessibility or in which the pools are coupled successively, for example, when a microbial biomarker (pool 2) is newly formed from the plant precursor (pool 1; for details and theoretical background, see Derrien and Amelung, 2011). Fresh lignin, for instance, dissipates rapidly (MRT1 ≈ 0.5 years; Rasse et al., 2006a; see also corroborating results from incubation experiments with ^{14}C labeled lignin; Stott et al., 1983), while the protected lignin decomposes slowly (Amelung and Zech, 1996; Glaser, 2005; Rasse et al., 2006a). According to the modeling of Rasse et al. (2006a,b), only 8% of the introduced lignin reached the protected pool, from where it dissipated at a rate of 0.05 years^{-1}, corresponding to a MRT2 of 20 years. Other studies found an MRT2 for the slow decomposing lignin in the range of 32–35 years (Hofmann et al., 2009). Also, the decomposition of carbohydrates and *n*-alkanes splitted into two fractions, one decomposing rapidly with a MRT1 of one year or shorter and the second one decomposing more slowly with an MRT2 of ~30 years (Derrien and Amelung, 2011). The short MRT1 may at least in part explain why shorter SOM turnover times are found in incubation experiments, which do hardly last longer than one year. On the other hand, even the longer MRT2 does not exceed that of bulk SOM (**Figure 14**), that is, also the 2-pool concept supports the hypothesis that the chemical structure of a molecule is not the main factor that decides on the duration of its persistence in soil.

Even if the turnover time of identifiable biomarkers is relatively short compared with the turnover time of some stable parts of bulk SOM, does that mean that we do not find a passive SOM pool in soil on the bases of its structural analysis? At least, there are a few indications that some organic N forms in soil may be pretty persistent. Gleixner et al. (2002) assigned soil proteins an average MRT of 54 years from $\delta^{13}C$ abundance analysis in specific GC–pyrolysis products. Bol et al. (2002) used the $\delta^{15}N$ signature of different amino acids as indicators of ancient management in the bronze ages. Amelung et al. (2006) concluded from the detection of racemized amino acids in biotic environments that significant parts of the soil protein pool are not seen by the soil microbial community and preserved for several decades if not even longer. Also, in British upland soils, it was found that the D/L ratio of amino acids increased with increasing radiocarbon age. As except for bacterial markers like D-alanine the respective amino acids are produced in L-forms, the slow inversion into the D-form may be seen as an evidence of a true in situ ageing. Particularly, D-lysine has been a promising age marker in this context (Amelung, 2003). Finally, Bol et al. (1996) and Huang et al. (1999) reported that radiocarbon ages of *n*-alkanes reached 10 000 years in these British upland soils that exhibited an aquic moisture regime. Assuming that there was no fungal resynthesis of these structures from old C remains, the authors therewith discovered a truly passive SOM fraction within these mainly anaerobic soils. However, the preservation of these structures was likely caused by the absence of oxygen and thus again by the specific soil environmental conditions. Only black C might persist in soils and sediments for millennia (Flessa et al., 2008; Masiello and Druffel, 1998; Schmidt et al., 2011).

In summary, it can be stated that biomarker analyses helps to identify the origin of SOM and thus the mechanisms of its transformation. Combining biomarker analyses with compound-specific isotope analyses helps to assess turnover times. No ^{13}C labeling experiment, however, yet lasted longer than a century. And in no case a biomarker MRT exceeded several hundred years. Some fractions of SOM, however, may survive in soils for millennia (e.g.,

Buyanovsky et al., 1994; Jenkinson and Rayner, 1977). Hence, none of the described methods mentioned earlier really succeeded in elucidating the fate of SOM in the very long-term run. Compound-specific radiocarbon dating might have provided a clue to the assessment of turnover times of a few thousand years. Yet, many of our soils are already contaminated with ^{14}C-free materials like lignite dust and residues from fossil fuel combustion, which at least in part may also have been assimilated by the soil microbial community (e.g., Brodowski et al., 2007; Kramer and Gleixner, 2006; Rethemeyer et al., 2004a,b).

The available data suggest that fungi appear to feed mainly on fresh plant material, while gram-positive bacteria also significantly recycle older SOM. The newly synthesized structures have apparent MRT of 1–80 years, while refractory plant-derived biomarkers may even dissipate faster. It is concluded that the hypothesis of selective preservation must be refuted to be a significant process in mineral soils. In contrast, bound residue formation adds to bulk MRT in a yet unresolved manner.

12.7.6 Soil-Specific Interactions of OM with the Mineral Phase

12.7.6.1 Soil Architecture and Its Effects on C Turnover and Stabilization

Soil structure is a crucial criterion of soil quality (Mueller et al., 2010), as it affects most soil processes and specifically soil organic C and N turnover and stabilization. A large part of the OM in soils is thermodynamically labile, but persists in soils due to the formation of inaccessible microstructures (Kleber et al., 2011; Kögel-Knabner and Kleber, 2011), that means it is not the thermodynamic properties of organic C itself, but rather the association of C with mineral surfaces and within aggregates that provides long-term stabilization. OM is stabilized most efficiently in microaggregates and associated organomineral associations, which are stable over long time periods. It has to be taken into account that also very fine particles in soils are often aggregates (Chenu and Plante, 2006), rather than primary organomineral associations (Christensen, 1992) (see **Chapter 12.12**). The OM stored additionally in macroaggregates has a much shorter turnover time (von Lützow et al., 2007).

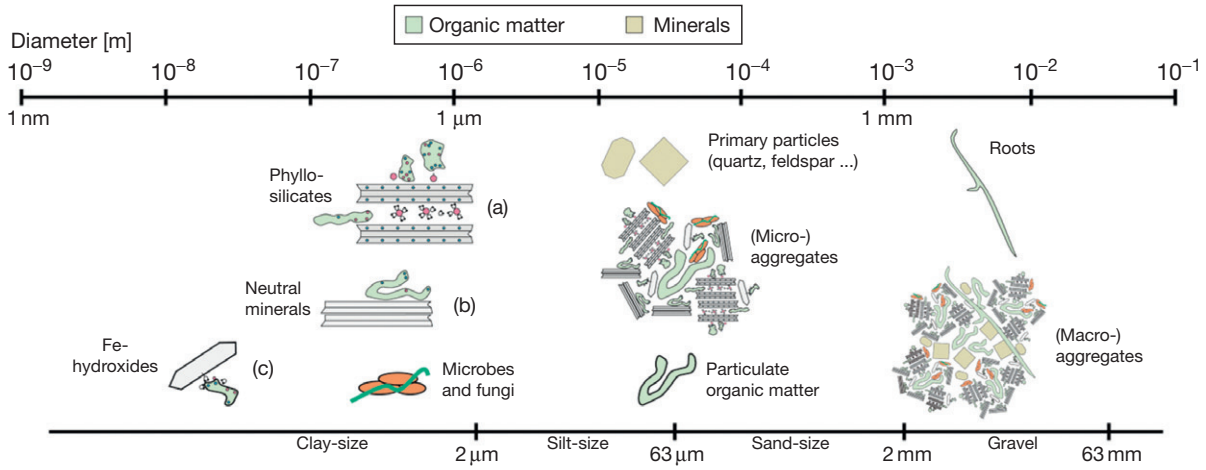
The soil matrix is separated into variable-sized compartments such that transfer rates of enzymes, substrates, water, oxygen, and microorganisms can be limited. Physical barriers due to the wetting resistance and chemical heterogeneity of surfaces, hydrophobic interfaces, and instable wetting fronts cause spatial heterogeneity of soil moisture and spatial inaccessibility for decomposer organisms. The input pathways as well as the location of OM within these compartments determine accessibility by the decomposer community. Specialization of decomposers toward preferred substrates and soil spaces (Ekschmitt et al., 2008) explains longer persistence of C substrates in nonpreferred soil spaces. In A horizons, OM is derived mainly from plant residues that are mixed into surface soils by tillage or by bioturbation, root residues, and exudates. In subsoils, C input occurs mainly through plant roots, bioturbation, and leaching of dissolved OM. Preferential flow paths of dissolved OM may be considered as 'hot spots' in soils, because they permit better nutrient and substrate supply compared to the whole soil matrix. With increasing depth, there is less probability for any point in a soil to be located near a preferential flow path or hot spot. This is consistent with the generally greater radiocarbon age of subsoil OM compared to surface soils (Chabbi et al., 2009). Important processes that reduce soil OM accessibility for decomposition are summarized here, a discussion in detail is given by von Lützow et al. (2006) and Kögel-Knabner and Kleber (2011). **Figure 15** gives an overview of the major modes of interaction of OM with the different mineral phases present in temperate soils as well as their association in aggregates.

