Soil Organic Matter

3

3.1 Origins, Distribution and Dynamics

In most topsoils, the mass of the soil **organic matter** only amounts to a few percent, but has an important influence on all soil functions and plays a central role in the global carbon cycle. For this reason, the **carbon content**, or the dark color value, is a differentiating criterion for soil descriptions in German and international classifications.

About 80 % of the terrestrial organic carbon reserves participating in the active C-cycle are bound in soils, and only about 20 % in the vegetation. Bound C is mainly returned to the atmosphere through soil respiration due to microbial oxidation processes. On the long term, the non-mineralized fraction remaining in the system is stored in the soil organic matter. This carbon is subject to stabilization processes in the soil, which protect it to a large extent against microbial decomposition. Under constant environmental and vegetation conditions, an equilibrium is reached in the soil between the supply and degradation of organic matter, resulting in a characteristic humus or organic matter content.

Due to its large surface area, soil organic matter is an important **sorbent** for organic and inorganic substances in the soil solution. It offers (mainly negative) charges and thus increases the cation exchange capacity, but also contains hydrophobic areas, where the less-soluble hydrophobic organic substances can be bound. At the same time, the organic matter is of central importance for the development of a stable soil structure through formation of soil micro- and macroaggregation. The organic matter content essentially determines the color of the topsoil and, especially in arable soils, has an effect on the soil heat balance. The mineralization of plant residues is a significant source of nutrients for plants and microbial biomass. Last but not least, soil organic matter is a source of C and energy for the soil fauna and microflora. Organic matter is the C and energy source for heterotrophic soil organisms, so that with constant environmental factors, there is a close correlation between organic matter content and biological activity. The maintenance of high biological activity requires constant replenishment of the consumed organic matter by adding plant residues to the soil (see Chap. 4).

The chemical composition of the organic matter is heterogeneous, because it consists of plant and animal residues at different stages of degradation. Soil organic matter comprises all of the dead plant and animal residues and their organic transformation products found on and in the mineral soil. It also includes substances introduced by human activities, e.g. synthetic organic substances (e.g. pesticides, organic wastes). Living organisms (edaphon, consisting of the soil flora and fauna) and living roots do not belong to the organic matter in soils.

The term humus is often used synonymous for the organic matter in soils. Soil organic matter is

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composed of a mixture of plant and microbial residues in different degrees of transformation. Humus is a complex organic material of brown to dark colored amorphous substances, which have originated during the decomposition of plant and animal residues by microorganisms, under aerobic and anaerobic conditions (Waksman 1938). Chemically, humus consists of certain constituents of the original plant material stabilized against decomposition, of substances modified during decomposition, either by processes of hydrolysis or by oxidation and reduction; and of various compounds synthesized by microorganisms.

In this chapter and in the rest of this book, the term **humus** refers to the dead **organic matter** in the soil as a whole. In mineral soils, the organic matter is mixed with the mineral phase, but it also forms the forest floor in many soils (ref. to humus forms). In addition to solid organic substances, the soil water also contains dissolved organic substances ("DOM" = *dissolved organic matter*).

The following components are often differentiated:

Plant litter: These are undecomposed or only weakly transformed plant residues, and the tissue structures are still morphologically recognizable. They include both aboveground dead **plant remains** and dead roots. These materials are found in the litter layer (L horizon) on the forest floor, but can also be isolated from the mineral soil as particulate or light organic fraction. They mainly consist of lipid, protein, polysaccharide and lignin compound classes. Their turnover time in the soil is short.

Partly degraded plant residues are found in the forest floor O horizons or occur inside aggregates. They are called occluded particulate organic matter as they can be isolated after destroying the soil aggregate structure. They have longer intermediate turnover rates.

Stabilized soil organic matter: These are strongly morphologically transformed substances without macroscopically perceptible tissue structures. They are stabilized against mineralization, i.e. they have a low turnover rate or a long residence time in soil. If they exist as organo-mineral compounds, they can be isolated from the mineral soil using particle size and density fractionation, and are then often referred to as heavy or fine organic fraction.

The decomposition of organic matter is also called **degradation**, and their transformation into humic matter is called **humification** or **stabilization**. **Mineralization** refers to complete microbial decomposition to form inorganic substances (CO_2, H_2O), where the plant nutrients (e.g. Mg, Fe, N, S, P) contained in the organic matter are also released. "Humification" is defined as the transformation and binding of organic matter in the soil, which leads to a stabilization against mineralization.

Humic substances can be isolated from soils by strong alkali and then further differentiated into acid soluble (fulvic acid) and acid-insoluble materials (humic acids). They are often used as model compounds for soil organic matter, but their occurrence in soils as defined macromolecular entities is questioned more and more (Piccolo 2001; von Lützow et al. 2006; Schmidt et al. 2011).

3.2 Contents and Quantities of Organic Matter in Soils

The carbon content of organic matter varies within individual substance classes, with polysaccharides containing about 40 % C, and lipids about 70 % C. The average C content is usually around 50 %. In addition to the nonmetals C, H, O, N, S and P, the organic matter in soils also contains metals. These occur either in an exchangeable form (especially Ca, Mg,), or are in the form of complexes, where they are generally firmly bound (e.g. Cu, Mn, Zn, Al and Fe).

The organic matter content in the individual soil horizons and the average organic matter content in different soils vary across wide ranges (Table 3.1, Chap. 7.2), and are also subject to a seasonal variation. The content of carbon in a soil is quantified by the concentration (mass of OC by mass of the soil, e.g. mg g^{-1}), and the amount of carbon by the stock (mass of OC, e.g. based on a

Table 3.1 Contents and stocks of organic matter in different soils of southern Germany; data from Wiesmeier et al. (2012)

Soil type Parent material Land use	Horizon	Depth (cm)	Bulk density (g cm^{-3})	Gravel content (%)	Texture sand/silt/clay (%)	OC content (g kg^{-1})	OC stocks (kg m^{-2})	OC stocks in the solum (kg m^{-2})
Calcaric Hyperskeletic Leptosol Limestone Mixed forest	O	0–3	0.20	0	–	382	2.3	7.3
	Ah	3–10	1.00	10	11/57/32	51	4.6	
	CAh	10–53	1.20	90	15/53/32	27	1.4	
Dystric Hyperskeletic Leptosol Quartzitic schists Coniferous forest	O	0–2	0.20	0	–	455	1.8	8.2
	Ah	2–12	1.00	28	58/38/7	74	5.3	
	AhC	12–37	1.00	60	58/38/7	11	1.1	
Dystric Cambisol Sandstone Deciduous forest	O	0–3	0.10	0	–	428	1.1	7.2
	Ah	3–8	0.48	2	61/32/7	58	1.4	
	AhBw	8–12	1.03	4	60/32/8	17	0.7	
	Bw1	12–43	1.53	8	59/32/9	8	3.5	
	Bw2	43–64	1.60	13	62/23/15	2	0.5	
Eutric Cambisol Loamy-sandy tertiary sediments Cropland	Ap	0–30	1.33	2	38/40/22	17	6.4	12.6
	Bw1	30–65	1.56	2	30/47/23	7	3.6	
	Bw2	65–89	1.57	4	18/55/27	5	1.8	
	C	89–105	1.59	10	30/46/24	3	0.8	
Luvisol Loess Cropland	Ep	0–33	1.33	0	6/66/28	13	5.8	10.2
	Bt1	33–45	1.52	0	2/53/45	7	1.2	
	Bt2	45–57	1.50	0	2/56/42	5	0.9	
	C	57–93	1.54	0	6/61/34	4	2.3	
Podzol Granite Coniferous forest	O	0–7	0.29	0	–	448	9.1	20.5
	Ah	7–10	0.80	20	59/30/11	46	0.9	
	Eh	10–37	0.92	40	65/28/7	30	4.5	
	Bhs	37–67	0.93	60	64/25/11	46	5.1	
	C	67–72	1.00	70	50/35/15	59	0.9	
Gleysol Fluviatile sediments Grassland	Ah	0–21	1.29	0	60/32/8	26	6.8	17.6
	2Ahl	21–29	1.31	0	47/40/13	21	2.7	
	3Alh	29–45	1.22	0	38/43/19	16	3.8	
	4Blr	45–69	1.23	0	42/36/22	13	3.0	
	5Brl1	69–81	1.61	0	67/19/14	3	0.5	
	6Brl2	81–100	1.73	0	75/13/12	2	0.8	
Planosol Deciduous forest	Ah	0–5	0.74	0	7/74/19	57	2.1	8.1
	Eg	5–35	1.18	2	8/73/19	12	4.1	
	2Bg	35–75	1.36	5	8/44/48	3	1.3	
	2C	75–90	1.58	20	12/52/36	3	0.6	

(continued)

Table 3.1 (continued)

Soil type Parent material Land use	Horizon	Depth (cm)	Bulk density (g cm^{-3})	Gravel content (%)	Texture sand/silt/clay (%)	OC content (g kg^{-1})	OC stocks (kg m^{-2})	OC stocks in the solum (kg m^{-2})
Ombric Histosol Raised bog	H1	0–20	0.10	0	–	533	10.7	52.3
	H2	20–40	0.10	0		533	10.7	
	H3	40–60	0.10	0		523	10.5	
	H4	60–90	0.10	0		507	15.2	
	H5	90–100	0.10	0		535	5.4	
Rheic Histosol Grassland	H1	0–6	0.23	0	–	403	5.6	69.2
	H2	6–20	0.16	0		513	11.5	
	H3	20–48	0.13	0		529	19.3	
	H4	48–100	0.12	0		525	32.8	

depth of 1 m over 1 ha). The quantity of organic matter, in turn, depends on the soil type, the bulk density and the content of stones and coarse fragments. Soils with finer textures generally store more organic matter than coarse-grained soils. Litter horizons have organic matter contents close to 100 %; their organic carbon content (OC) usually lies between 400 and 450 g kg^{-1}. The highest concentrations and turnover of organic matter are found in the topsoil. Ah horizons in forest and arable soils have C contents of 7.5–20 g kg^{-1}. In German arable soils, the organic matter stocks average 100–200 t ha^{-1}. They can be higher in colluvial soils, Chernozems, Andosols, Vertisols and Podzols. Higher contents can be found in the topmost horizons of permanent grassland soils (up to about 150 g kg^{-1}). The carbon concentrations in the subsoil, with the exception of colluvial soils, Fluvisols, Podzols, Vertisols and Andosols, are much lower and mostly lie between 1 and 10 g kg^{-1}. Recent inventories demonstrate that large amounts of organic matter, although in low concentrations, are stored in the subsoil (B and C horizons). Redoximorphic soils exhibit particularly high C concentrations, e.g. the A horizons of Gleysols contain up to 200 g kg^{-1}, H horizons of fens and bogs more than 200 g kg^{-1}, whereby raised bogs can contain up to almost 500 g kg^{-1} C. In contrast, the OC contents in soils of arid regions are much lower due to the low litter input, with typical values lying between 2 and 6 g kg^{-1}. The stocks of organic carbon in soils fluctuate across a wide range. They are regulated by, among other factors, the climate, vegetation and thus also the input of organic matter, the groundwater level, the rooting depth, and the soil type (Table 3.1).

Global estimations show that about 1500 Pg of organic carbon (1 Pg = 10^{15} g) are stored in the first meter of terrestrial soils, about 700 Pg of which is found in the top 30 cm (Table 3.2). When considering a soil depth of 0–2 m, Batjes (1996) obtained a total of about 2400 Pg OC. In comparison, the global C reserves in the plant biomass only amounts to about 500 Pg C. Changes or redistributions of the C stocks in the soil are thus very important for the **global C budget**.

Only a small fraction of the soil organic matter is water soluble and mobile, so it usually does not play a role for the C balance. The mobile, dissolved phase is still significant for pedogenic processes, e.g. podzolization, but also for the binding and translocation of contaminants. The soil solution contains between 1 and 100 mg L^{-1} of dissolved organic carbon (DOC).

The **quantitative determination** of the organic matter can be performed using different methods:

1. Oxidation by combustion in oxygen and determination of the liberated CO_2. In soils

Table 3.2 Global stocks[a] of terrestrial organic carbon (Pg C) by IPCC climate region in soil, and in above- and below-ground phytomass carbon pools (from Scharlemann et al. 2014)

Climate region	Soil		Total (%)	Phytomass (%)	Terrestrial carbon pool
	Topsoil	Subsoil			
Tropical wet	62.6	65.4	128.0 (47.7)	140.2 (52.3)	268.1
Tropical moist	78.6	72.3	150.9 (49.9)	151.7 (50.1)	302.6
Tropical dry	67.3	69.0	136.2 (76.2)	42.5 (23.8)	178.7
Tropical montane	29.6	26.5	56.1 (58.1)	40.5 (41.9)	96.6
Warm temperate moist	33.3	29.7	63.0 (68.7)	28.7 (31.3)	91.7
Warm temperate dry	38.9	39.6	78.5 (76.4)	24.2 (23.6)	102.7
Cool temperate moist	104.1	106.2	210.3 (88.1)	28.5 (11.9)	238.8
Cool temperate dry	52.2	50.0	102.2 (91.8)	9.1 (8.2)	111.3
Boreal moist	162.0	194.7	356.7 (93.8)	23.5 (6.2)	380.2
Boreal dry	32.0	37.0	69.1 (93.1)	5.1 (6.9)	74.2
Polar moist	30.6	21.7	52.4 (96.0)	2.2 (4.0)	54.5
Polar dry	8.0	4.3	12.3 (96.2)	0.5 (3.8)	12.8
Total	699.3	716.4	1415.7 (74.0)	496.6 (26.0)	1912.2

[a] Estimates of global soil OC stocks by topsoil (0–30 cm), subsoil (30–100 cm) and the combined layers (0–100 cm or when less to depth of soil layer)

containing carbonate and at combustion temperatures exceeding 650 °C, it is necessary to remove the carbonates prior the analyses, or to determine the concentration of carbonate-C separately (Kalbitz et al. 2013).

2. If the thermal method is not available, the oxidation of the organic matter using Cr(VI) (dichromate) in a sulfuric acid solution and photometric determination of the formed Cr (III) can be used (based on Walkley and Black 1934). Alternatively, the excess dichromate Cr(VI) or the CO_2 released by oxidation can be determined. The Walkley-Black method also requires the removal or separate determination of carbonate-C.
3. In organic soils and in soils where clays are largely absent, the determination of the loss on ignition at 400 °C provides sufficiently accurate values.

