
Preface to the Second Edition

Despite having been published about two years ago for the first time, the continuous demand for this book encouraged me to prepare this revised and enlarged edition. Many parts of the text have been rewritten, type errors traced and corrected, and the bibliography largely modified to include many of the references published about the subject of soil pollution in the previous ten years.

I should like to express my thanks to the staff of Springer-Verlag, Heidelberg, for their cooperative efforts in preparing this edition. I also would like to thank Mr. Michael Sidwell (B.A.) for the extreme but characteristic care with which he read and revised the proofs.

I hope that, in this new edition, the book may continue to serve the needs of students and professionals alike interested in the subject of soil pollution.

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Soil Constituents

Generally speaking soil is a three-dimensional system, made of a solid, a liquid and a gaseous phase, each in an amount depending on the abundance of its constituents and their kinetic roles in the complex series of reactions, leading to soil formation. Figure 2.1 illustrates the composition by volume of an average soil.

2.1 The Mineral Solid Phase

Mineral matter in soil depends largely on the nature and composition of the parent rock. However, since about three fourths of the Earth's crust is made up of silicon and oxygen, we find that silicate minerals occupy a central position in any description of the mineral constituents of a given soil. All silicates are formed of a fundamental structural unit, comprising one silicon ion (Si^{4+}) and four oxygen ions O^{2-} , closely surrounding the silicon in a tetrahedral lattice, as shown by Fig. 2.2.

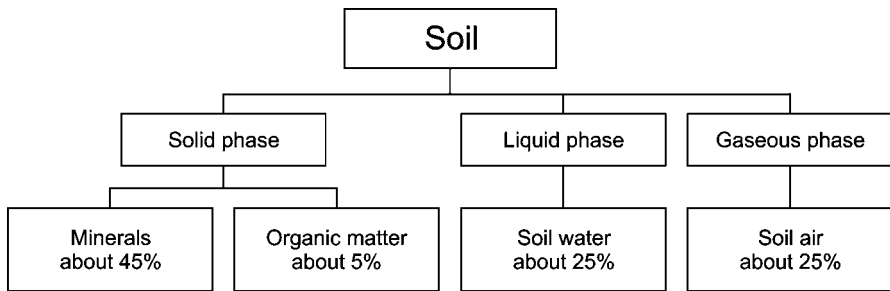
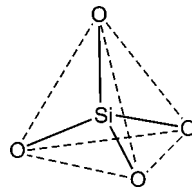


Fig. 2.1 Composition by volume of an average soil

Fig. 2.2 A silicate tetrahedron



The tetrahedra may, based on their net and residual charges, come together in a multiform of combinatorial structures and three-dimensional arrangements to form various kinds and varieties of silicates, which can be categorised into the following fundamental groups:

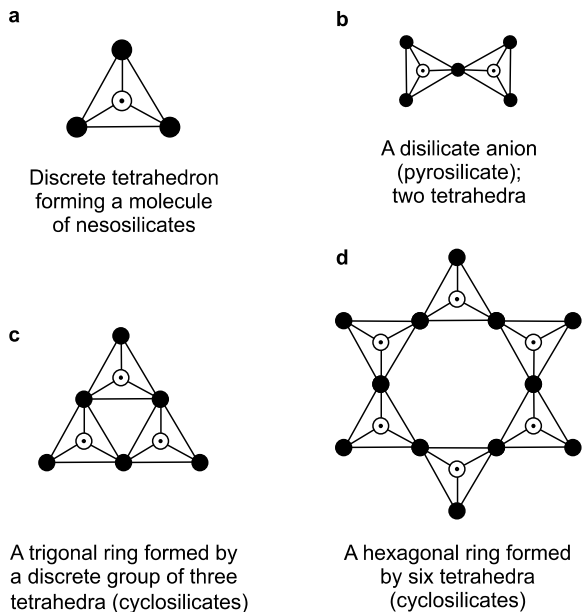
- *Orthosilicates*. These are discrete units of individual or grouped tetrahedra, made of one, two, three or six tetrahedra per unit – a property, which, as we can see later, is used for further classification of the group.
- *Chain silicates*. In this group, individual tetrahedra catenate together, by sharing the four tetrahedrally co-ordinated oxygen atoms with the neighbouring silicon atoms, to form infinite chains of formula $(\text{SiO}_3)_n^{2-}$.
- *Sheet silicates*. In this group, three co-ordinated oxygen atoms at the corners of a tetrahedron are shared with adjacent silicon atoms, resulting in the formation of a sheet or a layer of tetrahedra connected together at the three basal corners.
- *Framework silicates*. These are formed, if all four oxygen atoms per SiO_4 tetrahedron are shared with adjacent tetrahedra in a framework structure. In the following, each of these four silicate groups or classes will be discussed in some detail.