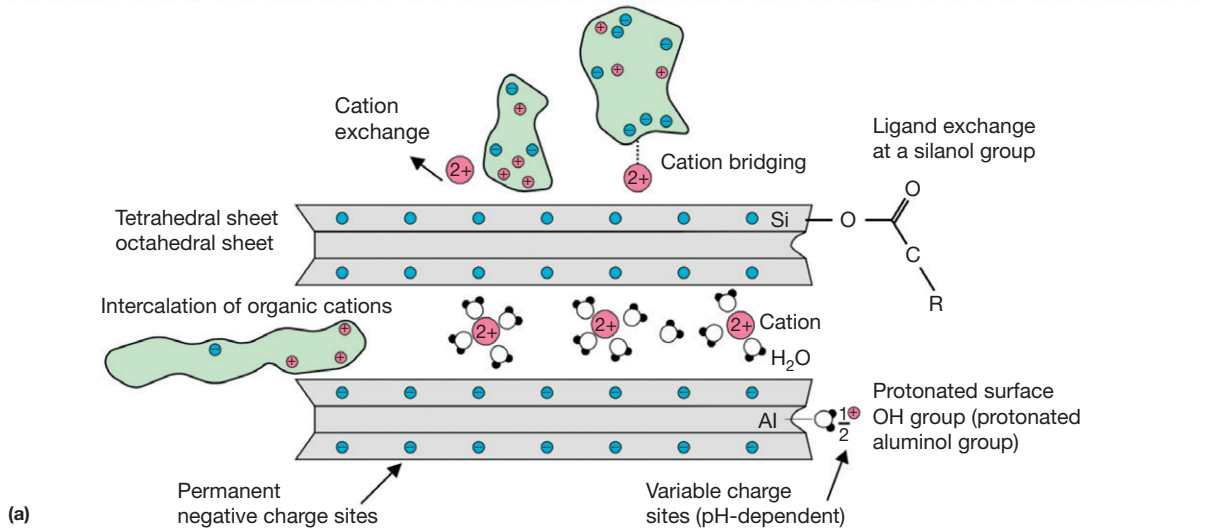
12.7.6.1.1 Accessibility/aggregation

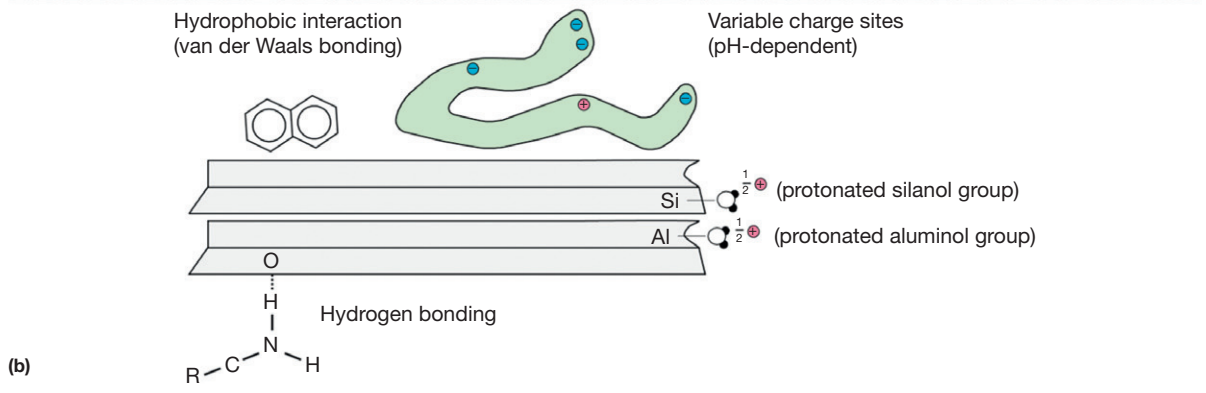
Observations of enhanced SOM mineralization following disruption of aggregates showed long ago that occlusion in aggregates has a retarding effect on SOM decomposition. Protection will be greatest where aggregate stability is high and aggregate turnover is low; thus, aggregation is the stabilization mechanism that is potentially most susceptible to disturbance. The fact that soil aggregation is a transient property and that aggregates are continually being formed and destroyed (Baldock and Skjemstad, 2000; Virto et al., 2010) suggests further that aggregation/accessibility is the stabilization mechanism controlling the size of the slow or intermediate pool of carbon turnover models, but not the dominant control on centennial or millennial turnover. Measured turnover times for carbon protected by aggregates indicate an inverse relationship between aggregate size and carbon turnover time (Balesdent, 1996; John et al., 2005; Liao et al., 2006; Skjemstad et al., 1993) with the highest reported turnover times in the lower centennial range (200–320 years) in the smallest aggregates <20 μm. Occlusion at the clay microstructure level (<20 μm) has been attributed to abiotic mechanisms, such as the precipitation of Fe and Al oxides or hydroxides (Duiker et al., 2003), but in general soil biota are thought to be strongly involved in the process of occlusion. Thus, microbial cells, secretions, root exudates, and faunal mucus act as cementing agents (**Figure 15**) and are at the same time occluded within microaggregates (von Lützow et al., 2006).

The presence of old, microbial-type organic materials in very small aggregates is often taken as evidence that the OM associated with microaggregates may not only be physically protected but also highly humified and biochemically recalcitrant. An increasing number of authors explain the mechanisms of long-term stabilization of energy-rich microbial residues or microbial products to be the result of an interaction with the mineral matter in small aggregates, rather than the production of newly formed 'humic substances' (see Kleber and Johnson, 2010 and Schmidt et al., 2011 for a detailed discussion and further references).

The very small microaggregates are major sites of OM stabilization. This is supported by measurements of microbial sugars in contact with pedogenic oxides by Spielvogel et al. (2008) and by contemporary theories about the structure of OM coatings in contact with mineral surfaces (Bachmann et al., 2008; Kleber et al., 2007; Wershaw et al., 1996). Carbon associated with mineral surfaces has a distinct composition related more to microbially processed OM than to plant-related compounds (Dümig et al., 2012; Grandy and Neff,







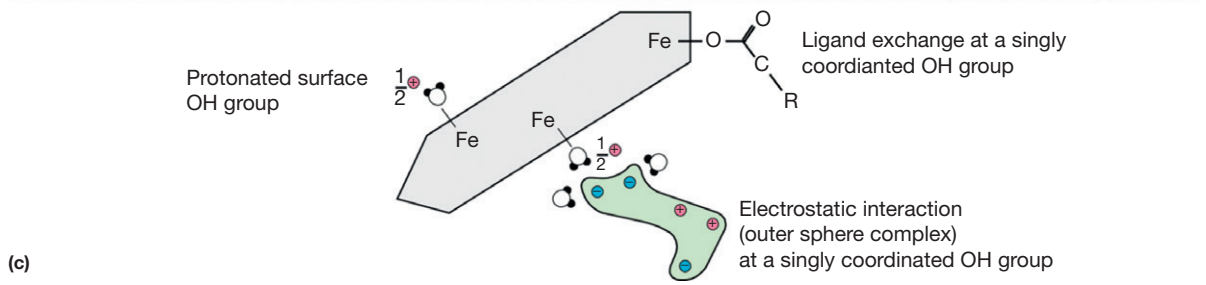


Figure 15 Models for the interactions of organic matter with minerals and aggregates at different scales, translated from Blume et al. (2010), concept by K. Eusterhues and A. Kölbl.

2008; Spielvogel et al., 2008). Frequently, the microaggregate-associated OM is thus rich in polysaccharide C (Cheshire, 1985).

12.7.6.1.2 Organomineral interactions

Organomineral interactions, or the protection of organic matter against decomposition through association with mineral surfaces, have received increasing attention over the past two decades and have been identified as the most likely mechanism to achieve long-term, that is, centennial or millennial, protection of OM (Kleber, 2010; Kögel-Knabner et al., 2008).

The SOM in fine silt and clay fractions has longer turnover times than OM in other soil OM fractions. Kalbitz et al. (2003) showed that sorption of soluble OM to subsoil material (Bw horizon) reduced OM mineralization to less than 30% compared with the mineralization in soil solution. A detailed mechanistic understanding of why sorption to soil minerals reduces decomposition rates is lacking and is complicated by artifacts in the experiments. Chenu and Stotzky (2002) suggest that small molecules sorbed to mineral surfaces cannot be utilized by microorganisms unless they are desorbed so that they can be transported into the cell. But they also caution that it is difficult to demonstrate the unavailability of adsorbed molecules because desorption can occur through microbial secretions during the experiments. The adsorption of macromolecules is considered to be associated with conformational changes that render macromolecules unavailable to the action of extracellular enzymes (Khanna et al., 1998; Theng, 1979). But as shown by Demaneche et al. (2001), degradation can also be hindered by the adsorption of the relevant enzyme to clay minerals rather than by adsorption of the substrate.

Long-term protection of organic molecules by sorptive interactions is limited to those organic materials directly bonded to the protecting mineral surface, which is of a finite size (Kleber et al., 2005). Abundant evidence that substantial parts of mineral surfaces are not covered by OM has led to the insight that organic materials must be stacked or clustered on mineral surfaces (Kaiser and Guggenberger, 2003) in small patches with some vertical extension. Such a multilayer architecture of organic coatings on mineral surfaces suggests that only the inner layer of organic molecules is able to participate in direct, strong mineral–organic interactions (Kleber et al., 2007). The degree of saturation of protective sites should thus affect the preservation potential of newly added carbon to the soil.