The C content is determined using method (1); the organic matter content is then calculated by multiplying this value by 2.0. The factor 1.724 is also sometimes used, which results from an assumed average C content of the organic matter of 58 %. Dichromate oxidation (2) also records other oxidizable substances, e.g. Fe(II) sulfides. The edaphon is also included to some extent in the determination of the organic matter, because it (except for larger animals or roots) hardly can be removed from the sample before analysis. However, the related error is seldom more than 10 %; it can be roughly estimated by determining the microbial biomass.

3.3 Plant Residues and Their Transformation During Decomposition

3.3.1 Composition and Structure of Organic Residues

3.3.1.1 Litter Type and Quantity

In addition to the **above-ground biomass** produced by green plants during photosynthesis (wood, leaves, needles, twigs) and falling to the ground as litter when they die, **the parent materials** for soil organic matter formation include dead roots, organic root exudates and residues (**rhizodeposition**) as well as dead soil fauna and microorganisms. These plant and edaphon residues are continuously added to the biologically active horizons of the soil. Plant residues and exudates are called primary resources, and those from microorganisms are secondary resources. In addition to the incorporation of crop residues, organic matter is also added to cultivated soils through fertilization and waste disposal (e.g. liquid manure, compost, sewage sludge). Soils in industrial-urban areas are often also contaminated with organic constituents from the petroleum and coal industry, as well as from coal combustion (e.g. tar oil, coal dust, black carbon).

The above-ground litter in forests mainly consists of leaves and/or needles. In deciduous forests of cool temperate climates, the twigs, bark and fruit only account for a fraction of about 20 %, and in coniferous forests of 20–40 % of the total litter falling on the surface. In temperate climate zones, the contribution from herbaceous vegetation to the total aboveground litter in forests amounts to less than 5 %. The fraction of the foliage in the total aboveground litter represents on average about 70 %. In coniferous forests, the total aboveground litter was estimated to be of 200–600 g dry mass m^{-2} a^{-1}. Similar ranges are also found for the aboveground input in deciduous forests, e.g. beech forests with 390–570 g m^{-2} a^{-1}. In coniferous forests, e.g. under spruce, litterfall is not restricted to a specific season. In general, the average quantity of aboveground litterfall in forests increases with decreasing latitude and increasing productivity from boreal coniferous forests (100–400 g m^{-2} a^{-1}) to the tropics (600–1200 g m^{-2} a^{-1}). In intensively managed forests, the proportion of leaf or needle litter is high compared to the woody constituents.

A considerable portion of the organic matter reaches the soil as below-ground input, i.e. as root litter and rhizodeposition. The predominantly low-molecular, usually N-rich organic matter that is secreted by plant roots (rhizodeposition) contributes significantly to the C input to the soil. Most of the root exudates are rapidly metabolized by microorganisms, and due to this constant C source, there is a high population density in the rhizosphere. About 30, 50, and 75 % of the root biomass are found in the topmost 10, 20 and 40 cm of the soil respectively; however, the maximum rooting depth, and thus also the range influenced by root residues and rhizodeposition, is much larger. In this way, root residues and exudates also reach greater depths, and together with translocated organic matter from the topsoil, contribute significantly to organic matter formation in the subsoil. Grassland and steppe soils generally exhibit a greater proportion of root mass in the total carbon input compared to forest ecosystems under comparable climatic conditions. In forests of cool temperate climates, the contribution of root litter to the input of organic matter, depending on the tree species and the life form (evergreen or deciduous), accounts for between 20 and 50 %. Under wheat cultivation, the subsurface input is around 25 % of the total C input, under grassland around 40 %.

3.3.1.2 Chemical Composition of Plant Residues

Essentially, there are two different types of tissues undergoing decomposition: parenchymatic tissues and woody tissues. Parenchymatic plant cells are found in the living, green tissues of leaves, and in the cortex of young twigs and fine roots. They consist mainly of cellulose and protein. Woody tissues form the woody parts (xylem) and the supporting tissue (sclerenchyma) of the stems, leaf epidermis, leaf veins and bark. Woody plant residues, such as straw or wood, contain mainly cellulose, hemicellulose and lignin (also called lignocellulose).

Cellulose makes up the cell wall and consists of glucose units that are linked to each other in linear chains through hydrolyzable, glycosidic bonds. The regular arrangement of the hydroxyl groups along the cellulose chain leads to the development of H bonds, and thus to the fibrillar structure with crystalline properties that is characteristic for plant organisms, accounting for around 85 % of the cellulose molecule. **Hemicellulose** and **pectin** are also cell wall components and differ from cellulose in their arrangement of various carbohydrate monomer types, namely pentoses, hexoses, hexuronic acids and deoxyhexoses (Fig. 3.1), with side chains and branching. Plant hemicellulose in the soil can hardly be analytically differentiated from microbial polysaccharides. The pentoses arabinose and xylose originate mainly from plant residues, while microorganisms mostly produce the hexoses galactose and mannose, as well as deoxyglucose (rhamnose and fucose). As a storage polysaccharide, **starch** is a component of the cell and consists of glucose monomers.

Lignin is a high molecular, three-dimensional substance made of phenylpropane units (Fig. 3.2a). In woody plants, it fills and strengthens the structure of the cell wall, which mainly consists of linear polysaccharides. The lignin from coniferous trees consists almost exclusively of coniferyl alcohol units, and that from deciduous trees has approximately equal proportions of coniferyl and sinapyl alcohol. The lignin found in grasses is formed from about equal proportions of the three monomers coniferyl, sinapyl and p-coumaryl alcohol. The various proportions of the individual phenylpropane units result in different methoxyl group contents, which are around 15 % for gymnosperm lignin and 21 % for angiosperm lignin. The monomers are linked by a multitude of non-hydrolyzable C–C and C–O bonds.

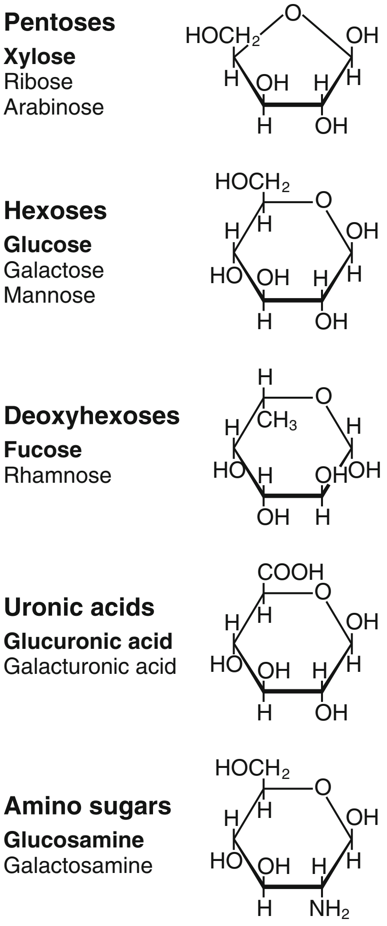


Fig. 3.1 Important sugar monomers in soils

Tannins are natural polyphenols with a great diversity of compositions. The hydrolizable tannins are esters formed by glucose and gallic acid. The more complex structure of non-hydrolyzable tannins or proanthocyanidins consists of up to 10 polyhydroxy-flavan-3-ol units. Organic compounds with tanning properties are capable of irreversibly linking proteins to one another. It is assumed that this effect also plays a role in the decomposition of litter in the soil, stabilizing proteins against degradation.

Cutin forms the macromolecular frame of the plant cuticle, which covers all of the aerial plant parts and is bound to the epidermis through a pectin layer. The cuticle consists of cutin, an

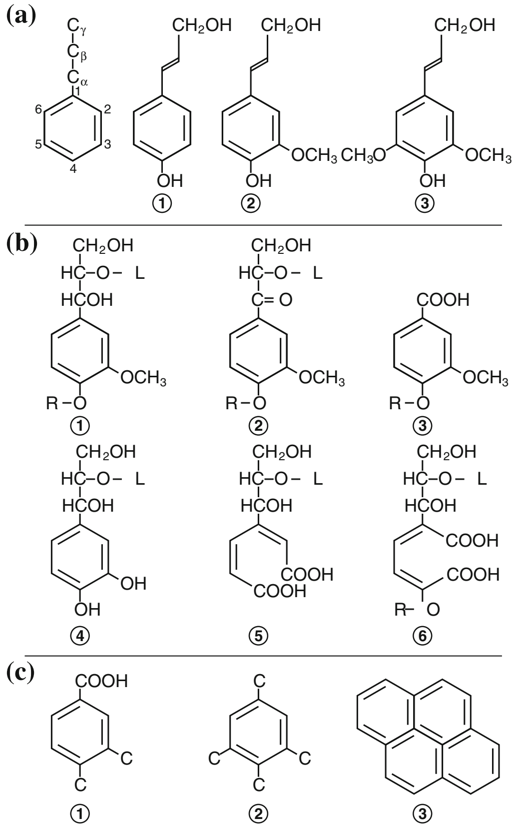


Fig. 3.2 Aromatic building blocks of organic matter. **a** Monomeric precursors of lignin (phenylpropane units): (*1*) p-coumaryl alcohol, (*2*) coniferyl alcohol, (*3*) sinapyl alcohol; **b** fragments of phenylpropane units modified by decomposition. (*1*) Intact phenylpropane unit in the macromolecule, (*2*) α-carbonyl formation, (*3*) splitting off of the side chain and oxidation of the Cα, (*4*) demethylation to o-diphenyl, (*5*, *6*) ortho-ring cleavage; **c** possible basic structures of the aromatic components in humic substances: C substituted (*1*, *2*) and condensed (*3*) aromatic C

insoluble polyester made of various hydroxy and epoxy fatty acids, mostly with chain lengths of C_{16} and C_{18}, in which low-molecular waxes and fats are embedded. These extractable **lipids** consist of a series of different substance classes, e.g. long-chain hydrocarbons, primary and secondary alcohols, ketones, triglycerides and wax esters. Similar to cutin, the *suberin* found in the root cortex and subsurface storage organs also has a polyester structure, however, it is embedded in the cell wall of the peridermal cells. In addition to aliphatic components, consisting of long-chain fatty acids and dicarboxy(lic) fatty acids (about 5–30 %), there is also a multitude of phenolic components, especially cinnamic acid.

Proteins are the most common intracellular compounds. They consist of a group of about 20 different amino acids that are connected with each other through peptide bonds. 99 % of the nitrogen in the remains of plants and animals are bound in organic form, mainly in proteins. Proteins also contain the majority of organically bound sulfur in the form of the amino acids cystine, cysteine and methionine.

N is also found in **DNA** (deoxyribonucleic acid), the carrier of genetic information, and in RNA (ribonucleic acid), responsible for the translation of the information for protein synthesis. The individual building blocks are deoxyribonucleotides, each consisting of one heterocyclic N compound (the purine or pyrimidine bases adenine, thymine, guanine, uracil and cytosine), the monosaccharide deoxyribose and one phosphoric acid molecule. They form the double helix structure of DNA.

P in plant residues occurs mainly in organic compounds as orthophosphate mono- and diesters, mostly in **inositol phosphates**, which are esters with hexahydroxycyclohexane, and **phospholipids**.

Root exudates contain a multitude of generally low-molecular components, whereby sugars and polysaccharides, organic acids, amino acids and peptides dominate.

The proportions of the individual contents in different raw materials are given in Table 3.3. The cell wall constituents cellulose, hemicellulose and lignin, as well as lipids, cutin/suberin and proteins are the most important components, accounting for more than 95 % both in the above-ground plant parts and the roots. In addition, plant residues contain a multitude of secondary constituents such as phenols, free sugars, amino acids, peptides and secondary metabolites, such as phenols and resins.

3.3.1.3 Microbial Residues

Here, the most important secondary resources are the residues from bacteria and fungi, which mainly serve as a source of C and energy

Table 3.3 Common composition of important C and energy sources for decomposition in the soil: plant residues, microorganisms; % dry matter (compiled from Haider 1992; Fengel and Wegener 1989; Swift et al. 1979)

	Cellulose	Hemicellulose[a]	Lignin % DM	Protein	Lipids[b]	C/N
Spruce (*Picea abies*)						
Wood	40	31	28	<2	1.4	100–400
Bark	48	17	38	<2	21	
Needles	15	13	14–20	3–6	7	40–80
Beech (*Fagus sylvatica*)						
Wood	32	43	24	2	0.8	100–400
Bark	38	23	39	2	11	
Leaves	20	17	11–16	6	5	30–50
Root wood	33	18	22	1.6	1.3	190
Fine roots	19	10	33	5.4	3.1	55
Ryegrass (shoot)	19–26	16–23	4–6	12–20		
Alfalfa (shoot)	13–33	8–11	6–16	15–18		
Wheat straw	27–33	21–26	18–21	3		50–100
Bacteria	0	4–32	0	50–60	10–35	5–8
Fungi	8–60 (chitin)	2–15	0	14–52	1–42	10–15
Phytoplankton (lakes)		18 + 50[c]	0	17	1.5	5–12

[a] and other non-cellulosic polysaccharides

[b] and/or other fractions that are extractable with solvents (e.g. waxes, resins, chlorophyll)

[c] non-structural carbohydrates

(Table 3.3). With the exception of lignin, tanning agents and cutin/suberin, all of the above-mentioned plant compound classes are also found in bacteria or fungi. Bacteria cell walls consist of murein, lipids and lipopolysaccharides. Murein is a peptidoglycan, which, in addition to amino acids, contains the bacteria-specific constituents galactosamine, muramic acid and diaminopimelic acid. High proportions of aliphatic biomacromolecules of lipidic nature were detected in the cell walls of various bacteria and algae, the precise structure of which is not yet known. Many bacteria produce extracellular polysaccharides consisting of neutral and acidic sugars. The cell walls of fungi contain proteins, chitin (an amino sugar polymer consisting of glucosamine, similar to cellulose), sometimes cellulose, and other polysaccharides containing a high fraction of mannose and glucose. The exoskeleton of arthropods (Chap. 4) is also made of chitin. Specific components of bacteria or fungi can be used as biomarkers to estimate the proportion of microbial residues in the soil. Glucosamine from fungi and bacteria, and galactosamine and muramic acid from bacteria are particularly well-suited for this purpose.

3.3.2 Decomposition and Transformation Reactions in the Soil

The degradation and mineralization of litter takes place in several closely interacting phases. Numerous organisms of the soil fauna and flora are involved in these decomposition and transformation processes. The first transformation processes take place already shortly before or immediately after plant organs or animals die, consisting of enzymatic reactions of the organism's own substances (senescence). Here, polymer compounds are broken down into individual components by hydrolysis and oxidation processes inside the cells (e.g. starch into glucose, proteins into amino acids). Chlorophyll is transformed into colorless decomposition products, while yellow carotenoids accumulate and red anthocyanins are formed, resulting in the autumn colors of leaves. Furthermore, a large portion of the mineral nutrients (K, Mg, Ca, u. a.) are liberated and can be leached or absorbed by plants.