2.1.1

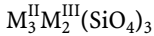
The Orthosilicates

The orthosilicates contain two subcategories: nesosilicates and sorosilicates. In the first category, the SiO_4 -tetrahedra occur as separate units, without shared oxygen atoms, linked by metallic cations. This structure (Fig. 2.3a) is not very common in minerals. However, some minerals like olivine, $(\text{Mg,Fe,Mn})_2\text{SiO}_4$, which is an important constitu-

Fig. 2.3 Structure of the orthosilicates



ent of basalt, adopt it. Other minerals, made of single silicon tetrahedra are zircon ZrSiO_4 , topaz $\text{Al}_2(\text{FOH})_2\text{SiO}_4$, and the garnets, with the general formula:



where M^{II} can be Ca^{2+} , Mg^{2+} or Fe^{2+} , and M^{III} is Al^{3+} , Cr^{3+} , or Fe^{3+} . This group of minerals occurs in soils formed on igneous rocks due to their higher resistance to weathering. The sorosilicates, themselves, may be further classified into two groups: the *pyrosilicates* and the *cyclosilicates*. In the pyrosilicates (also called *disilicates*), discrete groups of two tetrahedra share one of the co-ordinated oxygen atoms to form the disilicate anion Si_2O_7 (see Fig. 2.3b). An example is the mineral hemimorphite that has the general formula $\text{Zn}_4(\text{OH})_2\text{Si}_2\text{O}_7$; it sometimes occurs in soils formed on limestones. However, generally minerals having this structure are quite rare. In the cyclosilicates (the second category of the sorosilicates), three or six tetrahedra may share one or more of their co-ordinated oxygen atoms to form a trigonal ring, Si_3O_9 (Fig. 2.3c), or a hexagonal ring, Si_6O_{18} (Fig. 2.3d). Sorosilicates forming trigonal rings are represented by minerals like wollastonite, $\text{Ca}_3\text{Si}_3\text{O}_9$, or rhodonite, $\text{Mn}_3\text{Si}_3\text{O}_9$. Cyclosilicates having hexagonal ring structures are represented by minerals like beryl, $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$, or diopase $\text{Cu}_6\text{Si}_6\text{O}_{18} \cdot 6\text{H}_2\text{O}$. Figure 2.4 summarises the classification of the orthosilicates.

2.1.2

Chain Silicates or Inosilicates

This group derives its structure from the self-association of metasilicate anions (SiO_3^{2-}) into infinite chains of formula $(\text{SiO}_3)_n^{2n}$. The simplest of these is the string-like chain characteristic of the pyroxenes. In this arrangement, the silicon atoms share two of