Clay-sized particles like layer silicates (<2 μm), sesquioxides (crystals 5–100 nm), short-range ordered Fe oxides (3–10 nm), and amorphous Al oxides (<3 nm) provide the most significant surface area onto which OM can adsorb Basile-Doelsch et al., 2005; Eusterhues et al., 2005a,b; Jahn et al., 1992; Kaiser and Guggenberger, 2007; Kleber et al., 2005; Rasmussen et al., 2005; Spielvogel et al., 2008; Torn et al., 1997). Mineral reactivity, rather than mineral texture, consistently serves as a better predictor of the residence time and turnover time of stable soil OC and can be associated with two- to threefold differences in total soil C storage (Kahle et al., 2004; Kleber et al., 2005; Masiello et al., 2004; Mertz et al., 2005; Rasmussen et al., 2005; Torn et al., 1997). The extent to which microbial metabolites produced from decomposing plant residues are stabilized in different soils is controlled by specific surface area (SSA) provided by clay minerals (Saggar et al., 1996). The OM contents of coarse and fine clay subfractions depend on the mineralogy and, more specifically, on the surface reactivity of the mineral constituents. In the coarse clay fraction, silicate mineral surfaces (montmorillonite > vermiculite > illite > kaolinite) are more important for carbon storage than Fe oxides, which dominate in fine clay fractions and in acid subsoils (Anderson et al., 1981; Kahle et al., 2003; Kleber et al., 2004).

Mineralogical effects on carbon stabilization have been reported exclusively for secondary minerals, particularly such with abundant hydroxylated surfaces. Examples include Fe oxides (Kaiser and Guggenberger, 2007; Kögel-Knabner et al., 2008), Al-rich imogolite-type materials (Basile-Doelsch et al., 2005; Percival et al., 2000), short-range ordered Al hydroxides (Rasmussen et al., 2005; Spielvogel et al., 2008), and poorly crystalline materials in general (Jahn et al., 1992; Kleber et al., 2005; Torn et al., 1997). It seems that the same mineral surface type may function differently in different pedogenic environments, as a result of variations in pH, OM chemistry, cation availability, and other environmental controls.

12.7.6.1.3 Types of C and N in organomineral associations

In situ investigations show that the proportion of the mineral-bound OM and its ^{14}C age generally increase with soil depth. Stabilization by organomineral interactions operates at long-term scales and dominates during late decomposition phases and in subsoils (Kögel-Knabner et al., 2008). Little information is available on the relationship between mineralogy and the chemistry of bound OM. Kögel-Knabner (2000) found that OM in organomineral associations of fine fractions and loamy soils has a higher contribution of bacterial polysaccharides, whereas mineral-associated OM in acid sandy soils is more aliphatic. Kaolinite-associated OM from grassland and shrub surface soils was enriched in polysaccharide products, whereas smectite-associated OM, supposedly in interlayer spaces, was enriched in aromatic compounds (Wattel-Koekkoek et al., 2001). Laird et al. (2001) attributed differential carbon storage in clay subfractions to a shift in mineral composition from coarse to fine clay. The coarse clay fraction had stronger carboxyl and O-alkyl ^{13}C-NMR peaks and smaller concentrations of extractable amino acids, fatty acids, monosaccharides, and amino sugars than OM associated with the fine clay fraction (Kahle et al., 2003; Laird et al., 2001). Kleber et al. (2004) and Schöning et al. (2005) have found evidence for selective stabilization of O-alkyl C, especially by interactions with pedogenic oxides on mineral surfaces within the coarse clay subfraction. Ligand exchange might be the binding mechanism. In contrast, alkyl C and aromatic C responded to the duration of fertilizer deprivation but were indifferent to mineral surface reactivity (Kleber et al., 2004). Generally, the OM associated with soil minerals has a low C/N ratio (often around 8–12). This is attributed to the association of mainly proteins and peptides (Kleber et al., 2007; Knicker, 2004; Rillig et al., 2007) but, to a smaller extent, also of DNA (Pietramellara et al., 2009) with the mineral phase.

12.7.6.1.4 Phyllosilicate clay minerals

Organic anions are repelled from negatively charged surfaces in soils, but binding occurs when polyvalent cations are present on the exchange complex. Unlike Na^+ and K^+, polyvalent cations are able to maintain neutrality at the surface by

neutralizing both the charge on the negatively charged surface (e.g., in clay minerals) and the acidic functional group of the OM (e.g., COO^-) and thus act as a bridge between two charged sites. The major polyvalent cations present in soil are Ca^{2+} and Mg^{2+} in neutral and alkaline soils and hydroxypolycations of Fe^{3+} and Al^{3+} in acid soils. The Ca^{2+} ions do not form strong coordination complexes with organic molecules, relative to Fe^{3+} and Al^{3+}. For a long-chain organic molecule with multiple functional groups, multiple points of attachment to the clay particle (segment–surface contact) on permanent charge sites of layer silicates are possible. Microbially secreted polysaccharides frequently carry a negative charge due to the presence of uronic acids that adsorb strongly to negatively charged clay surfaces through polyvalent cation bridging (Chenu, 1995). The bonding efficiency of OM on phyllosilicates by cation bridges is weaker compared to ligand exchange on Al and Fe hydroxides.

Several nonexpandable layer silicates (e.g., 1:1 layer silicates like kaolinite) or quartz particles without layer charge and without interlayer spaces usually exhibit weaker bonding affinities. The negative charge on the siloxane surface of other clay minerals depends on the type and localization of the excess negative charge created by isomorphic substitution. In the absence of a layer charge, a siloxane surface may be considered uncharged. Nevertheless, the 1:1 clay minerals like kaolinite and halloysite may also be reactive due to available surface of Al-tetraeders (Kaiser and Guggenberger, 2003).

Uncharged but polar polysaccharides and extracellular enzymes or other proteins can form linkages via hydrogen bonding or van der Waals forces because of the presence of hydroxyl and other polar groups in the molecule (Quiquampoix et al., 1995). Their typically high molecular weight offers a large number of potential surface–segment contacts and thus strong binding between uncharged polysaccharides and clays can be established (Theng, 1979). Hydrophobic interactions become more favorable at low pH when hydroxyl and carboxyl groups of OM are protonated and the ionization of carboxyl groups is suppressed. Bonding interactions of apolar aromatic ring structures have long been considered as restricted to energetically weak, nonspecific, hydrophobic interactions. Over the last decade, an increasing number of authors have suggested specific (i.e., directed) and energetically stronger adsorption mechanisms between aromatic π-systems of organic compounds and sorption sites at mineral surfaces (Keiluweit and Kleber, 2009).

12.7.6.1.5 Pedogenic oxides

It is widely assumed that the energetically strongest associations between OM and mineral surfaces involve the mechanism of ligand exchange between carboxyl groups of OM and hydroxyl groups at the surfaces of mineral phases. Complexation of OM on mineral surfaces via ligand exchange increases with decreasing pH with maximal sorption between pH 4.3 and 4.7, corresponding to pK_a values of the most abundant carboxylic acids in soils. Therefore, ligand exchange between reactive inorganic hydroxyls (OH groups of Fe, Al, and Mn oxides and edge sites of phyllosilicates) and organic carboxyl and phenolic-OH groups is restricted to acid soils rich in minerals with protonated hydroxyl groups. The sorptive strength of hydroxyl-bearing phases, like Fe (hydr)oxides and poorly crystalline aluminosilicates, increases with decreasing pH and will therefore be particularly relevant in acidic soils. Sorption occurs preferentially at reactive sites such as edges, rough surfaces, or micropores (e.g., edges of illite particles where amphoteric Al OH groups are exposed, crystal surfaces of Fe oxyhydroxides with singly coordinated OH groups). Kleber et al. (2004) showed that singly coordinated, reactive OH groups on Fe/Al oxides and at edge sites of phyllosilicates, which are able to form strong bonds by ligand exchange, are a measure of the amount of OM stabilized in soils in organomineral associations. Kaiser and Guggenberger (2003) hypothesized that the molecules adsorbed first might be strongly stabilized by multiple ligand attachments. At larger surface loadings, sorption can then take place with fewer ligand attachments involved, which leaves parts of the molecule not attached to the surface and thus renders them more susceptible to degradation.

High OM contents are typical for soils derived from volcanic ash (Andosols), containing poorly crystalline aluminosilicates like allophane and imogolite. The striking ability of poorly crystalline aluminosilicate mineral matrices to contribute to soil carbon retention can be illustrated by comparing the organic C contents of Andosols with those of other mineral soils (see **Section 12.7.6.2**). On a global scale, Andosols have mean OC contents of 25.4 kg m^{-2} in the upper 100 cm (Batjes, 1996), which makes them the most carbon-rich FAO–UNESCO mineral soil unit. Such soils with significant proportions of poorly crystalline minerals also tend to have particularly long OM residence times compared with other soil taxa (Kleber et al., 2005). The different mechanisms to explain high OM storage and long OM residence times in soils containing poorly crystalline aluminosilicate phases are (1) strong ligand exchange type bonds combined with large SSAs, (2) formation of specific microaggregates, and (3) direct effects of Al^{3+} on microorganisms or enzymes (Kögel-Knabner and Kleber, 2011).