When the organic matter is deposited on or in the soil and is broken down by the soil fauna, it is rapidly mineralized to CO_2, while the majority of the mineralized N is incorporated into the microbial biomass. The C/N ratio therefore becomes narrower during the course of decomposition, and can reach values of about 10. The mineralization of organic matter to form CO_2 occurs from all soil organic matter compartments, with the highest rates from the decomposition of fresh litter and the turnover of the microbial biomass. Because of the properties of their chemical structures, certain macromolecular components of plants or microorganisms are not readily decomposable by microorganisms, and are called **recalcitrant**. Especially aromatic plant constituents, particularly lignin, but also long chain aliphatic compounds accumulate selectively in the soil during decomposition compared to other, more readily decomposable substances, such as polysaccharides. The availability of a N source probably plays an important role in the regulation of the decomposition of lignocellulosic substances in the soil. Lignin can only be decomposed under aerobic conditions and its decomposition is inhibited by oxygen deficiency, so that only low-molecular lignin components or lignin precursors are attacked. This causes the accumulation of lignin in anoxic soils or sediments (formation of peat and coal). During the course of the decomposition of litter, phenols can form recalcitrant polyphenol-protein complexes together with proteins and thus reduce N losses in N-poor sites. The condensed aromatic structures (Fig. 3.2c) resulting from vegetation fires are considered to be recalcitrant. In general, the following stability sequence can be derived for organic compounds originating from plants: sugars, starches, proteins < celluloses < lignins, wax, resins, tannins.

A considerable portion of the organic matter in soils can consist of finely distributed charred organic matter (*black carbon*, *charcoal*), originating from vegetation fires. The leads to an incomplete combustion of organic materials that leaves behind a continuum of charred aromatic structures condensed to different degrees. Both the chemical recalcitrance and interactions of the charred structures with minerals protect them from rapid degradation, so that estimates for the residence time of char in soils range from a few hundred to more than 10,000 years.

3.3.2.1 Decomposition Pathways for Various Plant Constituents

The decomposition of sugars, starches, proteins, hemicellulose or cellulose, and non-lignified parts (Fig. 3.3) in general takes place most rapidly. In contrast, lignocellulose is decomposed much more slowly, as well as already decomposed material, e.g. peat, manure or compost. Aquatic plants do not have any supporting tissue, and therefore do not contain lignocellulose. This is why the organic matter in subaquatic soils is generally much more strongly decomposed than peats or bogs in near-shore marine environments. Polysaccharides (cellulose, hemicellulose) and proteins serve as a C and energy source for microorganisms and are fully metabolized in the process. After extracellular enzymatic hydrolysis the resulting monomer or dimer fragments are absorbed by the microorganisms. These substances are oxidized by heterotrophic bacteria as a source of energy ("catabolism"). H_2O and CO_2 are produced as end products in aerobic environments, while the associated mineral salts are taken up by the bacteria or are released in the soil solution. The same products can be produced under anoxic conditions, provided that other oxidizing agents (electron acceptors) such as NO_3^-, SO_4^{2-}, Mn(IV) or Fe(III) are available. However, decomposition is then slower and usually incomplete, and results in low-molecular organic substances such as fatty

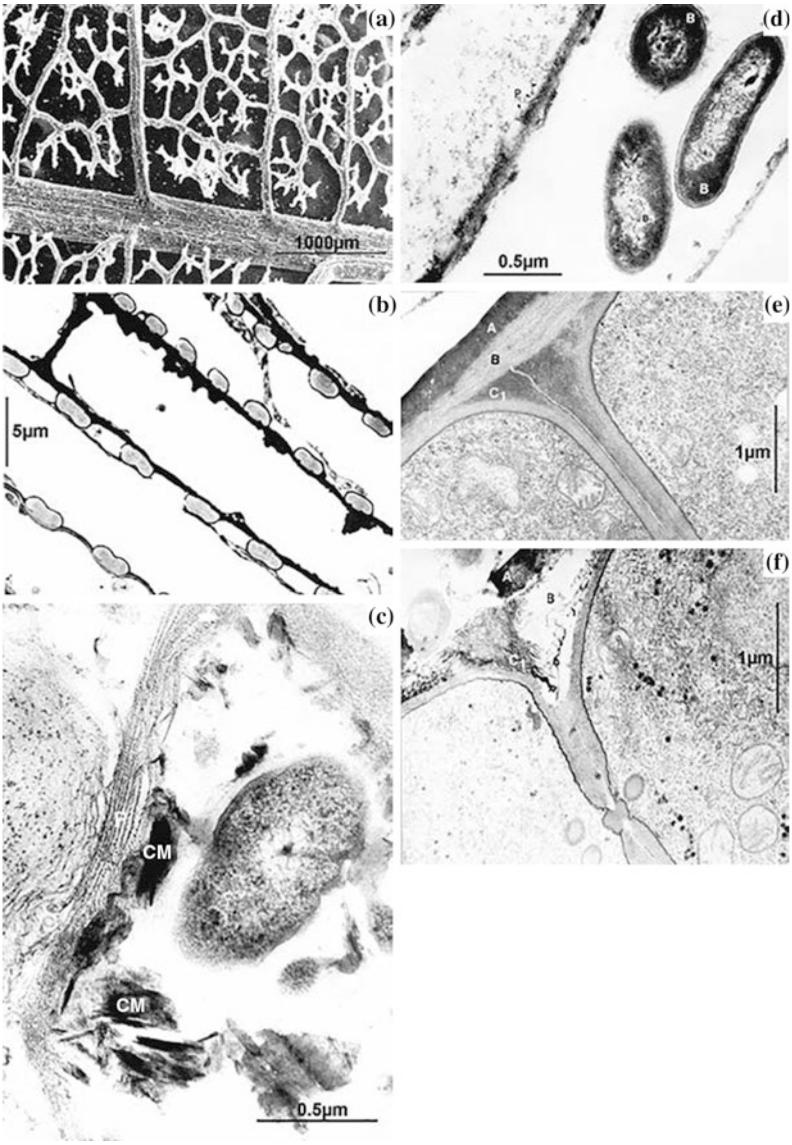


Fig. 3.3 Scanning electron microscope image of an oak leaf 4 weeks after falling off the tree (from Olah et al. 1978): **a** Preferential decomposition of parenchymatic tissues, the ligneous tissues remain behind; **b** fungi can be seen on the surface of the decomposed leaf. **c** Polysaccharide fragments (*P*) of an algae cell in close association with clay minerals (CM); decomposition of secondary resources: **d** invasion of a fungi (*Stropharia cubensis* Earle) by bacteria and decomposition of the cytoplasm after 7 days in the soil; **e/f** fungi cell wall before and after decomposition by bacteria

acids, methane, hydrogen sulfide or also hydrogen, with a lower energy gain for the microbes.

A portion of the easily digestible substrates is directly taken up by the microorganisms and used for the synthesis of their cells ("anabolism"). Labelling with radioactive or stable isotopes (usually ^{14}C, ^{13}C and ^{15}N) showed that the C and N from polysaccharides and proteins added to soils is found in the microbial biomass or their metabolites. Thus, plant polysaccharides and proteins are mainly subject to microbial resynthesis. A small fraction of the polysaccharides can be selectively accumulated due to "impregnation" with recalcitrant plant (lignin, cutin) or microbial constituents (melanin).

In contrast, the decomposition of lignin takes place much more slowly as an extracellular, co-metabolic process, i.e. the lignin does not serve as a C or energy source for microorganisms. For this reason, the decomposition of lignin requires the presence of a C and energy source (e.g. sugar, cellulose), since the lignin-decomposing microorganisms, mainly white rot and soft rot fungi, cannot grow with lignin as their only source of C. Brown rot fungi cause a modification of the lignin (e.g. demethylation), but no complete decomposition. Thus the fate of C from lignin is different to the fate of C from polysaccharides and proteins. Lignin decomposition takes place through a non-specific radical mechanism, which leads to the cleavage of bonds in the side chains and in the aromatic rings (Fig. 3.2b). On the one hand, a liberation of CO_2 is observed that indicates partial mineralization, and on the other, often only part of the lignin macromolecule is transformed in its structure. These modified lignin components are subject to further direct oxidative transformation. Especially the more easily degradable fractions of lignin, particularly those units that are linked by ether bonds, are strongly transformed. Lignin macromolecules that are modified by degradation consist of aromatic components with a high degree of C substitution, mainly carboxyl groups (Fig. 3.2c). Because of this and because of the opening of the rings during decomposition, the lignin molecule becomes increasingly soluble in bases and also in water. Thus a part of the partly degraded lignin components are leached. The recalcitrant lignin constituents, i.e. the ring units that are linked by C–C bonds, are selectively accumulated. Lignocelluloses in the soil are decomposed by a synergetic microbial community, where cellulose and lignin decomposing organisms work together. The microorganisms use both low-molecular lipids and cutin as a C and energy source, and at the same time, new microbial alkyl-C compounds are formed in the soil. Generally all recognizable plant or microbial components in a soil have turnover times lower than the turnover times of the total organic matter (Amelung et al. 2008).

3.4 Formation of Stable Organic Matter

Plant and microbial residues and their transformation products can be protected from further microbial degradation through various mechanisms. These stabilization processes have an effect on the mixture of fresh and transformed plant residues resulting from the decomposition phase, as well as on newly-formed microbial residues that were in turn transformed (Fig. 3.4). They lead to a significant deceleration of the initial rapid mineralization rate.

Parts of the litter can be protected from further decomposition inside aggregates where they are poorly accessible, and thus enter the moderately stable organic matter fraction. Poorly decomposable components (e.g. lignin or aliphatic compounds) can be selectively accumulated in these plant residues at different states of decomposition. The sorption of dissolved organic matter (DOM), resulting either directly from the

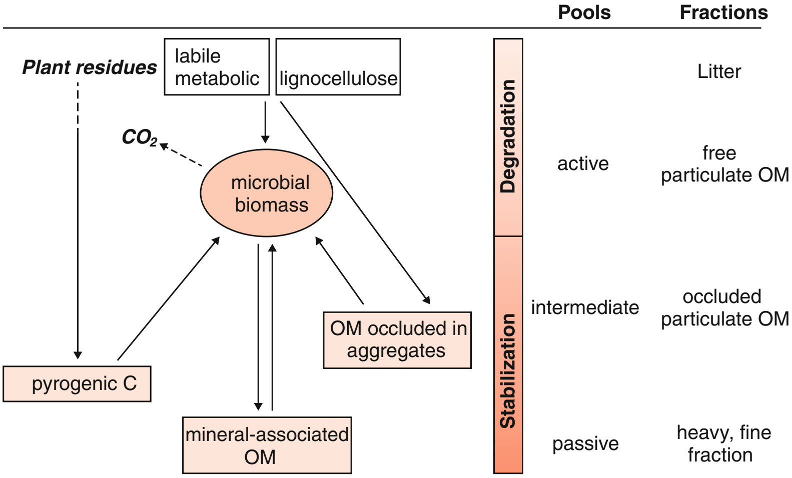


Fig. 3.4 Processes of transformation and stabilization (humification) of organic matter (OM) in the soil

decomposition of litter or from the microbial biomass, can lead to the transfer of carbon into the stable fraction. The development of organo-mineral compounds leads to the formation of stable organic matter products, which are mineralized only very slowly. Especially microbial polysaccharides and proteins are stabilized against further decomposition through binding onto the fine-grained minerals of the silt and clay fraction (Fig. 3.3c).

3.4.1 Stabilization by Interactions with the Mineral Phase

Organic substances can be stabilized and protected from microbial degradation through interactions with minerals. This mainly involves interactions with particles in the clay fraction (clay minerals, iron oxides). This leads to the formation of stable "**clay-organic matter associations**" or **organo-mineral compounds**. The binding between minerals and organic substances can take place through various mechanisms and depends on the one hand on the type of mineral and its surface charge, and on the other, on the type and charge of the functional groups in the organic matter. Therefore, pH value and base saturation are of great importance for the development of organo-mineral compounds. The following mechanisms play a role in binding of organic matter onto the mineral phase (Fig. 3.5):

1. Binding onto singly coordinated hydroxyl groups on the mineral surface, which can be either protonated or dissociated depending on the pH value of the soil. Through **ligand exchange**, inner-sphere complexes are formed between the carboxyl groups of the organic matter and protonated surfaces with positive partial charges. Here, the surfaces of Fe and Al oxides, allophanes and imogolites, and also the edge surfaces of clay minerals are most significant, whereas no ligand exchange reactions take place with silanol groups (SiOH) (Fig. 3.5a, b). Fe and Al oxides, allophanes and imogolites provide a particularly high specific surface area for such interactions. Because ligand exchange reactions only take place with protonated, singly-coordinated hydroxyl groups, they mainly play a role in acidic soils.
2. In soils with slightly acidic or neutral pH values, binding onto the siloxane surface of clay minerals (Chap. 2) with permanent charge increases in significance (Fig. 3.5a). The dominating mechanisms are the ionic bond between organic cations and the negative charges of clay minerals. The main organic cations involved are amines (alkyls etc.), amino sugars and amino acids, which accept a proton below the isoelectric point and thus have a positive charge. They are instead of the exchangeable inorganic cations bound by Coulomb forces. But also metal complexes of organic acids can be adsorbed. A polyvalent, usually hydrated metal cation forms a bridge and simultaneously neutralizes negative charges on the clay mineral and on the dissociated acidic groups of the organic molecule. An outer-sphere complex is formed. The exchangeable cations of clay minerals, especially polyvalent cations such as Ca^{2+} and Al^{3+}, can have an effect on the stability of the organo-mineral compounds. The adsorption of organic acids onto a smectite that is saturated with various cations increases in the sequence $Na^+ < K^+ < Ca^{2+} < Al^{3+} < Fe^{3+}$. Extractants, such as sodium pyrophosphate, which transform Fe, Al, and Ca into soluble complexes therefore also extract a relatively large amount of organic matter from the soil.
3. Weak interactions occur between the uncharged, nonpolar groups of the organic matter and the uncharged, neutral mineral surfaces (e.g. Si–O–Si groups) (Fig. 3.5c). Hydrogen bonds play a role in the binding of larger organic molecules. H bonds form preferentially via H_2O molecules of the exchangeable cations, or between molecules that are sorbed and those that are not yet sorbed. In contrast, they occur less frequently between these directly with the mineral