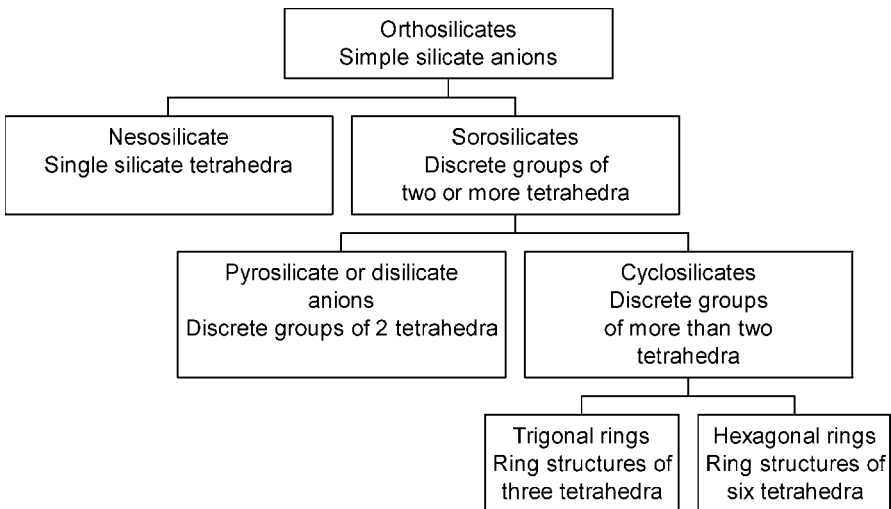


Fig. 2.4 Classification of the orthosilicates

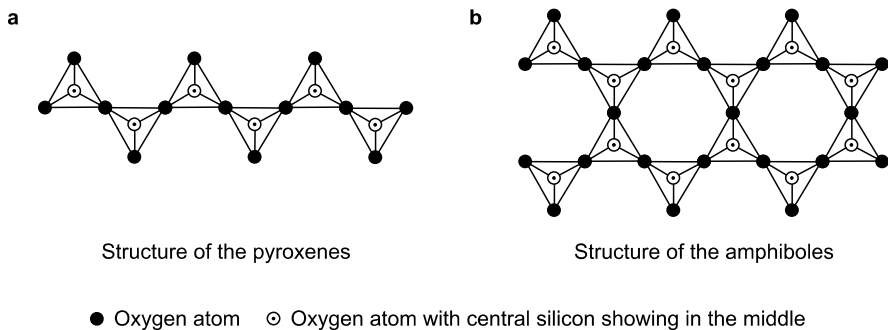


Fig. 2.5 Structure of the chain silicates

the four tetrahedrally co-ordinated oxygen atoms with adjacent silicon atoms (Fig. 2.5). Examples of the pyroxenes include enstatite, MgSiO_3 and diopside, $\text{CaMg}(\text{SiO}_3)_2$. If further sharing of the oxygen atoms by half of the silicon atoms occurs, a double chain or band structure is formed. This is the structure of the amphiboles. Amphiboles are more complicated, containing the basic $(\text{Si}_4\text{O}_{11})^6$ repeating unit as well as metal and hydroxide ions. Examples of the amphiboles are tremolite, $\text{Ca}_2\text{Mg}_5(\text{OH})_2\text{Si}_8\text{O}_{22}$ and actinolite, $\text{Ca}_2(\text{Mg,Fe})_5(\text{OH})_2\text{Si}_8\text{O}_{22}$.

2.1.3

Sheet Silicates or Phyllosilicates

If a complete sharing of the three basal oxygen atoms in a silicon tetrahedron is established, a layer or a sheet structure would result, made of various associated tetrahedra, and having an empirical formula $(\text{Si}_2\text{O}_5)_n$, creating a completely new type of silicates, known as *the phyllosilicates* or *the sheet silicates*.

Connections between the central silicon atoms in the individual tetrahedra lead to the appearance of a network of hexagonal holes on the sheets, lending them a pronounced pseudo-hexagonal symmetry (Fig. 2.6).

The apical atoms of the tetrahedra contemplating neutrality, form ionic-covalent bonds with other metal cations. They commonly associate themselves into octahedral sheets of gibbsite $(\text{Al}_2\text{OH}_6)_n$, or brucite $[\text{Mg}_3(\text{OH})_6]_n$. Gibbsite sheets are formed by edge-to-edge linking of two octahedra of Al equidistantly surrounded by six OH-groups (see Fig. 2.7). Edge-to-edge association of three octahedra of $\text{Mg}(\text{OH})_6$, results in the formation of *brucite sheets*, which are also of octahedral structure, having an empirical formula: $[\text{Mg}_3(\text{OH})_6]_n$.

The bonding of silica tetrahedral sheets (also known as *siloxane sheets*) with gibbsite or brucite octahedral sheets makes the basic structural units for the clay minerals, which are considered the most important group of mineral constituents of soils. These fundamental units (known as *layers*) are of two types; the first one (Fig. 2.8a), called here (for the sake of convenience) doublet structure while the other (also for convenience, called triplet structure) is made of a 2:1 lattice, comprising an octahedral brucite sheet sandwiched between two siloxane sheets (Fig. 2.8b).

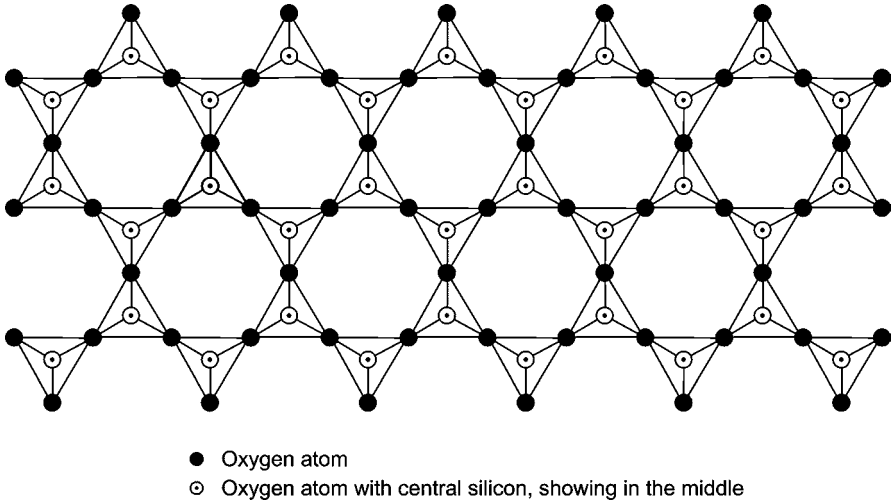
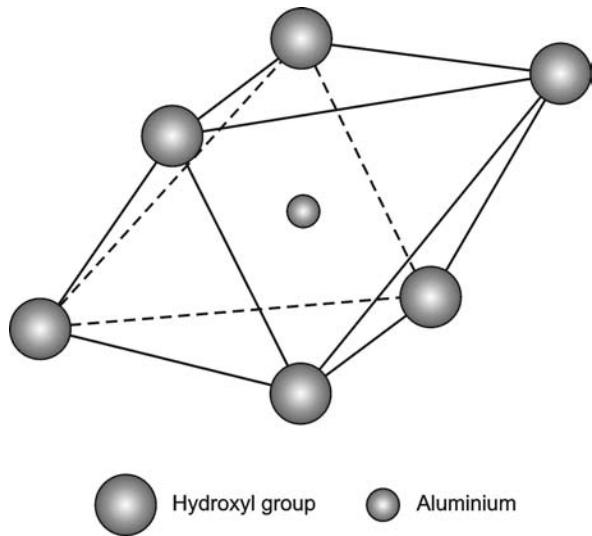