12.7.6.1.6 Interactions with metal ions

In comparison to the chemistry of metal binding, less information is available about the effect of metal binding (Ca^{2+}, Al^{3+} and Fe^{3+}, heavy metals) on soil OM stability or about the mechanisms involved. Several studies have shown effects of Ca^{2+} ions on the mineralization of soil OM and its solubility (Muneer and Oades, 1989), and the large OM content of calcareous soils is also attributed to the effect of Ca^{2+} ions (Oades, 1988). The interaction of soil OM with Al and Fe is considered to be the main reason for the stability of soil OM in Podzols (Lundström et al., 2000). The Al/C ratio of DOM seems to be an important parameter for its stability against microbial decomposition. In long-term incubation studies, Schwesig et al. (2003) showed that for natural DOM, Al/C ratios >0.1 increased the half-life of the stable DOM fraction up to fourfold. DOM in soils can be precipitated by metal ions and the precipitated DOM can be more stable than the DOM remaining in solution. Larger DOM molecules are precipitated preferentially, while smaller molecules stay in solution. Often, it is difficult to separate the complexing effect of metal cations (Ca, Mg, Al, and Fe) from their ability to form cation bridges.

12.7.6.2 SOM Formation in Major Soil Types

In this treatise, we are not able to discuss all soil types and their specific features of SOM formation and properties (see **Chapter 7.1**). Merely, we selected major soil types with specific pedogenetic properties and we describe how these are linked to

SOM formation and properties. The soils considered are examples for fertile and unfertile temperate soils (Chernozems and Podzols), tropical soils (Ferralsols), azonal soils derived from a specific parent material (Andosols), and man-made soils (Paddy soils and Terra preta). We refer to the soil types and horizon designations according to the major common soil classification system, the World Reference Base for Soil Resources WRB (IUSS Working Group WRB, 2006), but also give the soil type in the US soil taxonomy (Soil Survey Staff, 2010).

12.7.6.2.1 Chernozems

Chernozems (or Mollisols in the US soil taxonomy), commonly equated with black earth soils, are among the most fertile soils used in current agricultural production. They usually developed on aeolian and carbonaceous sediments, mostly loess. As a result, their clay mineralogy is dominated by high activity, three-layer clay minerals, contributing to a high CEC. The texture is silty to loamy, the base saturation ranges between 70% and 100%. The water-holding capacity is high due to the silty texture, frequently exceeding 150 mm. Besides, the soils usually contain high inherent amounts of potassium and phosphates, the availability of which depending on the degree of decalcification. In contrast to the so-called Phaeozems, the decalcification of the Chernozems is incomplete, and some of the dissolved carbonates are antecedently reallocated within the lower surface soil or subsoil, therewith forming secondary carbonate precipitates at mineral surfaces ('soft powdery lime') or within soil pores ('loess kindl'). The very surface soil, however, is free of lime, and pH values are slightly acidic.

The formation of the Chernozems has been favored by a climatic constellation specific for the steppe, that is, cold winters and hot summers, with the majority of plant growth occurring in moist spring. These specific constellations force larger soil animals like earthworms, mice, and ground squirrels to draw back into the deeper soil when living conditions are unfavorable in the surface soil, for example, during hot dry summer months. During humid times of the year, these animals are very active in the surface soil. As a result, these soils are characterized by a high degree of biological soil mixing, a process called bioturbation. It leads to the formation of biologically stabilized soil aggregates in the very surface soil (the concept of aggregate hierarchy has been developed for Chernozems; see **Section 12.7.6**), of so-called krotovinas (animal burrows) in the lower surface soil and subsoil, and altogether of the incorporation of OM into humus-rich, mighty black A horizons (Driessen et al., 2001). In its classical case, this dark A horizon is then underlain directly by the parent, calcareous loess, leading to the formation of a so-called A–C soil profile. Depending on the classification system, the A horizon obtains an appendix of a small capital 'p for plowing,' 'h for *h*umic,' and 'x for biological mixing' (**Figure 16**, Foto 1). The C horizon is usually a Cc, due to the existence of carbonates.

The occurrence of Chernozems is mainly restricted to the loess belt and former steppe climates around the world, that is, they are typically zonal soils. Chernozems are thus found in the US Great Plains and the Argentinian Pampa, in Central and Eastern Europe, for example, in Germany, Hungary, Romania and Ukraine, and in parts of Asia (Russia and China) around a latitude of about 50° N. They correspond to Mollisols in the US classification. Sometimes, these soils are underlain by Bt horizons, indicating clay lessivation at other stages of soil development, likely under a moister (forest) climate.

The depths of the A horizons, however, vary from >40 cm in Germany and some sites in the United States to >70 cm in some sites in Russia to >300 cm at selected sites in the Chinese Manchurian steppe (Rodionov et al., 2010). These variations in soil depth give support to the hypothesis that other processes than decalcification and bioturbation contributed to soil formation, such as wildfires or anthropogenic impacts correlating with slash-and-burn agriculture, erosion, and colluvium formation (see, e.g., Eckmeier et al., 2007, for a review, Gerlach et al., 2012). Also, the lack of homogenized radiocarbon ages in the surface soil, as it would have been expected from sole biogenic mixing, supports the idea that bioturbation alone may not explain the occurrence of thick dark A horizons (Scharpenseel et al., 1986). The origin of SOM even spans a few thousand years, which again conflicts with a monocausal soil formation theory at continental climates. Besides, there is no evidence for the presence of Chernozems in Central Europe in the Late Glacial, which also exhibited a continental climate (Eckmeier et al., 2007).

The black color of the mollic A horizon has attracted the geochemical community in the last years, since there is increasing evidence that it correlates with the occurrence of pyrogenic carbon (e.g., Eckmeier et al., 2007; Rodionov et al., 2010; Schmidt et al., 2002). Incomplete biomass burning leaves char and soot behind, its BC forms may explain the frequent aromatic nature of SOM (Haumaier and Zech, 1995; Schmidt et al., 2002). Glaser and Amelung (2003) even suggested that there might be a positive feedback loop: the high fertility of the Chernozems goes along with a high biomass production, which then leave more BC behind after vegetation fires than sites with lower primary productivity. Yet, not all of these BC must originate from natural vegetation burnings. Eckmeier et al. (2007) outlined that not only wildfires, which are a ubiquitous element of steppe environments, but also man-made fires, for example, used in early slash-and-burn agriculture contribute to the origin of SOM and thus soil formation. And more recently, Kiem et al. (2003), Rethemeyer et al. (2004b), and Brodowski et al. (2007) gave evidence that at least in lower Saxony (Germany), dust from diagenetic coals as well as burning of fossil energy sources already comprised up to 50% of the topsoils' organic C. High radiocarbon ages are then no longer an indicator of a long residence time of the SOM but rather reflect contaminations from fossil fuels, which may not be neglected in SOM characterization.

In summary, the SOM found in Chernozems is prone to stabilization by biologically mediated aggregate formation. The concept of aggregate hierarchy is fully valid. The SOM may thus be rich in saccharides, which are primary binding agents in microaggregates and which in Chernozems may even be preserved in preference to lignins (Amelung et al., 1997; Cheshire, 1985). The stabilization processes are driven by these organomineral interactions and not by selective preservation mechanisms of selected SOM moieties (Flessa et al., 2008; von Lützow et al., 2007). Yet, a significant part of the SOM also originates from biomass burning. This BC is stable in soil, may accumulate relative to other SOM constituents, and is aromatic in nature. Since Chernozems are usually used for agricultural

Figure 16 Representative soil profiles of the world (1) Chernozem.

(Continued)

purposes, prone to erosion, these SOM forms may also enter the rivers in colloidal forms, then becoming part of the regional biogeochemical element dynamics.

12.7.6.2.2 Podzols

In contrast to Chernozems, Podzols are not suited for high-input crop production. These soils are strongly acidified and water-holding capacity is low (frequently <100 mm). They usually developed on permeable sandy materials with low contents of Fe and low base saturation and under vegetation, which produces a slowly degrading, nutrient-poor litter. The potential vegetation therefore comprises, for example, *Calluna*, *Erica*, *and Vaccinium* species as well as coniferous forests. It forms an organic litter above a bleached A horizon with typical pH values between 2.5 and 4.5. The texture of the mineral soil is commonly sandy to loamy sand, the structure of the surface soil is single-grained, the cation exchange capacity is low, and earthworm casts are absent. Quartz is the dominating mineral in all horizons. The few clays remaining typically consist of pedogenetically transformed minerals like illite or secondary chlorites.