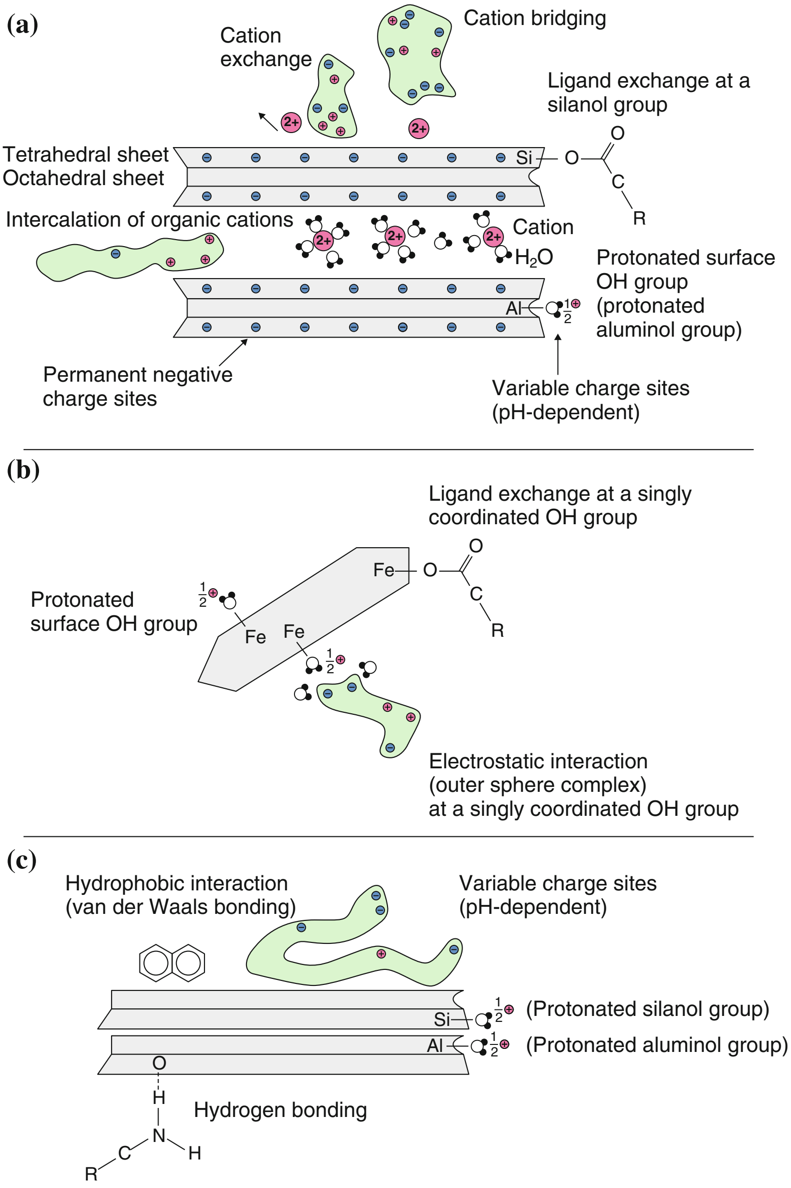


Fig. 3.5 Binding mechanisms of clay-humus coupling in the soil. **a** On phyllosilicates with permanent charge, **b** on (hydr)oxide surfaces with variable charge, **c** on minerals with neutral surfaces

surface. Despite the weaker and short-ranging individual bonds compared to the interactions mentioned above, Van der Waals interactions are probably mainly responsible for the binding of larger molecules onto the uncharged surfaces of clay minerals, e.g. kaolinite, pyrophyllite, or quartz. Hydrophobic interactions can then lead to additional binding of organic substances onto already sorbed molecules. They are most significant at low pH values, because the hydroxyl and carboxyl groups are then protonated.

4. The decomposability of organic matter can also be strongly reduced by complex formation with metal cations. In this case, the bonding of metal cations (Ca, Al, Fe, heavy metals) onto the organic matter inhibits attack by enzymes.

This strong association between organic and mineral matter in soils is evidenced by the fact

Table 3.4 Properties and composition of organic matter in the particle size fractions of the A horizon of a Cambisol (Guggenberger et al. 1994)

Characteristic	2000–63 µm	63–2 µm	<2 µm
Composition (%)	Plant residues		
Alkyl C (e.g. lipids)	40–46	31–44	46–50
O Alkyl C (mainly polysaccharides)	35	26–30	22–25
Aryl C (aromatic C)	24–26	16–27	13–14
C/N ratio	Wide	Medium	Narrow
Degree of transformation of lignin	Low	Medium	Strong
Origin of polysaccharides	Mainly plant	Plant/microbial	Mainly microbial

that it is impossible to fully separate the organic matter from the mineral phase. It is possible to use an alkaline solution (0.1 N NaOH, humic substance extraction) to partially extract the organic matter from the soil, but a non-extractable fraction (the so-called humic fraction) always remains in all soils. A further portion can be extracted when the minerals are previously dissolved using hydrofluoric acid. Even through oxidation with H_2O_2 or NaOCl, it is not possible to completely destroy the bound organic matter.

There are many simple organic compounds that can be bound onto minerals of the clay fraction. These include alcohols, sugars, amino acids and amines, as well as simple aromatic compounds such as benzene, phenols etc. If the clay fraction is isolated from the soil and its composition is investigated, mainly alkyl compounds and polysaccharides are found, however, only low concentrations of aromatic compounds, such as strongly transformed lignin fragments (Table 3.4). Bound organic matter is also rich in carboxyl and amide groups.

The stabilization in organo-mineral compounds is also highly significant for the organic nitrogen, the majority of which is bound in the clay fraction in the form of slowly mineralizable peptide structures. Some of these compounds are also enzymes. Their activity and the decay rate are reduced by binding onto the minerals of the clay. For this reason, the C/N ratio in the clay fraction is often between 8 and 12. However, it must also be considered that this also includes the NH_4^+ that is bound to the clay minerals. The association of organic substances and clay minerals becomes visible under the electron microscope (Fig. 3.6). The high stability of organo-mineral compounds is reflected by the fact that the temperature of thermal decomposition of organic matter increases after binding onto the mineral phase, and at the same time, the **decomposition rates** of these bound organic substances decline strongly.

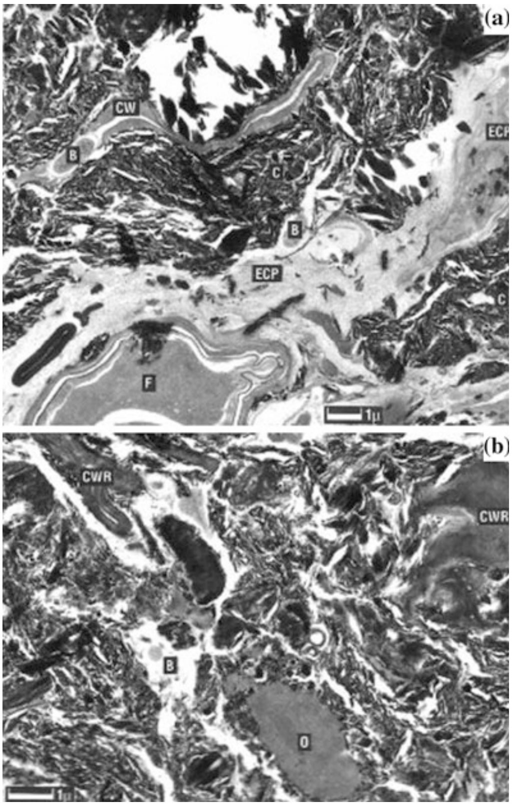


Fig. 3.6 Scanning electron microscope images of the association between organic matter and mineral particles in the soil; *B* bacteria cells, *C* clay minerals, *ECP* extracellular polysaccharides, *F* fungi, *CW* cell wall of a collapsed cells, *CWR* cell wall remains, *O* amorphous, humified organic matter (after Ladd et al. 1996)

The cation exchange properties of clay minerals apparently hardly change through bonding/binding with humic substances. In contrast, organic substances can effectively compete with the sorption of inorganic anions onto clay minerals and oxides. Furthermore, the crystallization ("aging") of pedogenic Al and Fe oxides can be delayed or inhibited, if adsorbed organic substances combine in very stable complexes with Al and Fe ions. The polarization of the adsorbed organic molecules and the high charge density of the clay minerals may promote catalytic reactions (protonation, oxidation, polymerization).

3.4.2 Stabilization by Spatial Separation

Stabilization of otherwise readily decomposable substrates in the soil can result from the spatial separation of the substrate from the decomposers, which thus prevents degradation. The spatial localisation of organic matter in aggregates hinders access by microbes and enzymes. Inaccessibility is mainly caused by occlusion of OM in aggregates and entrapment of OM in pore spaces. This usually involves partially decomposed plant residues that are occluded inside the aggregates and are inaccessible to microorganisms. It was observed that the plant residues occluded inside aggregates are enriched in lignin, while the polysaccharides had already been degraded.

Soil aggregation has a strong effect on the physical separation between substrate and decomposers. The distribution and composition of organic matter is regulated by the aggregation, which in turn is determined by, among other things, the soil type, the pedogenesis and the activity of the soil fauna. The aggregation of mineral soil particles by organic matter is a complex series of interactions, taking place at various spatial scales (Fig. 3.7). Particles in the clay fraction are aggregated into packages of <20 µm, which are then in turn bound to form stable microaggregates with a size of 20–250 µm. These are bound together to form macroaggregates (>250 µm). Mainly polysaccharides, secreted by roots and microorganisms, are responsible for the formation and stabilization of microaggregates. Microaggregates are stable over decades. Macroaggregates result from the effects of roots, fungal hyphae and other plant residues, which link the microaggregates together to form larger aggregates. For this reason, stable macroaggregates have a high proportion of relatively young particulate organic matter. The stabilizing effect of these organic constituents in the macroaggregates only lasts for a few years. The composition and properties of the macroaggregate surface therefore differs significantly from those inside the aggregates.

The formation of organo-mineral compounds in soils as well as aggregation are promoted by high biological activity, because microorganisms

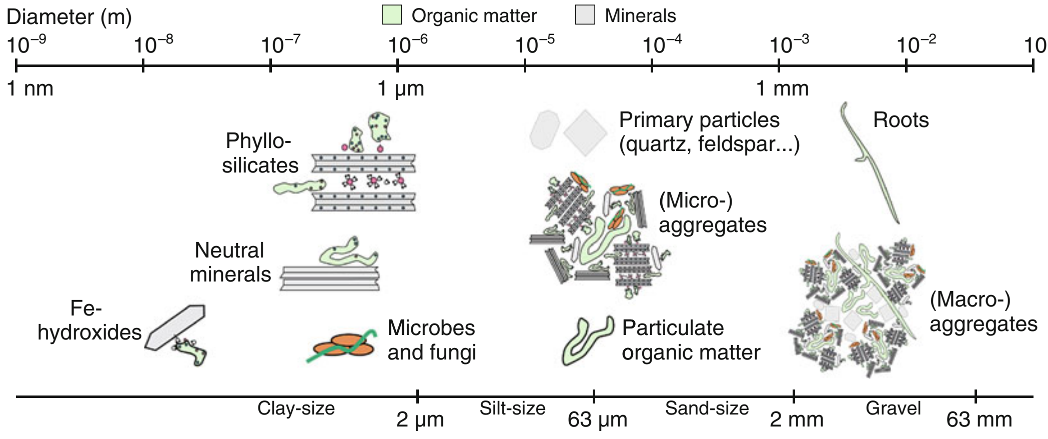


Fig. 3.7 Diagram of the association of organic matter in micro- and macroaggregates in soils of temperate climates

constantly form reactive organic substances (e.g. mucus) and soil fauna mixes organic matter closely with mineral particles (see bioturbation). Here, the formation of organo-mineral compounds in the intestines of earthworms is of special importance. The combination of poorly degradable organic substances (e.g. peat) with clay minerals under sterile conditions, in contrast, does not result in any stable organo-mineral compounds, even after a longer period of exposure. The significance of organo-mineral compounds for soils lies mainly in the fact that the organic matter binds mineral particles together and thus makes a considerable contribution to the structure formation. Accordingly, the formation of stable aggregates is closely linked to the development of organo-mineral compounds. If the supply of organic residues is reduced or even totally eliminated, the structure formation is strongly impaired. This is associated with an initial depletion of the organic matter, especially in the fraction of the occluded plant residues.

3.4.3 Organic Matter in Functional Soil Fractions

Physical fractionation, based on a separation resulting from differences in density or particle size, is used to separate the plant residues from organo-mineral compounds. It is generally performed following pre-treatment consisting of agitation or ultrasound to destroy the aggregates. The obtained fractions are then separated using sieves, sedimentation and/or density fractionation (Christensen 2001). With **density fractionation**, the sample is suspended in a liquid with a density between 1.6 and 2.4 g cm^{-3} (organic solvent mixtures or inorganic salts), so that the light, floating organic material can be separated. For **particle size fractionation**, the material in the >63 µm fraction (sand fraction) is separated, which can be further fractionated by sieving. The organo-mineral compounds <63 µm are separated using sedimentation in water, and the <2 µm fraction can be further separated via centrifugation. Fractionation according to the particle size and the density are often combined. Using such combined particle size and density fractionation, it is possible to separate specific organic matter fraction from mineral soils. The particulate organic matter can be found in the light or coarse fraction, which mainly consists of partly decomposed plant residues. The heavy and fine fractions mainly contain organo-mineral compounds. If the aggregation is selectively destroyed by ultrasound, the occluded particulate organic matter, mainly plant residues with a higher degree of decomposition, can be isolated.

The OC fraction in organo-mineral compounds, which cannot be separated from the clay by ultrasonic treatment (to destroy the aggregates) and subsequent density separation, lies between 10 and 95 % in various soils. In general, organo-mineral compounds account for high proportions of the total carbon especially in the subsoil, while in the topsoil, a larger fraction of plant residues can be found in a form that is free and/or occluded in aggregates. The content of this particulate organic matter is higher in topsoils under forest or grassland than under cultivated land. Plant residues are mainly added to the topsoil; this is why their proportion in the organic matter here is also the highest, while organo-mineral compounds dominate in the B horizon. For this reason, the degree of decomposition generally increases from top to bottom. However, it must be considered that root litter and leaching of particulate and dissolved organic matter have an influence on the composition of the organic matter in the subsoil.