The low pH value in the A horizon facilitates the dissolution of primary silicates and clay minerals, resulting in a release of Al, Fe, and Si. This process is promoted by the production of water-soluble acids and other chelating agents in the litter layer. These elements and the mobile OM are then leached into the subsoil, leading to the formation of an illuvial B horizon with humic materials (Bh) or sesquioxides (Bs) or both (Bhs, Bsh). Left behind is an ash-colored E horizon (Ae in, e.g., the German classification system), with bleached quartz grains and depleted in OM (**Figure 16**, Foto 2). These characteristic features were traditionally the basis for the name Podzol, which is a combination of the Russian words 'pod' (= under; под) and 'zola' (= ash; зола). The illuvial B horizon is thus internationally designated as 'spodic' horizon or 'spodic B horizon,' and diagnostic for Podzols in the WRB or 'Spodosols' in the US soil taxonomy system, respectively. If strongly developed, it may finally consolidate and become hard when dry.

There are different theories about the mobilization and translocation mechanisms involved in the podzolization process (see, e.g., Sauer et al., 2007, for a review):

- Formation of water-soluble chelates between the DOM and Fe, Al, and Si ions
- Reduction of Fe and migration of in reduced metal–organic complexes
- Colloidal transport of Fe, Al, and Si

Several other processed then favor the reimmobilization and stabilization of OM and sesquioxides in the B horizon, such as precipitation and flocculation at increased pH, filtering in small pores (e.g., in layered substrates), degradation of the organic complex partner, or as a second step, readsorption on

Figure 16 (Continued) Representative soil profiles of the world (2) Podzol.

subsoil oxide coatings. As outlined by Sauer et al. (2007), likely not one sole process but several different processes are involved in the translocation and immobilization of the metals. It should also be kept in mind that the occurrence of specific forms of the metals in the illuvial B horizon (e.g., as metal–organic complexes) does not necessarily imply that this was the main form of translocation. Many of the Al and Fe complexes, for example, found in the Bh and Bs horizons are possibly also formed *in situ*. In any case, the Podzols are one of those soils, where due to the illuviation/ process the biogeochemical surfaces in the subsoil may be more reactive than in the surface soil, even clustering to stable microaggregates, whereas the surface soil is usually not aggregated.

Podzols cover 485 million hectares worldwide (Driessen et al., 2001). The occurrence of the Podzols is correlated with that of its parent material and potential vegetation. Well-developed profiles are mainly found in cool and semihumid to humid climates, particularly in the boreal zone, such as in Scandinavia, Russia, and Canada. However, Podzols are also found in high mountain regions, such as the lower Rocky Mountains or Appalachian Mountains (USA), the Alps, or the Himalayan region (Sauer et al., 2007). Some Podzols also occur in humid to perhumid tropical regions, where sometime the bleaching of the A horizon was so severe that only a sandy soil remained in the first 1–2 m (Giant Podzols; then to be classified as Arenosols due to the lack of specific B horizon features). In subarctic tundra and polar desert, but also in alpine regions, Nanopodzols have been found, which are frequently only a few millimeter to centimeter thick (Blume et al., 1996). The time needed for their formation spans from several decades (incipient E horizon) to 6000 years (Sauer et al., 2007).

In summary, the SOM found in Podzols is prone to different stabilization mechanisms in the different soil horizons. In the litter layer and in well-bleached E horizons, it is likely the refractory nature and unfavorable low pH value and Al toxicity (in the E horizon) rather than many organomineral interactions that contribute to the preservation of SOM. Lignins, tannins, and particularly aliphatic waxes as well as branched alkyl moieties are decomposed less rapidly than other compounds, such as structural carbohydrates (Kögel et al., 1988; Kögel-Knabner and Hatcher, 1989; Ziegler et al.,

1986). In the spodic horizons, the OM may coat the mineral surfaces (Amelung et al., 2002a). The lignins and phenols are depleted, but carbohydrates may be stabilized by penetration into or interactions with the Fe-rich microaggregates (Eusterhues et al., 2005a,b, 2011; Mikutta et al., 2006; Schmidt et al., 2000). Still, high contents of DOM (between 115 and 500 kg m^2; representing 35% of annual litterfall) may be lost from the surface soils, leached to the groundwater, or stored in the mineral subsoil (between 19% and 52% of the total C; Kalbitz and Kaiser, 2008).

12.7.6.2.3 Ferralsols

Ferralsols are very highly weathered soils that are found primarily in the intertropical regions of the world. Ferralsols are the 'classical,' deeply weathered, red or yellow soils of the humid tropics. These soils have diffuse horizon boundaries, a clay assemblage dominated by low activity clays (mainly kaolinite), and a high content of sesquioxides, that is, Fe and Al oxide minerals. Ferralsol is derived from Latin terms *ferrum*, iron, and *alum*, aluminum. Internationally, Ferralsols are known as Oxisols (Soil Taxonomy, USA), Latosols (Brazil), Sols ferralitiques (France), and Lateritic soils.

Ferralsols form principally in humid tropical zones under rainforest, scrub and thorn, or savanna vegetation on flat to gently sloping uplands. They are typically found on old landscapes that have been subject to shifting cultivation for millennia. Their parent material is strongly weathered material on old, stable geomorphic surfaces. The typically occur in level to undulating land of Pleistocene age or older, whereas they are less common on younger, easily weathering rocks. Ferralsols are generally associated with perhumid or humid tropical conditions, and minor occurrences elsewhere are considered to be relics from past eras with humid tropical climate.

The worldwide extent of Ferralsols is estimated at some 750 million hectares, almost exclusively in the humid tropics on the continental shields of South America (Brazil) and Africa (Zaire, southern Central African Republic, Angola, Guinea, and eastern Madagascar). Outside the continental shields, Ferralsols are restricted to regions with easily weathering basic rock and a hot and humid climate, for example, in southeast Asia. Oxisols occupy ~7.5% of the global ice-free land area.

Ferralsols have an ABC profile. Deep and intensive weathering has resulted in a high concentration of residual, resistant primary minerals alongside sesquioxides and well-crystallized kaolinite. This mineralogy and the low pH explain the stable microstructure (pseudosand) and yellowish (goethite) or reddish (hematite) soil colors (**Figure 16**, Foto 3).

Ferralsols have the following characteristic features:

- A *deep solum* (usually several meters thick) with *diffuse or gradual* horizon boundaries
- A '*ferralic*' *subsurface horizon*, reddish (hematite) or yellowish (goethite) in color, with weak macrostructure and strong microstructure ('pseudosilt' and 'pseudosand') and friable consistence
- *Deep internal drainage* and absence of conspicuous mottles

These soils are characterized by relative accumulation of stable primary and secondary minerals; easily weathering primary minerals such as glasses and ferromagnesian minerals and even the more resistant feldspars and micas have disappeared completely. Quartz is the main primary mineral (if originally present in the parent rock). The clay assemblage is dominated by kaolinite, goethite, hematite, and gibbsite in varying amounts, in line with the kind of parent rock and the drainage conditions. *Ferralitization* is hydrolysis in an advanced stage. If the soil temperature is high and percolation intense (humid climate!), all weatherable primary minerals will ultimately dissolve and be removed from the soil mass. Less soluble compounds such as iron and aluminum oxides and hydroxides and coarse quartz grains remain behind. Ferralitization (or *desilication* as it is also called) is furthered by the following conditions:

- *Low soil pH and low concentrations of dissolved weathering products* in the soil solution promote desilication and buildup of high levels of (residual) Fe and Al. CO_2 in the soil (from respiration by roots and soil organisms feeding on OM) and percolating rainwater depress the pH of the soil and lower the concentrations of weathering products.
- *Geomorphic stability* over prolonged periods of time is essential. Ferralitization is a very slow process, even in the tropics where high temperatures increase reaction rates and solubility limits. *Note that* old erosion surfaces are more common in the tropics than in temperate regions where recent glacial processes reshaped the landscape.
- *Basic parent material* contains relatively much iron and aluminum in easily weatherable minerals and little silica. Ferralitization proceeds much slower in acidic material that contains more quartz. Even though most silica is leached from the soil (hence 'desilication'), the silica content of the soil solution remains higher than in soils in basic material. This silica combines with aluminum to the 1:1 clay mineral kaolinite (*kaolinitization*), in particular where internal drainage is impeded and dissolved silica is less quickly removed.

Ferralsols have good physical properties but are chemically poor. Most Ferralsols are characterized by extremely low native fertility, resulting from very low nutrient reserves, high phosphorus retention by oxide minerals, and low CEC. Most nutrients in Oxisol ecosystems are contained in the standing vegetation and decomposing plant material. In natural systems, the limited stock of plant nutrients is in a constant process of 'cycling' with most nutrients contained in the biomass. Many Ferralsols are still used for shifting cultivation. Liming and full fertilization are required for sustainable sedentary agriculture. The well-structured aggregates of Ferralsols are composed of a mixture of kaolinite and Fe oxides (hematite). Stable microaggregates explain the excellent porosity, good permeability, and favorable infiltration rates measured on Ferralsols. Despite their low fertility, Ferralsols can be quite productive with inputs of lime and fertilizers. Intensive plantation agriculture is possible if lime and fertilizers are applied with careful management to prevent erosion. In weathered tropical soils, such as Ferralsols, rates of C loss caused by cultivation are often considered many times faster than those for temperate

Figure 16 (Continued) Representative soil profiles of the world (3) Ferralsol.

soils, with a substantial deterioration in soil quality often in less than 10 years, thus proper OM management is necessary for sustainable agriculture on these soils (Shang and Tiessen, 1997). Nonetheless, they contain a substantial proportion of rather stable OC. Skjemstad et al. (2008) found between 17.1% and 31% of the total organic C in an Australian Oxisol to be derived from C3 rainforest after cultivation under C4 pasture for 90 years.

The structure of Ferralsols is stabilized by oxides and OM, but no aggregate hierarchy is observed, in contrast to many temperate soils. Generally, it is considered that Ferralsols are more stabilized by inorganic cementing agents (iron and aluminum oxides) rather than OM (Oades and Waters, 1991). However, recent research has shown that OM stabilization in Ferralsols occurs to 58–60% through organomineral associations (Basile-Doelsch et al., 2009). This indicates that binding of organic compounds at the surface of mineral phases is a major stabilization process in Ferralsols, and thus, the accumulation of OM is enhanced by the formation of organomineral associations (Dalmolin et al., 2006). In contrast, Shang and Tiessen (1997, 1998) and Skjemstad et al. (2008) reported that protection within microaggregates is the major mechanism for protection of OC in Oxisols. Baldock et al. (1997) pointed out that in soils with variable charge, the interaction of OM with the mineral matrix may protect it against microbial attack, retarding the mineralization of OM and affecting its chemical composition as well, Oxisols being dominated by both O-alkyl and alkyl carbon. Polysaccharide-type OM associated with kaolinite (Wattel-Koekkoek et al., 2001) and that from iron-rich Ferralsols in central Brazil (Neufeldt et al., 2002) seem to be preserved mainly by a surface complexation between variable-charge minerals and OM.

12.7.6.2.4 Cryosols

Cryosols (Gelisols in the Soil Taxonomy) develop in association with near-surface permafrost. They are the zonal soils of the polar and subpolar regions, as well as higher elevations of other regions. Thus, they are widely distributed in northern Eurasia and northern North America and are also the dominating soils in the ice-free Antarctic, covering more than 8% of

the ice-free land surface on earth. Cryosols are formed under tundra, boreal forest, and cold desert vegetation. A comprehensive treatment of cryosols is found in Kimble (2004).

Cryosols develop under specific conditions from cryogenic processes that include cryoturbation, ice segregation, or cryodessication in the presence of permafrost. Cryosols are influenced by physical and chemical weathering to a larger degree than thought earlier, but the cryopedogenetic processes are dominating (Bockheim et al., 2006). The cryosol profile (**Figure 16**, Foto 4) is differentiated in an upper part, the so-called active layer, which freezes and thaws periodically. The lower part of the profile is constantly frozen and is the top of the permafrost layer (Cf horizon), which can reach depths of several hundred meters. The active layer often consists of an organic layer (O horizon) on top of the mineral soil (A/B horizons). Cryosol formation is characterized by cryoturbated soil profiles with warped or broken horizons, weak weathering, redoximorphic features in the lower active layers due to saturation above the permafrost, and OM moved into the lower active layer and the upper permafrost by frost churning. The permafrost table acts as a barrier to leaching so that weathering products accumulate in the active layer (Bockheim et al., 2006).

Michaelson et al. (2004) outlined that the Arctic and boreal zones hold about 12–13% of the total terrestrial carbon stocks in soils. Accumulation of organic C is strongly associated with cryosol formation, with major factors low temperatures and frost action (Ping et al., 2008). The major effect of frost is the formation of ice wedge polygons, resulting in patterned-ground soil surfaces and frost churning/mixing or cryoturbation. The litter produced aboveground or in the active layer (root litter) is drawn down to deeper layers. Once buried, unfavorable conditions due to soil freezing prevent decomposition of the OM. Preservation and protection of SOM is enhanced by cryoturbation, as the OM mixed into the lower mineral horizons is exposed to mineral interactions, low temperatures, more reducing redox conditions, and also encasement in the permafrost. Michaelson et al. (2004) report a ratio of 1:1:2 for the distribution of OC stocks between active-layer organic horizons, active-layer mineral horizons, and permafrost down to 1 m. A recent study suggests that in the northern circumpolar permafrost region, at least 61% of the total soil C is stored below 30 cm depth (Tarnocai et al., 2009). The OC stocks in the B/O and Cf horizon often result from cryogenic processes in such patterned-ground soils. In addition to cryoturbation, OC can also be incorporated in deeper layers due to repeated deposition of organic-rich alluvial material or long-term deposition of OM in peats.

A large proportion of the cryosol OM is composed of detrital plant residues in different stages of decomposition, including cell wall components and remnants. These materials are mainly composed of cellulose and hemicellulose components. They account for 50–57% of OC in organic horizons, 35–49% of OC in B horizons, and 49–77% of OC in the Cf horizons (upper permafrost; Michaelson et al., 2004). Cryosols are also reported to contain high proportions of low molecular weight soluble components (Michaelson et al., 2004). As these materials are easily decomposed under warmer conditions, climate change that affects the temperature and moisture conditions of cryosols will lead to higher release of organic C through increased decomposition rates, as the thickness of the active layer increases (Beer, 2008).

12.7.6.2.5 Andosols

Andosols have distinctive physical, chemical, and mineralogical properties that are not found in most other soil types. These specific properties are largely attributable to the formation of short-range order minerals with variable-charge surfaces that are strongly associated with the accumulation of OM. Andosols have the highest OC contents among the mineral soil orders and thus play an important role in the global C cycle. Soils with andic properties occur in all climatic regimes and cover about 120 million ha, which is nearly 1% of the world land surface (Dahlgren et al., 2004), but contain about 5% of the total OM stored in soils (Eswaran et al., 1993). The fine fraction of Andosols consists mainly of allophane, imogolite, and ferrihydrite associated with Fe- and Al-OM complexes. Andosols are characterized by a combination of features, which are together called 'andic' properties. These are very low bulk density, high OM contents, variable charge, high water-holding capacity, thixotropy, and high phosphate retention, due to their specific mineralogy.

Andosols (**Figure 16**, Foto 5) are differentiated in allophanic Andosols dominated by allophane and imogolite, whereas nonallophanic Andosols have mainly Al–humus complexes and 2:1 layer silicates. Allophane-containing Andosols (silandic Andosols in WRB) are soils formed from volcanic ashes and ejecta. The development of these specific minerals is directly related to the properties of the volcanic parent materials, which consists to a large extent of volcanic glassy particles. Rapid chemical weathering of these materials leads to the formation of a colloidal fraction dominated by short-range order and poorly crystalline constituents. The second group of Andosols develop from nonvolcanic parent materials but show the same andic properties as young volcanic ash soils. Nonallophanic Andosols dominated by Al–humus complexes are denominated in WRB as aluandic Andosols.

Due to the high productivity of Andosols, there is typically a large annual OM input via aboveground and belowground plant litter as well as root exudates into these soils. Radiocarbon age of OM in Andosols is often rather high, and it is considered that MRTs for OM in Andosols are considerably higher than in other soil types such as Mollisols or Cambisols (Aran et al., 2001; Inoue and Higashi, 1988; Nierop et al., 2005; Tonneijck et al., 2006). This also implies that Andosols preserve OC originating from previous land use for a long time as demonstrated by Dümig et al. (2009) in a study combining chemolytic and ^{13}C NMR spectroscopic analyses with stable isotope analyses. More than in other soil types knowledge of vegetation cover and changes in the past is necessary to interpret SOM composition, because of the possible preservation of OM components from earlier vegetation and land use.

Stabilization of OM in Andosols results from interactions with polyvalent cations and noncrystalline inorganic materials, specifically allophone, imogolite, or ferrihydrite. These mineral materials in turn impart a high amount of microaggregates to Andosols, which are responsible for the protection of OM. Thus, a significant fraction of OM in Andosols is inaccessible to decomposing organisms (Dahlgren et al., 2004; Tonneijck et al., 2010). In a nonallophanic Andosol, the minerals form

Figure 16 (Continued) Representative soil profiles of the world (4) Cryosol.

aggregated nanosized domains, most probably agglomerated nanosized $Al_x(H_2O)_y(OH)_z$ clusters. These extended micropores are combined with a mesopore network and form the unique physicochemical properties of this Andosol (Filimonova et al., 2011). In addition, stabilization of OM in Andosols often also occurs by burial of the topsoil due to repeated addition of fresh volcanic ash.