3.5 Composition and Properties of Soil Organic Matter

3.5.1 Binding Forms of C, N, P and S in Soil Organic Matter

Characteristic changes in the composition of the organic matter take place during the course of decomposition and stabilization processes. The relative proportion of aromatic compounds generally remains constant or decreases, the polysaccharides or O/N-alkyl C fraction decreases, and the alkyl C (long-chain aliphatic C compounds) fraction increases. These conversion processes lead to an increase in the alkyl C to O/N-alkyl C ratio, a parameter often used for the degree of decomposition of organic matter. These typical changes can be observed both in the organic layers of forest soils and in the particle size fractions of mineral soils (Table 3.4). The proportion of carboxyl groups also increases considerably during the course of humification. This higher oxidation state is responsible for the high, pH-dependent cation exchange capacity of organic matter.

Vegetation and forest fires are observed on about 530×10^6 ha of land annually worldwide. These fires convert approximately 90 % of the biomass to CO_2 and NO_x; however, charcoal is also formed due to the incomplete combustion, which represents a relevant C and N sink when entering the soil. It is assumed that charcoal is mainly formed in steppe and savanna soils through (natural) fires, but it also plays a role in soils of temperate and boreal zones. This *black carbon,* the decomposition product of charcoal resulting from vegetation fires, is stored in the soil and remains stable over long periods of time. For this reason, in addition to the morphologically identifiable pieces of charcoal often found in soils, high proportions of aromatic C and N compounds can also be found in the finely distributed soil organic matter. This pyrogenic carbon probably mainly contributes to the organic matter in particularly dark humic soils. High proportions of black carbon have been documented in Chernozems and Chernozem-like soils, and in anthropogenic soils (Terra preta). The charcoal residues are most probably responsible for the condensed aromatic structures (Fig. 3.2c) observed in many soils. Their formation from the lignin of plant residues or other precursors during biochemical conversion processes has not been documented. Condensed aromatic structures in the soil organic matter are increasingly used as an indicator for vegetation fires. Soils at the periphery of industrial areas often also contain organic components originating from industrial sources, such as coal dusts, ashes and soot.

Nitrogen is an important constituent of soil organic matter. While most of the C is liberated as CO_2 over the course of decomposition, N is initially mainly stored in the microbial biomass, more than 95 % of which is stabilized in organic matter on the long term. The C/N ratio of the organic matter therefore becomes increasingly narrow during the course of degradation and associated soil organic matter formation, reaching values of 10–12 in soils or soil fractions which have been intensively processed. The major part of the organically bound nitrogen is probably stabilized in the form of amide structures. The majority of the nitrogen is found in the form of peptide groups, a smaller portion in the form of free amino groups. Wet chemical analyses demonstrate that amino acids and amino sugars, together accounting for about 30–70 % of the total organic nitrogen, represent the majority of the molecular units containing N. However, because the hydrolysis is not complete, the total content of peptide structures cannot be determined. Proteins and enzymes are sorbed onto the clay fraction of soils, and are probably responsible for the narrow C/N ratio of the organic matter in this fraction. Contrary to former beliefs, the proportion of nitrogen in heterocyclic aromatic compounds is considered to be low with a maximum of 5–10 %. However, soils affected by vegetation fires exhibit higher proportions of heterocyclic N compounds, especially pyrrole and indole structures.

Sulfur is also always a component of soil organic matter. The C/S ratio is of about 200 in grassland and forest soils, and about 130 in cultivated soils. Up to 90 % of the sulfur is bound in organic form, about 30–75 % of which as sulfate ester. Another important binding form that is found is C-bound sulfur at various oxidation levels. Reduced organic S (oxidation level $< +1$) includes organic mono- and disulfides as well as thiols, e.g. as a component of proteins and peptides; intermediate organic S (oxidation level +2 to +5) includes sulfoxides; sulfones and sulfonates; oxidized organic S (oxidation level +6) includes ester sulfates and sulfamates. According to Prietzel et al. (2007), the distribution of the S binding forms depends on the land use and the O_2 availability in the soil. The proportion of reduced organic S binding forms increases in the sequence: Arable land < forest soil < moor.

Phosphorus is also found in soils with more than 60 % in organic form. Although a portion of the organically bound phosphorus could not yet be identified, more than 50 % of the total P in soils has been found to be in the form of phosphate esters. Analysis using nuclear resonance spectroscopy (^{31}P) demonstrated that the most important chemical forms are orthophosphate monoester R–OPO_3^{2-} (inositol phosphates, mononucleotides, sugar phosphates), orthophosphate diester R_1–OR_2–OPO^{2-} (phospholipids, DNA and RNA, teichon acids) and phosphonate (C–P binding).

3.5.2 Properties of Soil Organic Matter

The properties of the humic substances determine the soil's characteristics in many ways. Of course, the influence of organic matter on the properties of mineral soils is highest in the A horizons.

The **adsorption capacity** of humic substances is significant for the binding of many nutrients that are present as cations in the soil. During the course of the humification process, the CEC increases through oxidation and the formation of carboxyl groups. In general, a sufficient humus supply is particularly important for maintaining the CEC in clay-poor soils, or soils where the clay fraction mainly consists of clay minerals with low CEC, e.g. kaolinite. This is particularly true for organic layers and moors, where the CEC is almost exclusively attributed to the organic matter, as well as sandy soils, which owe about 75 % of their cation exchange capacity to organic matter. The CEC of isolated humic substances lies between 300 and 1400 $cmol_c\ kg^{-1}$, but it is strongly pH-dependent. The CEC of soil organic matter is much lower at 60–300 $cmol_c\ kg^{-1}$, because the less transformed litter substances only have a low CEC. In addition, part of the charges can be protonated or is not available for the CEC due to interactions with the mineral phase or complex formation.

Table 3.5 Sorption capacity of the mineral and organic components of an Ah horizon with different organic matter contents for heavy metals (Lair et al. 2007)

	Sorption capacity ($mmol^2\ kg^{-1}\ L^{-1}$)		
	Cu	Cd	Zn
Mineral phase	10.7	2.5	3.5
Soil organic matter			
Bare fallow 10.0 mg C g^{-1}	65.2	21.4	25.4
Grassland 26.0 mg C g^{-1}	87.5	33.0	37.7

Metal ions, especially Cu^{2+}, Mn^{2+} and Zn^{2+}, but also other polyvalent cations (e.g. Fe^{3+}, Al^{3+}), can also be found in stable complexes with organic compounds. In water-soluble form, these chelates can be transported downwards through the soil with seepage water (e.g. within the scope of podzolization). They also increase the availability of chelated micronutrients for plants.

Organic matter also has a great significance for the **binding of inorganic and organic pollutants** in soils. The binding of pollutants onto organic matter regulates their bioavailability and thus also their persistence. On the one hand, this prevents direct harm to organisms, and on the other, it also reduces or retards their translocation to deeper soil layers or to the groundwater. Investigations in soils with different humus contents show that the organic matter is mainly responsible for the binding of heavy metals. Depending on the humus content, the organic matter in the Ah horizon of a Cambisol provides 6–16 times more sorption capacity for Cu, Cd and Zn than the mineral phase (Table 3.5).

Soils with higher organic matter contents are characterized by a higher **porosity** and lower **bulk density**. This results in a linear relationship over a wide range, only small changes are observed at high OC contents, which are attributed to the organic matter's low density.

Organic matter has considerable effects on the soil's wettability. Plant residues and strongly transformed humic substances have hydrophobic properties. The binding of organic molecules to the surface of (hydr)oxides and clay minerals generally causes these surfaces to be more water repellent. This has an effect on the development of flow paths in the soil.

Organic matter has a positive effect on the structural stability of soils. It favors the formation of a **stable aggregate structure**, particularly in Cambisols, Luvisols and Chernozems. The binding of organic matter onto the surfaces of (hydr)oxides and clay minerals leads to the development of very stable microaggregates (<250 μm), which serve as building blocks for the less stable macroaggregates (>250 μm) (aggregate hierarchy). The development of macroaggregates is particularly characteristic for clayey soils and requires the continuous input of organic residues. This promotes microbial activity and thus the production of microbial polysaccharides, which are mainly responsible for the stabilization of macroaggregates.

This effect is less pronounced in Ferralsols and Andosols, because here mainly oxides and hydroxides have a stabilizing effect in primary organo-mineral compounds, while macroaggregation is largely lacking. Increased aggregate stability counters the effects of erosion, since there is less tendency towards soil surface sealing. Furthermore, the stability towards heavy loads is improved.

Humus has a high **water storage capacity**; it can store about 3–5 times its own weight in water. Through the aggregating effect, organic matter also has an indirect effect on the pore size distribution and water balance. This is why the humus content determines the field capacity in sandy soils. By adding large amounts of barn manure, it was possible to increase the humus content in such soils from 0.93 to 1.38 % within a period of 18 years, whereby the pore volume increased from 38.4 to 41.4 %. Mulch covers also decrease evaporation and increase the infiltration of water. A high soil organic matter content shifts the soils' **consistency limits** towards higher water contents, so that soil tillage can be performed at a wider soil moisture range without structural damage.

Humic substances are the source of the dark color of the topsoil, and thus promote the warming of the soil in the spring in cool climate regions (longer vegetation period). On the other hand, an organic layer or mulch can lead to insulation of the mineral soil against temperature fluctuations.

3.6 Soil Organic Matter Dynamics

3.6.1 Turnover Rates and Turnover Time of Organic Matter in Soils

The **turnover time** is defined as the quotient of the humus in the soil with the annual input of organic matter:

Turnover time (*a*) = amount of OM (kg m^{-2})/annual net input (kg m^{-2} a^{-1})

Under the assumption of steady state conditions, one obtains information on the turnover time of organic matter in the soil, i.e. the period of time that is required to completely transform the organic matter one time. The annual input of organic matter represents about 3–5 % of the stocks; about the same amount of C is liberated back into the atmosphere. This results in estimated average turnover times of several decades. Depending on the data used, it is estimated to be of 26–40 a, but large differences are observed in different climate and vegetation zones. Estimated turnover times are of 18 a for soils under grassland, 16 a for deciduous forests, 6 a for tropical forests, 7 a for agricultural soils, and more than 2000 a for tundra soils.

The inverse of the turnover time delivers the **decomposition rate** k (a^{-1}) = annual net input (kg m^{-2} a^{-1})/amount of OM (kg m^{-2}).

Depending on the composition and site conditions, decomposition rates can vary across a wide range. They fluctuate between 0.03 a^{-1} in tundra soils and 6 a^{-1} in tropical rainforests. Decomposition rates of up to 2–3 % d^{-1} are known to exist for readily degradable crop residues on field sites. In forest soils of temperate zones, rates of approx. 0.1 % d^{-1} are given for readily decomposable substances, and up to 10^{-5} % d^{-1} for poorly decomposable substances, which then represent an (almost) inert fraction.

3.6.2 Estimation of the Turnover Time

3.6.2.1 ^{14}C Content of Organic Matter

The **radiocarbon age** of the soil organic matter is derived from the natural ^{14}C activity. The radiocarbon method is based on the measurement of the ratio of the quantity of the carbon isotope ^{14}C to ^{12}C in a sample. The average turnover time of OC in the soil or in soil fractions can then be calculated from the decay constant or the half-life of ^{14}C. The ^{14}C content of a sample can be either determined by counting the decaying ^{14}C nuclei with a Geiger counter or by counting the still existing ^{14}C nuclei using accelerator mass spectrometry. The latter method requires less material, but is more complex and expensive. The results are given in pmC (percentage of the modern C fraction) or as ^{14}C age in years before present, and are based on a standard from the year 1950. The determination the ^{14}C/radiocarbon age enables an estimate of the average turnover time of the organic matter in soils or individual fractions. Meanwhile, it is possible to determine the ^{14}C contents for individual components of the organic matter, e.g. for the microbial biomass and also for the mineralized CO_2 (Fig. 3.8). The use and atmospheric testing of nuclear weapons between 1945 and 1963 strongly increased amount of ^{14}C in the atmosphere. Still today, the $^{14}C/^{12}C$ ratio has not yet dropped back to levels from before 1945. This bomb (radio)carbon can be detected in soils and generally changes the ^{14}C signature of the organic matter to "younger" values, however, due to its penetration behavior into deeper soil horizons and in various organic matter classes, it can be considered as a tracer enabling conclusions about current pedogenic processes, e.g. bioturbation in Chernozems, pedoturbation in Vertisols, cryoturbation in Cryosols, and percolation into the aquifer.

The organic/litter layers of forest soils are recent, as is also the topmost layer of Ah horizons, with a ^{14}C age of less than 500 years, because the organic matter in the topmost profile section is continuously being renewed by the addition of fresh plant litter. The impact of C losses through the cultivation of native soils became obvious in the Great Plains, where the average ^{14}C age was increased by 900 years. This demonstrates that cultivation mainly liberates C from fractions with a low ^{14}C age.

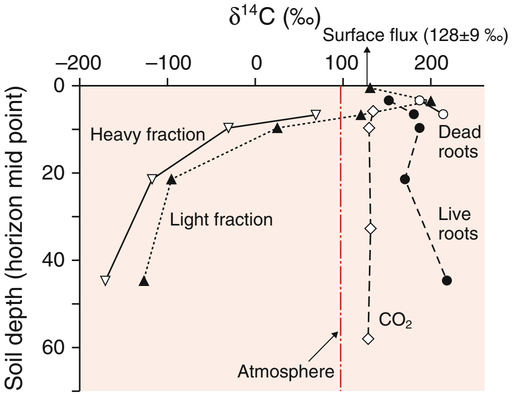


Fig. 3.8 $\delta^{14}C$ contents ($^o/_{oo}$) of various organic matter fractions in a forest soil in temperate climates (after Trumbore 2000)

With increasing depth, the radiocarbon age achieves values between 2500 and 4000 years before present. Both in cultivated and in native Phaeozems, the organic matter at a depth of 10–20 cm demonstrates a 1200-year higher ^{14}C age than at a depth of 0–10 cm. This is coupled with a lower mineralization rate of the organic matter from deeper soil horizons. ^{14}C ages of up to 5000–6000 years BP were observed in the subsoils of Chernozems and Luvisols, while the Bh horizons in Podzols have a younger ^{14}C age due to constant additions of recent OC.

In general, the ^{14}C age of the individual organic matter fractions increases with increasing profile depth (Table 3.6). As expected, smaller, still poorly decomposed fragments of lignin and polysaccharides are usually only 10–100 years old. Organic matter that is bound in organo-mineral associations is particularly well stabilized against decomposition. The oldest organic matter is found in the fine silt and clay fractions, e.g. in the illuvial horizon of Luvisols.