The capacity for stabilizing OC via organomineral interactions is high in Andosols, due to the high SSA of their short-range order mineral material. Accumulation of OC is therefore related to concentrations of noncrystalline materials, as was shown for soils formed from basaltic lava in Hawaii (Torn et al., 1997) and for allophonic Andosols on La Reunion (Basile-Doelsch et al., 2005). But metal–OM complexes with multivalent cations (Al^{3+} and Fe^{3+}) also play a major role for C sequestration in Andosols, specifically in nonallophanic Andosols (Tonneijck et al., 2010). Only few studies have characterized the OM composition in Andosols. Pyrolysis studies found no indication for the preservation of plant-derived OM, but high amounts of microbial polysaccharides and chitin point to a stabilization of secondary, microbial components in both allophanic and nonallophanic Andosols (Buurman et al., 2007; Nierop et al., 2005). Consistent with these results, the amount of lignin in Andosols is low, high aromatic carbon contents are found in Andosols that have undergone vegetation fires (Dümig et al., 2009; Golchin et al., 1997a,b). In acidic nonallophanic Andosols, an accumulation of aliphatic lipid-type materials is observed, probably due to toxic levels of Al^{3+} for microorganisms (Tonneijck et al., 2010).

12.7.6.2.6 Man-made soils (Anthrosols)

12.7.6.2.6.1 Paddy soils

Paddy soils make up the largest anthropogenic wetlands on earth. They may originate from any type of soil in pedological terms but are highly modified by anthropogenic activities. The formation of these Anthrosols is induced by specific paddy management operations (Kögel-Knabner et al., 2010). These are artificial submergence and drainage, plowing and puddling (= plowing and leveling the surface layer of a

Figure 16 (Continued) Representative soil profiles of the world (5) Andosol, by courtesy of Peter Schad.

submerged soil), organic manuring (animal manure, rice straw, and other crop residues, often fermented with sediments taken from the river or channel), liming, and fertilization. The specific flooding and drainage regime is associated with the development of a plow pan and redoximorphic features. Redox potential oscillations due to paddy management control microbial community structure and function and thus short-term biogeochemical processes. After flooding, microbial reduction processes sequentially use NO_3^-, Mn^{4+}, Fe^{3+}, and SO_4^{2-} as electron acceptors, accompanied by the emission of the trace gases like N_2O, H_2S, CH_4, and – due to reduction-induced increasing pH – NH_3. The management-induced change of oxic and anoxic conditions results in temporal and spatial (vertical, horizontal) variations in reduction and oxidation (redox) reactions affecting the dynamics of organic and mineral soil constituents (Cheng et al., 2009).

Paddy management leads to the development of pedogenetic horizons that are specific for paddy soils (**Figure 16**, Foto 6). Paddy soils are thus classified as Hydragric Anthrosols (IUSS Working Group WRB, 2006) and may originate from different reference soil groups. The specific soil management and the continuing paddy soil use lead to alternating redox conditions and therefore to soil properties and morphologies that are independent from the initial soil unit. Thus, paddy soil development is driven by the specific soil management practices that mask the soil's original character (Kirk, 2004).

The formation of a dense plow pan as a typical feature of paddy soils plays a decisive role for the accumulation of SOM in topsoils. The typical exchange with subsoil horizons will be prohibited, resulting in larger OC enrichment of topsoils but at the same time in decreased C input to subsoils by roots and DOM. Much steeper gradients in SOC concentrations in the

soil profile in paddy than in nonpaddy soils indicate such limited input of OC to subsoil horizons (Wissing et al., 2011).

High concentrations and fluxes of DOM in paddy soils from plant debris trigger the microbial activity and thus the emission of greenhouse gases. Retention of DOM by soil minerals and its subsequent stabilization against microbial decay depend on the redox state (e.g., DOC precipitation by Fe^{2+} under anaerobic conditions). Oscillation in redox conditions may enhance retention and stabilization of DOM by Fe oxyhydroxides.

Paddy soil management has a clear effect on the accumulation of SOM. After land embankment, organic C and N concentrations of the topsoils increased continuously with increased duration of paddy management, however, after 110 years a maximum was reached for N (Roth et al., 2011; Wissing et al., 2011). The SOM storage in paddy soils exceeded SOM storage in corresponding nonpaddy soils, which is in accordance with Wu (2011) and Shang et al. (2011), whose data also indicated higher OC concentrations and stocks in paddy soils compared to other arable ecosystems in China. Many studies confirm that SOM decomposition and the formation of stable SOM proceed at a slower rate in hydromorphic soils than in well-drained, aerated soils. However, as paddy soils are usually also prone to wet-and-dry cycles, the overall OM decomposition is not necessarily retarded in these soils. Wissing et al. (2011) found that a reduced crystallization of Fe oxides is accompanied by higher proportions of SOM stabilized in paddy soil. The higher accumulation of OC in paddy soils seems to be a result of OC accumulation by Fe oxides and – in turn – may hamper the crystallization of Fe oxides. OM accumulation in paddy soils also derives from high input of residues, partly also in the form of charred residues, under intensive management. Due to high silica demand of rice plants, the cycling of silicon is a special feature in paddy soils. Thus, phytoliths may play an important role for carbon stabilization, but it remains to be investigated whether carbon trapped in phytoliths is available to microbial attack or not.

In summary, the large accumulation of SOM observed in some, but not all paddy soils, is considered to be due to high input of plant residues and charred material associated with retarded decomposition under anaerobic conditions. There is also evidence for the stabilization of SOM via occlusion into aggregates and phytoliths as well as interactions with clay minerals and iron oxides. SOM accumulation in paddy subsoils can be explained by downward movement of DOM and its stabilization by interaction with iron oxides. A specific feature of paddy soils is the coupling of OM turnover with mineral transformations and fluxes, which seem to be intensified by the alternating redox conditions with increasing age of paddy soil development.

12.7.6.2.6.2 Terra preta

Another important Anthrosol that is distributed widely throughout Amazônia and gained increasing attraction in the last years is the so-called Indian black earth or Terra Preta do Indio. This soil occurs in patches of <1 ha to 350 ha and has been formed by the indigenous pre-Columbian population – about 500–8700 years ago (Liang et al., 2006; Neves et al., 2003; Smith, 1999). Surprisingly, these patches sustained a productivity that even today exceeds by far that of the surrounding Ferralsols. Hence, this soil is preferred by local farmers for the production of nutrient-demanding crops (Woods and McCann, 1999).

The typical Terra Preta soil is characterized by a dark thick A horizon, usually 70 cm deep but occasionally even reaching 2 m (Smith, 1980; Woods and McCann, 1999). This top layer is enriched in OM and, in contrast to the Ferralsols, has elevated contents of plant-available P and Ca, a less acidic pH value, and a high CEC (Glaser et al., 2001a,b; Lehmann et al., 2003; Liang et al., 2006; see also **Figure 16**, Foto 7). Ceramic and lithic debris witness their anthropogenic origin, though also related dark soils without these cultural artifacts exist. These rather brown than black soils are called Terra Mulata and they usually encircle the darker Terra Preta sites. They contain lower amounts of plant-available P and Ca but similar contents of organic C (Sombroek, 1966; Woods and McCann, 1999). For Latin America, both soils have been summed under the heading Amazonian Dark Earth (Lehmann et al., 2003). But it has been suggested that similar soils probably also exist in other areas of the world, for example, in Africa (Fairhead and Leach, 2009).

As the parent material of the Terra Preta is similar to that of the surrounding soil, it is the addition of the specific type of OM and its resistance against decay that must be responsible for its sustainable productivity in the last centuries. The OM of the Terra Preta is very aromatic (Zech et al., 1979), likely reflecting an input of charred OM (BC; Glaser et al., 2001b). Such BC particles are stable in soil, but its surfaces slowly oxidize or adsorb OM so that polar functional groups are nowadays found around the BC particles (Brodowski et al., 2005a,b; Lehmann et al., 2005; Liang et al., 2006). These functional groups finally explain the large potential CEC of the Terra Preta soils (Cheng et al., 2008). They do not yet explain the elevated nutrient contents like P and Ca. They are likely the result of the additional input of different kinds of wastes like ash, bones, excrements, and compost (Birk et al., 2011; Glaser et al., 2007).

Since the pre-Columbian population only possessed stone axes, it is unlikely that shifting cultivation had been the cause for the enrichment of charred material (Denevan, 2001; Glaser et al., 2001a). It is more likely that the Amerindians took advantage of forest clearing, which were then expanded by hand and controlled burning for the farming of maize, manioc, and other cultures in the shadow of remaining or planted trees, the cultures being possibly additionally fertilized with composted household debris (Denevan, 1996, 2001; Hecht, 2003; Schmidt and Heckenberger, 2009).

In summary, the Terra Preta soils are one of the rare but prominent examples, how the addition and alteration of OM to (oxidic) soils may change their properties so dramatically that they turn into fertile fields for centuries. The high fertility is therewith related to a favorable constellation of several processes, such as the preservation of recalcitrant aromatic C forms in a tropical environment, the transformation of BC to particles with high CEC, the long-term increase of the soil pH and the associated mobilization of nutrients, the strong interactions of the added and transformed OM to Fe and Al oxides, and the addition of nutrients like P and Ca with waste residues to a soil ecosystem that is usually P and Ca deficient.

Figure 16 (Continued) Representative soil profiles of the world (6) Paddy soil, by courtesy of Peter Schad.

12.7.7 Peculiarities

SOM comprises a vast range of different organic structures with a MRT in soils ranging from days to millennia. The dynamics of SOM in terrestrial and semiterrestrial environment, however, is controlled by processes that are different to those occurring in marine and other aquatic environments.

First, terrestrial precursor materials that form SOM comprise larger fractions of structures that are usually produced in much smaller amounts in aquatic ecosystems, such as lignins, tannins, cellulose, and some lipids (see also **Sections 12.7.2** and **12.7.3**).

Second, many of the soils are aerobic, whereas in marine and other aquatic environments, anaerobic conditions frequently limit the decay of OM. Hence, the residence time of the individual molecules in soil is usually shorter than under subhydrical conditions. While free monomers, such as root exudates, may be decomposed within hours, the residence time of SOM macromolecules usually ranges in the timescale of years to decades (Amelung et al., 2008). There is hardly any selective enrichment of these structures in the mineral soil. Hence, it is therefore the specific environment but not the inherent stability of the OM that contributes to C sequestration in soils in the long-term run (see also Schmidt et al., 2011, and **Section 12.7.6.1**).

Third, most soils are aggregated, frequently even hierarchically (see **Section 12.7.6.1**). The aggregates are also prone to turnover processes, for macroaggregates usually in the timescale of weeks to several decades, for some microaggregates even longer (Buyanovsky et al., 1994). The spatial separation of soils into zones or domains with different physicochemical properties and different accessibility for organisms implies that

Figure 16 (Continued) Representative soil profiles of the world (7) Terra Preta. Reproduced from Schmidt MJ and Heckenberger MJ (2009) Amerindian Anthrosols. Amazonian Dark Earths Formation in the Upper Xingu. In: Woods WI, Lehmann J, Rebellato L, Steiner C, Teixeira WG, and WinklerPrins A (eds.) *Terra Preta Nova – Where to from Here? Amazonian Dark Earths. Wim Sombroek's Vision*, pp. 163–191. Dordrecht: Springer, with permission.

the actual position of OM in this hierarchic architecture or the lifetime of aggregates often controls the turnover of organic compounds to a larger extent than their chemical structure.

At the nano- and micrometer scale, organic molecules have a patchy distribution on mineral surfaces and within soil aggregates (Figure 17(a)). Many organic molecules are stored within pores smaller than the soil biota or even exoenzymes,

thus being inaccessible for decay (see Section 12.7.6.1). However, unlike sediments in marine and other environments, soils exhibit also a pronounced heterogeneity at larger scales. At the millimeter and centimeter scale, it is mainly the growth of roots that creates hot spots of microbial activity in the rhizosphere and a priming of cometabolic SOM decay due to the release of available C sources from the plant roots (see Section 12.7.6.1). At the decimeter to meter scale (= scale of a soil profile), highest SOM contents are usually found in the surface soil (A horizon), where there is also the highest microbial activity. As soil depth increases, the degree of soil weathering declines, that is, the amount and availability of reactive biogeochemical surfaces decreases in the various subsoil horizons. Again, limited bioaccessibility but also unfavorable conditions for microbial growth contribute to the storage of old SOM in different subsoil horizons (see Section 12.7.6).

Besides, there is also a pronounced heterogeneity beyond the meter scale, that is, at the plot scale (several meters to hectares) or within the landscape, which affects stocks and turnover of SOM (Kölbl et al., 2007). Heterogeneous deposition of the geological substrate, erosion, and colluvium formation and also heterogeneous management and plant growth (Kölbl et al., 2011) result in a significant spatial variability of SOM (Figure 17(b), plot heterogeneity). At the microscale level, contents and turnover of SOM vary by a few orders of magnitude, which must be considered when modeling soil C and N dynamics. At plot scale, SOM contents still vary up to a factor of 2–3, sometimes even more, which must particularly be considered when sampling a soil. All conclusions about changes in SOM dynamics may be wrong, if not considering that the analytical result may be just different when sampling would have been performed a few meters

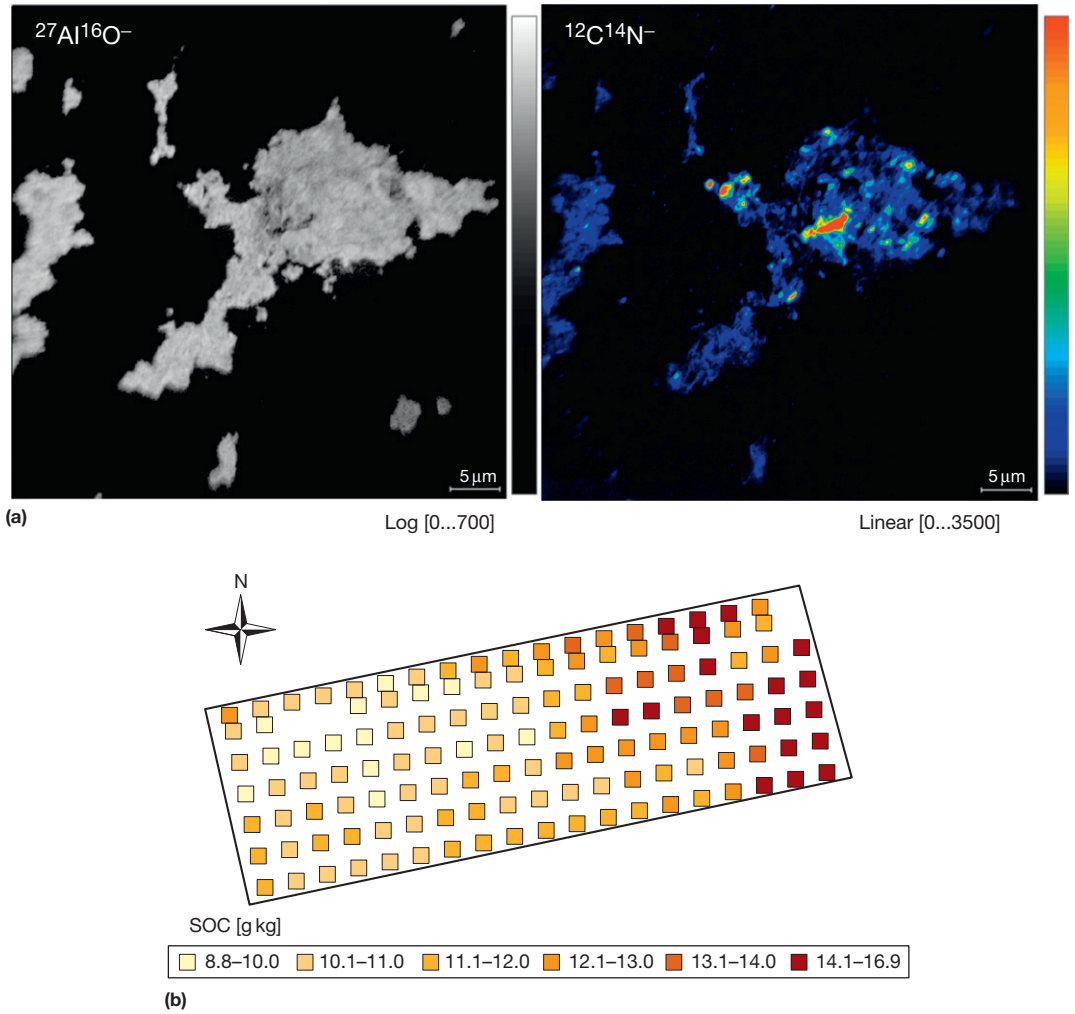


Figure 17 (a) Nanoscale secondary ion images for $^{27}Al^{16}O^-$ and $^{12}C^{14}N^-$, achieved on a Cameca NanoSIMS 50 L (TU München, Germany), of a clay-sized SOM fraction obtained from the Ap horizon of a Luvisol under agricultural use. The $^{27}Al^{16}O^-$ image indicates the distribution of the clay minerals on the sample mount (Si wafer), whereas the $^{12}C^{14}N^-$ map demonstrates the spatially heterogeneous distribution of organic matter (detected as cyanide ions) on the clay minerals at the microscale (Vogel et al., unpublished data). (b) Heterogeneity of soil organic carbon (SOC) contents at an arable field near Selhausen, Germany (Bornemann et al., 2010). Each square represents a sampling point, taken in a 10 by 10 m grid, with a 5 by 10 m grid for the northern border.

aside. Geostatistical procedures and noninvasive sensing tools are therefore increasingly needed to derive effective parameters of, for example, soil CO_2 release, to enable us to integrate the process understanding in soils into global models of biogeochemical element cycles (Herbst et al., 2012).

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