Table 3.6 Characteristic parameters for various organic matter fractions in soils: organic C contents and stocks

Horizon	Depth (cm)	OC concentration (g kg^{-1})	OC stock (kg m^{-2})	Fraction < 1.6 g cm^{-3}.$^{a)}$	Fraction > 1.6 g cm^{-3}	Fine soil		Fraction < 1.6 g cm^{-3}.$^{a)}$		Fraction > 1.6 g cm^{-3}	
				(g kg^{-1} OC)		^{14}C activity (pmC)	^{14}C age (years BP)	^{14}C activity (pmC)	^{14}C age (years BP)	^{14}C activity (pmC)	^{14}C age (years BP)
Steinkreuz (*Cambisol*)											
Ah	0–5	82.6	4.29	770	230	112.3	Modern	112.4	Modern	111.9	Modern
Bv1	5–24	9.8	2.41	500	500	101.3	Modern	104.8	Modern	98.0	160 ± 25
SdBv2	24–50	3.0	0.79	230	770	92.1	655 ± 25	119.0	Modern	84.2	1375 ± 30
IISd Bv3	50–80	1.4	0.40	190	810	80.9	1700 ± 30	122.8	Modern	69.8	2890 ± 30
IIICv	85–115	1.1	0.14	160	840	80.6	1758 ± 56	117.2	Modern	70.8	2780 ± 45
IVC1	115–140	0.5	0.07	150	850	76.3	2165 ± 30	116.4	Modern	69.1	2960 ± 30
Waldstein (*Podzol*)											
Ae	0–10	38.1	2.90	750	250	93.6	525 ± 30	92.0	655	98.5	120 ± 25
Bh	10–12	92.8	1.04	270	730	98.5	120 ± 25	95.8	435	99.5	30 ± 20
Bs	12–30	52.0	5.47	210	790	91.1	745 ± 40	87.0	1010	92.2	700 ± 25
Bv	30–55	7.7	2.09	120	880	82.2	1570 ± 25	87.3	980	81.5	1640 ± 20
C1	55–70	1.7	0.25	100	900	62.0	3840 ± 70	90.8	730	58.8	4265 ± 30
C2	70–80	1.9	0.19	80	920	62.0	3840 ± 70	112.8	Modern	56.5	4580 ± 30
Rotthalmünster (*Luvisol*)											
Maize Ap	0–30	12.9	5.35	186^{a}	814	102.7	Modern 54^{b} (±4)	nd	nd	106.5 ± 0.3	Modern 58^{b} (+9/-8)
	30–45	6.7	1.55	232^{a}	768	nb	144^{b} (+9/-8)	nd	nd	97.5 ± 0.3	205 ± 22 151^{b} (+23/-18)
Forest	0–7	40.5	2.57	563^{a}	437	108.3	Modern	nd	nd	nd	nd

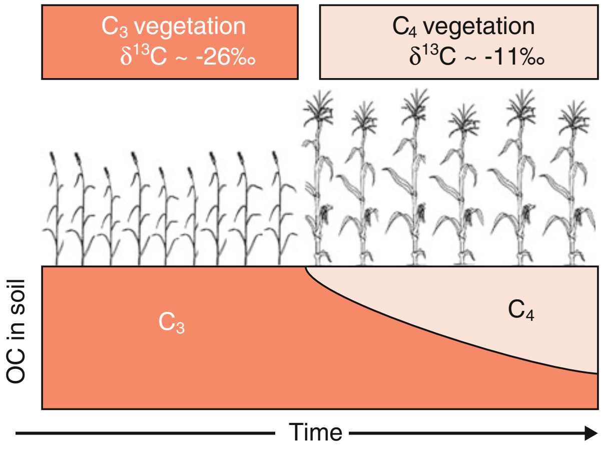
Radiocarbon content and the resulting calculated mean ^{14}C age in different humus fractions (from Eusterhues et al. 2003, 2005; Kaiser and Guggenberger, unpublished; Rethemeyer 2004)

[a] Difference calculation

[b] ^{13}C turnover time (John et al. 2005)

nd not determined

Fig. 3.9 Recording of the turnover time of organic soil carbon based on the change in the δ^{13}C signature after the change from C3 to C4 vegetation, as well as the quantity and mean turnover time of OC in density fractions of a Luvisol from loess, 24 years after the conversion from wheat cultivation to grain maize cultivation (after John et al. 2005)



OC fraction	Amount ($g\ C\ kg^{-1}$)	Proportion maize-derived OC (%)	Turnover time* (years)
Total OC	13.0	35.7	54
OC bound to mineral surfaces (heavy fraction, > 2 $g\ cm^{-3}$)	11.3	31.4	63
OC in free particulate organic matter (light fraction, < 1.6 $g\ cm^{-3}$)	0.5	64.8	22
OC in occluded particulate organic matter (light fraction in aggregates, 1.6 ... 2 $g\ cm^{-3}$)	1.1	38.3	49

*mean turnover time assuming homogeneous C pools and first oder decomposition kinetcs

3.6.2.2 ^{13}C Isotope Signature of Organic Matter

The transformation and turnover time of organic matter can also be determined through the measurement of the **^{13}C isotope signal** in the soil (Fig. 3.9). This method takes advantage of the fact that the **^{13}C signature** of plants with C4 photosynthetic metabolism (C4 plants, e.g. maize) is significantly different from that of C3 plants. The average δ^{13}C difference between C3 and C4 vegetation is about 15 $^{o}/_{oo}$. For example, after many years of maize cultivation, the fraction of maize C in a soil can be determined where the soil organic matter previously had a C3 signature. This method makes it possible to measure the C turnover in situ over longer periods of time. In a Luvisol, the fraction of maize OC in the soil organic matter was of 36 % after 24 years of maize cultivation, corresponding to a turnover time for the soil organic matter of 54 years. This also then enables the detection of the carbon fixed in different fractions. While mainly maize C was found in the light fraction, only 31 % of the carbon in the mineral-bound fraction came from the maize residues with a turnover time of 63 years. The light fraction occluded in the aggregates has substantially longer turnover times. This confirms that the turnover times of carbon in the clay and fine silt fraction are much longer than in the coarse or light fractions.

The use of tracers (model substances or plant residues) labeled with ^{13}C or ^{15}N, which differ from the natural background in terms of their isotope composition, enables tracing of the development of specific components in the soil, both in laboratory experiments and in field trials. A special advantage of this method is that the use of stable isotopes enables the recording of long-term processes, and in combination with thermal or chemolytic degradation, also enables a component-specific isotope analysis on a molecular basis.

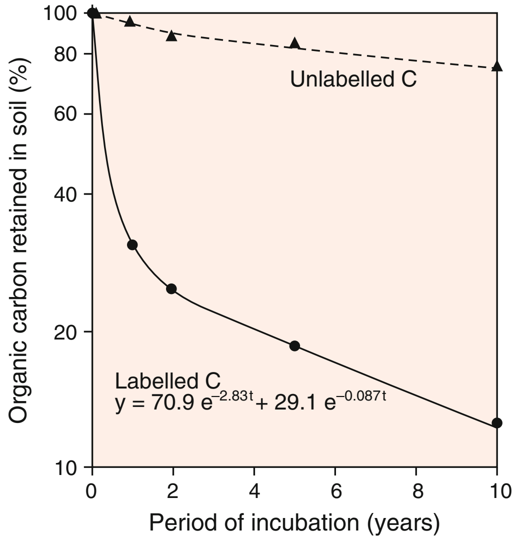


Fig. 3.10 Loss of soil C and C from ^{14}C labelled rye straw over the course of a 10-year open field incubation (after Jenkinson 1977)

3.6.3 C Turnover Modeling

The turnover of fresh organic matter added to the soil can be described with an equation, where the turnover rate is proportional to the amount of existing substrate:

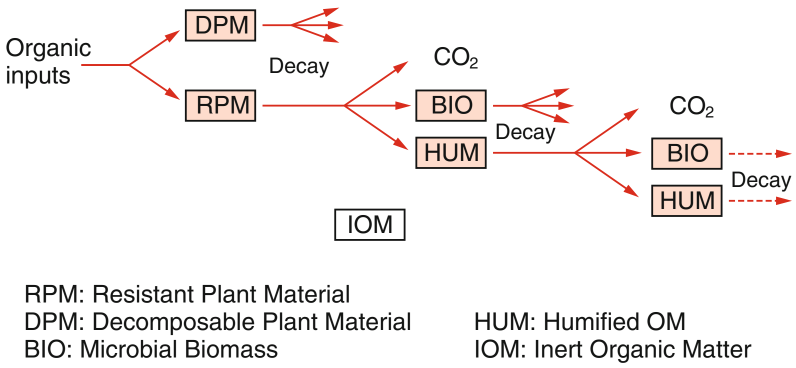
$$A_t = A_0 e^{-kt}$$

Here, A_t and A_0 are the quantities of organic C in plant residues at the time 0 and at the time t, and k is the reaction constant per unit of time. In this 1st order equation, the quantity of added organic matter is reduced respectively by half (half-life) within a specific period of time. This enables a good description of the decomposition of plant residues during the first years (Fig. 3.10).

To describe and predict **C storage** and dynamics in the soil, one must take account of the varying stability of the different SOM pools, which results from the turnover times described above. For this reason, the organic matter in most turnover models is found in a finite number of compartments or pools. Current **carbon turnover models** (Fig. 3.11) use three or more functional pools that are characterized by different carbon turnover rates. In addition, the turnover rates are often described using relationships with the soil moisture, temperature, clay content, pH value and the N availability. The organic matter is generally differentiated into three pools: rapid turnover (labile), slower turnover (intermediate), and very slow turnover rate (passive). The quantitative description of the turnover behavior in the different pools is based on the empirically obtained turnover rates described above.

The labile **pool** is transformed very rapidly, within a few months or years, but only accounts for about 1–5 % of total soil organic matter. The labile fraction of soil organic matter consists of undecomposed, readily available residues from plants and microorganisms, and is mainly significant for the short-term nutrient supply in soils. In soils used for arable farming, about half of the organic matter has an average turnover time of 10–50 a, i.e. it corresponds to the intermediate pool. The intermediate pool mainly consists of partially decomposed plant residues, where the lignin accumulated compared to the

Fig. 3.11 The Roth C model, example for a multi-component model to simulate the C turnover in soils (after Coleman and Jenkinson 1999)



more readily degradable polysaccharides. This fraction is probably protected against decomposition through aggregation, and is therefore strongly influenced by various management and soil tillage methods (Fig. 3.4). This fraction can be successfully isolated using the above-mentioned combined fractionation according to the particle size and density.

The passive pool has average turnover times in the range of hundreds to thousands of years. Some model approaches also contain an inert pool, which is considered to be non-decomposable and is therefore included as a constant. The stable humus fraction accounts for the passive pool in the models and is most significant in terms of quantity. The very stable fractions of soil organic matter probably mainly consist of charred organic matter and organic substances in organo-mineral compounds. Organo-mineral compounds are dominated by polysaccharides and alkyl-C compounds, whereas aromatic constituents are of secondary importance.

The multitude of processes that lead to very long-term stabilization of organic matter in the passive pool has made the prediction of the magnitude and degradation behavior of the passive carbon pool difficult until now. For this reason, it has not yet been possible to establish a satisfactory relationship between the conceptual pools of the model and the measurable fractions of the soil organic matter, and to selectively isolate them from soil. In addition to insufficient fractionation and characterization methods, this is mainly due to the fact that organic matter in the soil exists as a continuum, and not in discrete fractions. Nevertheless, the fundamental components of the individual pools are meanwhile described in such widely used models.

3.6.4 Soils as a Carbon Reservoir and Source

Within the framework of climate protection, the soil's function as a carbon reservoir has gained major interest, because building up the **soil carbon pool** leads to a sequestration of atmospheric CO_2. At the same time, CO_2 storage as well as all biogenic greenhouse gases, i.e. also nitrous oxide (N_2O) and methane (CH_4) must also be considered (Lal 2004). Figure 3.12 shows the C pools and fluxes of the soil C cycle. In every soil under natural vegetation or with long-term unchanging use, a steady-state is established between the supply and decomposition of organic matter according to the climatic conditions (Table 3.7). The production of CO_2 in soils is almost entirely from root respiration and microbial decomposition of organic matter. Like all chemical and biochemical reactions, these processes are temperature-dependent (Fig. 3.13). The question as to

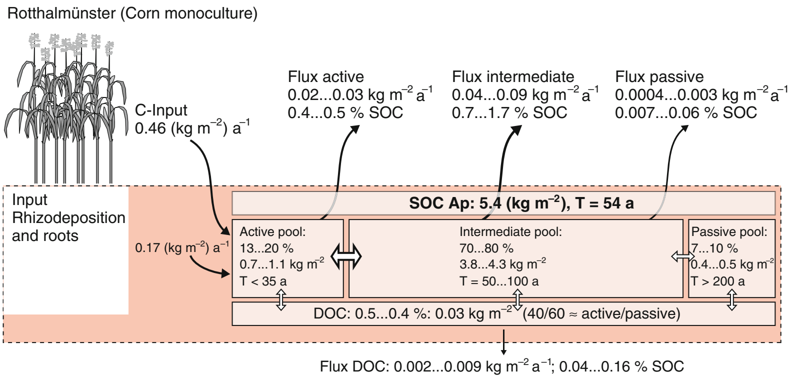


Fig. 3.12 Mineralization rates in different soil organic matter pools. Active, intermediate, passive pool: determined using the particle and density fractionation. Calculation of the turnover times (*T*) using $\delta^{13}C$ measurements in C3/C4 conversion soils (Flessa et al. 2008), C stocks and C input from maize straw (Kögel-Knabner et al. 2008a, b), C input underground (roots and rhizodeposition) (Ludwig 2005), DOC: guideline values from Haynes (2005), von Lützow et al. (2007)

Table 3.7 Turnover time for soil organic matter in different climatic zones

Climatic zone	Ecosystem	Turnover time (a)	References	Method
Boreal	Boreal coniferous forest	220[b]	Trumbore (2000)	Calculation[b]
Temperate	Mean value 31 sites	63 ± 7	Six et al. (2002)	^{13}C method
	Temperate forests	12[b]	Trumbore (2000)	Calculation[b]
	Temperate forests	11–31[c]	Garten et al. (2006)	Calculation[c]
	Cool temperate forests	30[a]	Jenkinson (1981)	Calculation[a]
Humid	Subhumid savanna	34[a]	Jenkinson (1981)	Calculation[a]
	Humid savanna	37[a]	Jenkinson (1981)	Calculation[a]
Maritime (Rothamsted UK)	Wheat, unfertilized	22[a]	Jenkinson (1981)	Calculation[a]
	Wheat, NPK	30[a]	Jenkinson (1981)	Calculation[a]
	Grassland, unfertilized	77[a]	Jenkinson (1981)	Calculation[a]
Tropical	Mean value, 23 sites	36 ± 5	Six et al. (2002)	^{13}C method
	Tropical rainforest	9	Jenkinson (1981)	Calculation[a]
	Tropical rainforest	2.5[b]	Trumbore (2000)	Calculation[b]

[a] Estimated from the ratio of the net primary production to the OC content of the soil

[b] Calculated from OC stocks and soil respiration

[c] Calculation based on measured OC stocks and estimated C input

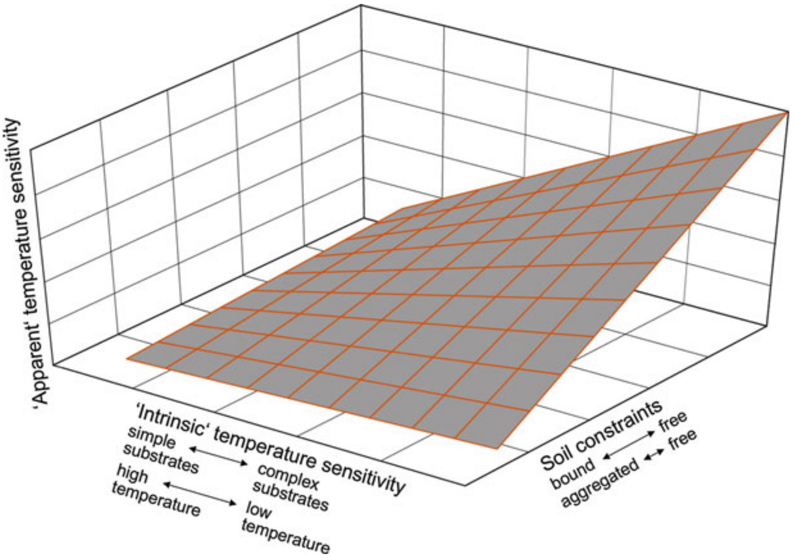


Fig. 3.13 The intrinsic temperature sensitivity of decomposition of an organic-C substrate is a function of the decomposability of the molecule and the ambient temperature. In general, more complex molecular structures have higher activation energies and, hence, higher temperature sensitivity. Environmental and soil constraints on decomposition will dampen or obscure the intrinsic temperature sensitivity by reducing substrate availability, often causing the measured (or 'apparent') temperature sensitivity to be less than expected. Modified from Davidson and Janssens (2006)

whether the build up of soil organic matter (e.g. through higher organic matter input or changes in land use) would ultimately lead to a net CO$_2$ fixation can only be assessed on an ecosystem level, in conjunction with the net primary production (NPP) (net biome productivity =

NPP − respiration losses). The role of soils as a source or sink for greenhouse gases can thus only be evaluated through simultaneous consideration of the losses through heterotrophic respiration and gains through biomass production and litter incorporation. If carbon stored belowground is transferred to the atmosphere by a warming-induced acceleration of its decomposition, a positive feedback to climate change would occur. Conversely, if increases of plant-derived carbon inputs to soils exceed increases in decomposition, the feedback would be negative (Davidson and Janssens 2006). Soil moisture, temperature and soil texture, as well as the quantity and quality of the supplied litter as a substrate for soil organisms, are important site factors for the intensity of biological turnover processes, which produce CO_2, N_2O and CH_4 (see Chap. 4.2).

Under the same climatic conditions and with the same C supply, clay-rich soils often have higher humus contents than sandy or silty soils. This is probably due to a combination of stabilizing processes through direct interactions with the solid phase and aggregation. The higher humus contents in fine-grained soils are explained by (a) the capacity of clay minerals, aluminum and iron oxides to adsorb organic substances and thus reduce microbial decomposition; (b) the higher content of aggregates, where the enclosed carbon compounds are protected from decomposition by microorganisms, and (c) the resulting more frequently occurring anoxic conditions. Therefore, a smaller fraction of the organic matter is mineralized in clay-rich soils than in clay-poor soils (Fig. 3.14). Here, the significance of the clay fraction is particularly high when the clay contents are low. As shown in Fig. 3.15, the accumulation of C and N in the fine fractions decreases with increasing clay and silt content. Long-term field experiments demonstrate the dependence of the soil organic matter content on the organic matter inputs (Table 3.8; Fig. 3.16). Inorganic fertilization has a direct influence on the organic matter content in soils through the yield quantities and thus the crop residue supply. Under comparable crop rotations, the soil organic

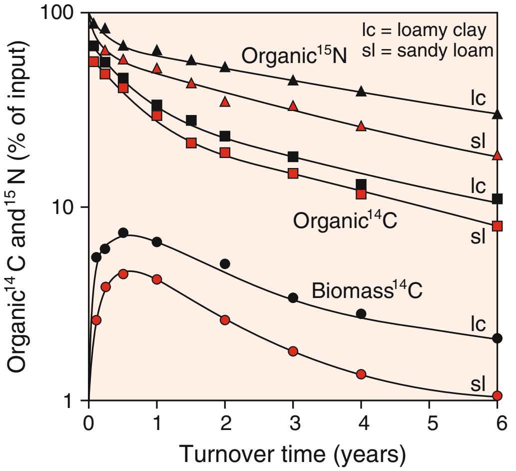


Fig. 3.14 Residual ^{14}C and residual ^{15}N and biomass ^{14}C in a clay (Cl) and a sandy loam (Ls) during the decomposition of labelled legumes under field conditions (after Ladd et al. 1996)

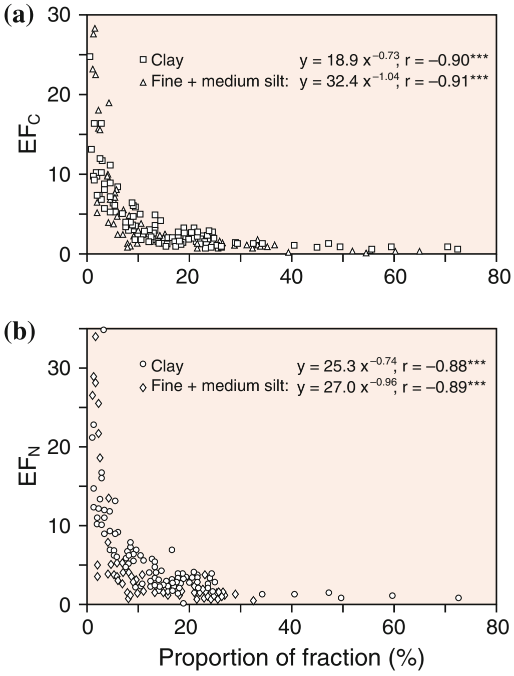


Fig. 3.15 Enrichment factors (Anreicherungsfaktoren) for **a** organic carbon (AF_C) and **b** nitrogen (AF_N) in the clay, fine silt and medium silt fractions of soils with various clay and silt contents. AF_C = % C in fraction/C in the bulk soil, AF_N = % N in fraction/N in the bulk soil (from Schulten and Leinweber 2000)

Table 3.8 Long-term effects of farmyard manure (FYM) application, mineral fertilization (N, NP, PK, NPK) and bare fallow on OC concentrations (mg g^{-1}) of agricultural topsoils

Site	Germany Bad Lauchstädt	Spain Madrid	Sweden Ultuna	UK Rothamsted	India Ranchi	China Yangling/ Shaanxi
Climate	Cool temperate	Mediterranean	Cool temperate	Temperate maritime	Sub-tropical	Semi-arid
Duration (years)	108	26	53	155	30	20
Crop rotation	Sugar beet/ spring barley/ potato/winter wheat	Sugar beet/ potato/cereals	Spring cereals/ fodder crops	Winter wheat	Soybean/ winter wheat	Winter wheat/ maize
Clay content (%)	21	27	37	25	25	na
pH	7.0	na	6.6	6.3	5.3	na
Unfertilized control	15.7	5.5	15.0	10.3	3.5	7.4
FYM	20.6	9.5	22.1	27.3	na	na
Application FYM (t ha^{-1} $year^{-1}$)	10	10	8	35	na	21
N	19.4	–	–	–	3.4	8.5
NP	20.4	–	–	–	4.2	10.2
PK	18.5	–	–	–	–	8.4
NPK	20.9	6.1	–	10.3–12.4	4.5	10.0
FYM + NPK	22.9	10.0	–	26.3	4.7	13.9
Bare fallow	–	–	9.7	–	–	7.9

From Blair et al. (2006), Börjesson et al. (2012), Körschens et al. (2013), Manna et al. (2007), and Yang et al. (2012)
na Not available

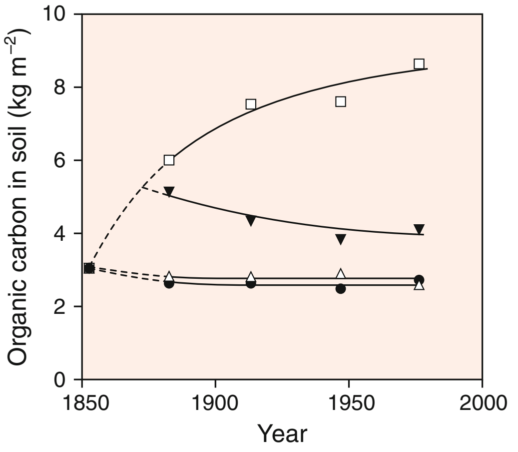


Fig. 3.16 Temporal change in the humus content in loamy Cambisols from the long-term trials in Rothamsted under different management since 1852; *Square box* (□) barn manure, *filled circle* (●) unfertilized, *triangle* (Δ) NPK, *black down pointing triangle* (▼) barn manure, unfertilized since 1871 (after Jenkinson 1988)

matter content of the soil increases with increasing yields through fertilization. In wet soils (peat) and soils with thick forest floor layers, the strongly retarded biological decomposition of organic matter in these soils results in carbon storage (Figs. 3.12 and 3.13).

Although they are difficult to predict, boreal thawing processes are an important influencing factor on the global soil C balance. The top 3 m of all permafrost-zone soils within the northern circumpolar permafrost zone contain about 1024 Pg C. This C accumulated over thousands of years under cold and sometimes waterlogged conditions, but becomes partly susceptible to thawing as the climate changes to warmer conditions. If these soils thaw, the ancient C stored in the permanently frozen layer is available for decomposition by soil organisms and is released to the atmosphere. The progressive mineralization of previously conserved organic matter stocks in the soil could affect one quarter to one third of the global soil C resources. However, the extent to which these changes have an effect on the soil C stocks mainly depends on the soil moisture conditions. Some of this C is easily metabolized and will be consumed quickly by microorganisms while other fractions are more difficult to break down because the stabilization processes described above also take effect here and will thus remain within the soil for much longer. How much greenhouse gas is released will depend on the balance between the release of carbon dioxide (CO_2) or methane (CH_4), i.e. the prevalence of aerobic or anaerobic conditions after thawing and the subsequent decomposition (Schuur et al. 2013). The greenhouse effect of methane is 20–30-fold higher than that of CO_2. Where the tundra is transformed into active moors, they can continue to grow. While the humus body continues to grow, so do the methane emissions.

Changes in land use disturb the steady state between the supply of organic matter and decomposition. Deforestation and the cultivation of previously forested areas, or the conversion of steppe or grassland into arable land as well as inverse measures have a strong effect on the organic matter dynamics, with changes preferentially in the topsoil. The temporal changes in the organic carbon occurring here follow the same course as those of organically bound nitrogen. The global soil C stocks have been continuously reduced since the beginning of soil cultivation about 10,000 years ago. About 20 % of the current atmospheric CO_2 concentration can probably be attributed to the cultivation of natural sites, 24–32 % of which to the decomposition of soil organic C. The most important factors are, as shown in the following examples, deforestation and the conversion of grassland or forest to cropland, soil tillage, and drainage. Conversion of native grassland or forest to cropland, resulted in losses of 20–40 % of the soil organic matter stocks, mainly from the topsoil (Scharlemann et al. 2014). The reduction of the OC content in the topsoil after the conversion of steppe or grassland into arable land is due to the combined effect of erosion losses, biochemical decomposition of the organic matter, and dilution effects through tillage (deepening of the ploughed A horizon). Soils under permanent grassland or forest often contain more organic matter than neighboring arable land, because litter input is higher and the topsoil is not tilled. When land has been taken into cultivation, the subsequent loss of organic matter does not take place uniformly, but rather preferentially from the particulate organic matter fraction, which mainly contains younger, poorly decomposed plant residues.

If the natural aggregation state of a soil is disturbed, e.g. due to soil tillage and the cultivation of natural soils, the turnover rate of the physically protected fraction increases, and there are particularly high C losses from the coarse fraction. The more often the soil is tilled during the course of the season, and the more ploughings are used, the more the humus content decreases. In doing so, the mineralization of previously physically protected organic matter from aggregates is stimulated. This degradation, caused by intensive aeration and destruction of the aggregates, can be reduced if loosening, non-inversion tillage is used instead of ploughing.

Managing soil carbon is considered to produce multiple benefits and improve soil properties as well as soil fertility. Actual management concepts suggest to increase soil carbon contents by appropriate management and at the same time enhance a range of ecosystem services (Table 3.9). Increasing the soil OC of degraded soils could simultaneously ensure high agricultural productivity, sequester CO_2 whose emissions might otherwise exacerbate climate change, and enhance water capture. Based on the discoveries of long-lasting fertility of the Terra preta, application of biochar to soils is considered a strategy that would increase stable soil organic matter, increase bioavailable water, lower bulk density, act as a liming agent, and reduce leaching of pesticides and nutrients to surface and ground water. Biochar is a carbon-rich product resulting from pyrolyzing biomass. When applied to the soil it is considered to be resistant to decomposition, effectively

Table 3.9 Management options to promote C sequestration in agricultural topsoils

Management option	Potential C sequestration ($t\ ha^{-1}\ year^{-1}$)
Conservation/zero tillage	0–0.8
Incorporation of crop residues	0.2–0.7
Application of manure/slurry	0.2–1.5
Improved rotations/intermediate crops	0.1–0.6
Organic farming	0–0.5
Bioenergy crops	0–0.6
Improved grazing management	0.2–0.7
Conversion cropland to grassland	0.3–1.9
Conversion cropland to forest	0.5–1.9

Based on data from Smith (2004), Vleeshouwers and Verhagen (2002), Dendoncker et al. (2004), Freibauer et al. (2004)

sequestering the applied carbon and mitigating anthropogenic CO_2 emissions. Other promoted benefits of biochar application to soil include increased plant productivity and reduced nutrient leaching. However, the effects of biochar are variable and it remains unclear if recent enthusiasm can be justified (Gurwick et al. 2013). Although biochar application to soil has been considered to be long-lasting carbon capture strategy, only few data are available to date to evaluate the stability of biochar in situ and show variable and uncertain results. But despite the variability introduced by soil and climate, the addition of biochar to soils resulted, on average, in increased aboveground productivity, crop yield, soil microbial biomass, rhizobia nodulation, plant K tissue concentration, soil phosphorus (P), soil potassium (K), total soil nitrogen (N), and total soil carbon (C) compared with control conditions. Soil pH also tended to increase, becoming less acidic, following the addition of biochar. Thus, although there remain many uncertainties biochar addition to soils holds promise in being a win-win-win solution to energy, carbon storage, and ecosystem function (Biederman and Harpole 2013).

References

Supplementary Reading

Baldock JA, Broos (2011) Soil organic matter, chap. II-1. In: Hunag PM, Li Y, Sumner ME (Hrsg) Handbook of soil science. CRC, Boca Raton

Doerr SH, Ritsema CJ, Dekker LW, Scott DF, Carter D (2007) Water repellence of soils: new insights and emerging research needs. Hydrol Process 21:2223–2228

ECCP (European Climate Change Programme) (2003) Working group sinks related to agricultural soils. Final report, 76 p

Gregorich EG, Beare MH, Mckim UF, Skjemstad JO (2006) Chemical and biological characteristics of physically uncomplexed organic matter. Soil Sci Soc Am J 70:975–985

Hedges JI, Eglington G, Hatcher PG, Kirchman DL, Arnosti C, Derenne S, Evershed RP, Kögel-Knabner I, De Leeuw JW, Littke R, Michaelis W, Rullkötter J (2000) The molecularly-uncharacterized component of nonliving organic matter in natural environments. Org Geochem 31:945–958

Helfrich M, Flessa H, Mikutta R, Dreves A, Ludwig B (2007) Comparison of chemical fractionation methods for isolating stable soil organic carbon pools. Eur J Soil Sci 58:1316–1329

Jenkinson DS (1990) The turnover of organic carbon and nitrogen in soil. Phil Trans R Soc B 329:361–368

Kalbitz K, Glaser B, Bol R (2004) Clear-cutting of a Norway spruce stand: implications for controls on the dynamics of dissolved organic matter in the forest floor. Eur J Soil Sci 55:401–413

Kalbitz K, Meyer A, Yang R, Gerstberger P (2007) Response of dissolved organic matter in the forest floor to long-term manipulation of litter and throughfall inputs. Biogeochemistry 86:301–318

Knicker H (2007) How does fire affect the nature and stability of soil organic nitrogen and carbon?—a review. Biogeochemistry 85:91–118

Knorr W, Prentice I, House JI, Holland EA (2005) Long-term sensitivity of soil carbon turnover to warming. Nature 433:298–301

Kögel-Knabner I (2002) A review on the macromolecular organic composition in plant and microbial residues as input to soil. Soil Biol Biochem 34:139–162

Lal R (2008) Soils and sustainable agriculture. A review. Agron Sustain Dev 28:57–64

Marschner BS, Brodowski A, Dreves G, Gleixner P-M, Grootes U, Hamer A, Heim G, Jandl R, Ji K, Kaiser K, Kalbitz C, Kramer P, Leinweber J, Rethemeyer MWI, Schmidt L Schwark, Wiesenberg GLB (2008) How relevant is recalcitrance for the stabilization of organic matter in soils? J Plant Nutr Soil Sci 171:91–110

Neumann F (1979) Böden in Landschaftsausschnitten Bayerns. II. Südliches Tertiär-Hügelland und Ampertal. Bayer Landw Jb 56:960–971

Oades JM (1988) The retention of organic matter in soils. Biogeochemistry 5:35–70

Rumpel C, Kögel-Knabner I, Bruhn F (2002) Vertical distribution, age, and chemical composition of organic carbon in two forest soils of different pedogenesis. Org Geochem 33:1131–1142

Schöning I, Kögel-Knabner I (2006) Chemical composition of young and old carbon pools throughout Cambisol and Luvisol profiles under forests. Soil Biol Biochem 38:2411–2424

Smith P, Powlson DS, Smith JU, Falloon P, Coleman K (2000) Meeting Europe's climate change commitments: quantitative estimates of the potential for carbon mitigation by agriculture. Glob Change Biol 6:525–539

Cited References

Amelung W, Brodowski S, Sandhage-Hofmann A, Bol R (2008) Combining biomarker with stable isotope analyses for assessing the ttransformation and turnover of soil organic matter. Adv Agron 100:155–250

Batjes NH (1996) Total carbon and nitrogen in the soils of the world. Eur J Soil Sci 47:151–163

Biederman LA, Harpole WS (2013) Biochar and its effects on plant productivity and nutrient cycling: a meta-analysis. Glob Change Biol Bioenergy 5:202–214

Blair N, Faulkner RD, Till AR, Poulton PR (2006) Long-term management impacts on soil C, N and physical fertility—part 1: broadbalk experiment. Soil Tillage Res 91:30–38

Börjesson G, Menichetti L, Kirchmann H, Kätterer T (2012) Soil microbial community structure affected by 53 years of nitrogen fertilisation and different organic amendments. Biol Fertil Soils 48:245–257

Christensen BT (2001) Physical fractionation of soil and structural and functional complexity in organic matter turnover. Eur J Soil Sci 52(3):345–353

Coleman K, Jenkinson DS (1999) RothC-26.3, a model for the turnover of carbon in soil: model description and user's guide. Lawes Agricultural Trust, Harpenden, UK

Davidson EA, Janssens IA (2006) Temperature sensitivity of soil carbon decomposition and feedbacks to climate change. Nature 440:165–173

Dendoncker N, Van Wesemael B, Rounsevell MDA, Roelandt C, Lettens S (2004) Belgium's CO_2 mitigation potential under improved cropland management. Agric Ecosyst Environ 103:101–116

Eusterhues K, Rumpel C, Kleber M, Kögel-Knabner I (2003) Stabilisation of soil organic matter by interactions with minerals as revealed by mineral dissolution and oxidative degradation. Org Geochem 34:1591–1600

Eusterhues K, Rumpel C, Kögel-Knabner I (2005) Organo-mineral associations in sandy acid forest soils: importance of specific surface area, iron oxides and micropores. Eur J Soil Sci 56:753–763

Fengel, D, Wegener G (1989) Wood: chemistry, ultrastructure, reactions. De Gruyter, Berlin

Flessa H, Amelung W, Helfrich M, Wiesenberg GLB, Gleixner G, Brodowski S, Rethemeyer J, Kramer C, Grootes P-M (2008) Storage and stability of organic matter and fossil carbon in a Luvisol and Phaeozem with continuous maize cropping: a synthesis. J Plant Nutr Soil Sci 171:36–51

Freibauer A, Rounsevell MDA, Smith P, Verhagen J (2004) Carbon sequestration in the agricultural soils of Europe. Geoderma 122:1–23

Garten J, Charles T, Hanson PJ (2006) Measured forest soil C stocks and estimated turnover times along an elevation gradient. Geoderma 136:342–352

Guggenberger G, Zech W, Haumaier L, Christensen BT (1994) Land use effects on the composition of organic matter in particle-size separates of soils. II. CP-MAS and solution ^{13}C-NMR analysis. Eur J Soil Sci 46:147–158

Gurwick NP, Moore LA, Kelle C, Elias P (2013) A systematic review of biochar research, with a focus on its stability in situ and its promise as a climate mitigation strategy. PLoS ONE 8(9):e75932

Haider K (1992) Problems related to the humification processes in soils of the temperate climate. In: Bollag J-M, Stotzky G (Hrsg) Soil biochemistry, vol 7. Dekker, New York, pp 55–94

Haynes RJ (2005) Labile organic matter fractions as central components of the quality of agricultural soils: an overview. Adv Agron 85:221–268

Jenkinson DS (1977) Studies on the decomposition of plant material in soil. V. The effects of plant cover and soil type on the loss of carbon from 14C-labelled ryegrass decomposing under field conditions. J Soil Sci 28:424–434

Jenkinson DS (1981) The fate of plant and animal residues in soil. In: Hayes MHB (ed) The chemistry of soil processes. Wiley, Chichester, pp 505–561

Jenkinson DS (1988) Soil organic matter and its dynamics. In: Waid A (Hrsg) Russel's soil conditions and plant growth, 11th edn. Longman, Harlow, pp 564–607

John B, Yamashita T, Ludwig B, Flessa H (2005) Storage of organic carbon in aggregate and density fractions of silty soils under different types of land use. Geoderma 128:63–79

Kalbitz K, Kaiser K, Fiedler S, Kölbl A, Amelung W, Bräuer T, Cao ZH, Don A, Grootes P, Jahn R, Schwark L, Vogelsang V, Wissing L, Kögel-Knabner I (2013) The carbon count of 2000 years of rice cultivation. Glob Change Biol 19:1107–1113

Kögel-Knabner I, Guggenberger G, Kleber M, Kandeler E, Kalbitz K, Scheu S, Eusterhues K, Leinweber P (2008a) Organo-mineral associations in temperate soils: integrating biology, mineralogy and organic matter chemistry. J Plant Nutr Soil Sci 171:61–82

Kögel-Knabner I, Ekschmitt K, Flessa H, Guggenberger G, Matzner E, Marschner B, von Lützow M (2008b) An integrative approach of organic matter stabilization in temperate soils: Linking chemistry, physics, and biology. J Plant Nutr Soil Sci 171:5–13

Körschens M, Albert E, Armbruster M, Barkusky D, Baumecker M, Behle-Schalk L, Bischoff R, Cergan Z, Ellmer F, Herbst F, Hoffmann S, Hofmann B, Kismanyoky T, Kubat J, Kunzova E, Lopez-Fando C, Merbach I, Merbach W, Pardor MT, Rogasik J, Ruhlmann J, Spiegel H, Schulz E, Tajnsek A, Toth Z, Wegener H, Zorn W (2013) Effect of mineral and organic fertilization on crop yield, nitrogen uptake, carbon and nitrogen balances, as well as soil organic carbon content and dynamics: results from 20 European long-term field experiments of the twenty-first century. Arch Agron Soil Sci 59:1017–1040

Ladd JN, Foster RC, Nannipieri P, Oades JM (1996) Soil structure and biological activity. In: Bollag J-M, Stotzky G (Hrsg) Soil biochemistry, vol 9. Dekker, New York, pp 23–78

Lair GH, Gerzabek MH, Haberhauer G (2007) Sorption of heavy metals on organic and inorganic soil constituents. Environ Chem Lett 5:23–27

Lal R (2004) Soil carbon sequestration impacts on global climate change and food security. Science 304:1623–1627

Ludwig B, Helfrich M, Flessa H (2005) Modelling the long-term stabilization of carbon from maize in a silty soil. Plant Soil 278:315–325

Manna MC, Swarup A, Wanjari RH, Mishra B, Shahi DK (2007) Long-term fertilization, manure and liming effects on soil organic matter and crop yields. Soil Tillage Res 94:397–409

Olah G-M, Reisinger O, Kilbertus G (1978) Biodégradation et humification. Atlas ultrastructural. Presses de l'université Laval, Quebec

Piccolo A (2001) The supramolecular structure of humic substances. Soil Sci 166:810–832

Rethemeyer J (2004) Organic carbon transformation in agricultural soils: radiocarbon analysis of organic matter fractions and biomarker compounds. Dissertation, Christian-Albrechts-Universität

Scharlemann JPW, Tanner EVJ, Hiederer R, Kapos V (2014) Global soil carbon: understanding and managing the largest terrestrial carbon pool. Carbon Manage 5:81–91

Schmidt MWI, Torn MS, Abiven S, Dittmar T, Guggenberger G, Janssens IA, Kleber M, Kögel-Knabner I, Lehmann J, Manning DA, Nannipieri P, Rasse DP, Weiner S, Trumbore SE (2011) Persistence of soil organic matter as an ecosystem property. Nature 478:49–56

Schulten H-R, Leinweber P (2000) New insights into organo-mineral particles: composition, properties and models of molecular structure. Biol Fertil Soils 30:399–432

Schuur EAG, Abbott BW, Bowden WB, Brovkin V, Camill P, Canadell JG, Chanton JP, Chapin FS III, Christensen TR, Ciais P, Crosby BT, Czimczik CI, Grosse G, Harden J, Hayes DJ, Hugelius G, Jastrow JD, Jones JB, Kleinen T, Koven CD, Krinner G, Kuhry P, Lawrence DM, McGuire AD, Natali SM, O'Donnell JA, Ping CL, Riley WJ, Rinke A, Romanovsky VE, Sannel ABK, Schädel C, Schaefer K, Sky J, Subin ZM, Tarnocai C, Turetsky MR, Waldrop MP, Walter Anthony KM, Wickland KP, Wilson CJ, Zimov SA (2013) Expert assessment of vulnerability of permafrost carbon to climate change. Clim Change 119:359–374

Six J, Feller C, Denef K, Ogle SM, de Moraes Sa JC, Albrecht A (2002) Soil organic matter, biota and aggregation in temperate and tropical soils—effects of no-tillage. Agronomie 22:755–775

Smith P (2004) Carbon sequestration in croplands: the potential in Europe and the global context. Eur J Agron 20:229–236

Swift MJ, Heal OW, Anderson JM (1979) Decomposition in terrestrial ecosystems. Blackwell, Oxford

Trumbore SE (2000) Age of soil organic matter and soil respiration: radiocarbon constraints on belowground dynamics. Ecol Appl 10:399–411

Vleeshouwers LM, Verhagen A (2002) Carbon emission and sequestration by agricultural land use: a model study for Europe. Glob Change Biol 8:519–530

von Lützow M, Kögel-Knabner I, Ekschmitt K, Flessa H, Guggenberger G, Matzner E, Marschner B (2006) Stabilization of organic matter in temperate soils: mechanisms and their relevance under different soil conditions—a review. Eur J Soil Sci 57:426–445

von Lützow M, Kögel-Knabner I, Ekschmitt K, Flessa H, Guggenberger G, Matzner E, Marschner B (2007) SOM fractionation methods: Relevance to functional pools and to stabilization mechanisms. Soil Biol Biochem 39:2183–2207

Waksman SA (1938) Humus: origin, chemical composition and importance to nature. Baillière, Tindall & Cox, London

Wiesmeier M, Spörlein P, Geuß U, Hangen E, Haug S, Reischl A, Schilling B, von Lützow M, Kögel-Knabner I (2012) Soil organic carbon stocks in southeast Germany (Bavaria) as affected by land use, soil type and sampling depth. Glob Change Biol 18:2233–2245

Yang XY, Ren WD, Sun BH, Zhang SL (2012) Effects of contrasting soil management regimes on total and labile soil organic carbon fractions in a loess soil in China. Geoderma 177:49–56