Fig. 2.6 Structure of the phyllosilicates. Observe the hexagonal network of holes

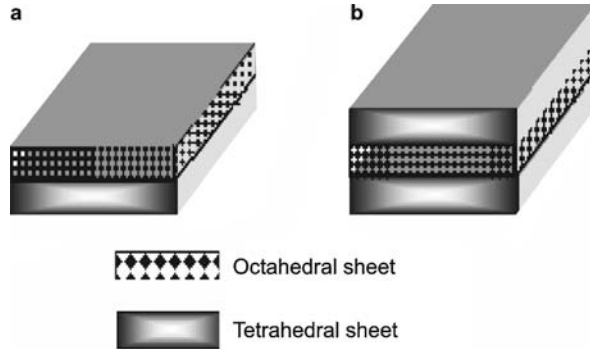
Fig. 2.7 Diagrammatic representation of an alumina octahedron



Classification of the Clay Minerals

Before explaining the fundamentals of clay mineral's classification in detail, the terms used henceforth will be shortly recapitulated. There are three fundamental elements delineating the structure of clay minerals: *sheets*, *layers* and *stacks*. The sheets are structurally of two types (tetrahedral silica and octahedral Al-OH or Mg-OH sheets). Combinations of sheets make the layers, of these there are also two types – “doublets”, made

Fig. 2.8 a A doublet layer (1:1), an octahedral sheet linked to a tetrahedral (siloxane) sheet; **b** a triplet layer (2:1), an octahedral sheet sandwiched between two tetrahedral sheets



of a tetrahedral sheet linked to an octahedral one and “triplets” made of an octahedral sheet sandwiched between two tetrahedral ones. A stack is a combination of layers alternating in a vertical direction. Layers in a stack may all be of the same type or they may be different, in which case the clay mineral is called a *mixed layer-clay*. The alternation of layers in a stack may follow a regular rhythm or may be random. Figure 2.9 summarises these relations.

Clay minerals are classified according to the type of layer structure (doublets or triplets), the interlayer or basal spacing between the unit layers, and the interlayer components or species. Accordingly, the following groups are identified:

- *The kaolinite group.* This group is made of stacks of doublets (see above). The main member of the group is the mineral kaolinite, which has the composition $(\text{OH})_8\text{Al}_4\text{Si}_4\text{O}_{10}$. Another member of this group is halloysite, having almost the same composition except for having two layers of water molecules within the stack. Figure 2.10 represents the structure of the group.
- *The montmorillonite group.* This group is made of triplets stacked in vertical direction (Fig. 2.11). It has the empirical formula $(\text{OH})_4\text{Al}_4\text{Si}_8\text{O}_{10} \cdot n\text{H}_2\text{O}$. Mg^{2+} , Fe^{2+} , or any other divalent cations substitute generally for Al^{3+} in the octahedral sheet, producing a rest charge, which is normally balanced by accommodating Ca^{2+} , or Na^+ , between the layers. The interlayer space in this group provides a shelter not only for neutralising ions, but also for organic material as well as for varying amounts of water, making the lattice expandable to accommodate variable numbers of water molecules. The interlayer ions may be displaced by other dissolved ions when their solutions enter the interlayer space. This property makes members of this group suitable for use as ion exchangers. Other members of the montmorillonite group include smectite, in which Fe^{2+} and Mg^{2+} substitute for Al^{3+} and nontronite with Fe^{3+} replacing Al^{3+} .
- *The illite (Hydromica) group.* The illite or hydromica group (also known as *muscovite group*) is represented by its main member illite. It has the general formula: $\text{OH}_4\text{K}_y(\text{Al}_4\text{Fe}_4\text{Mg}_4\text{Mg}_6)(\text{Si}_{8-y}\text{Al}_y)\text{O}_{20}$ and has a structure made of stacked triplets (Fig. 2.12). However, about three quarters of the tetrahedral positions in the siloxane sheets are occupied by Al^{3+} rather than Si^{4+} , leaving a net layer charge of about -2

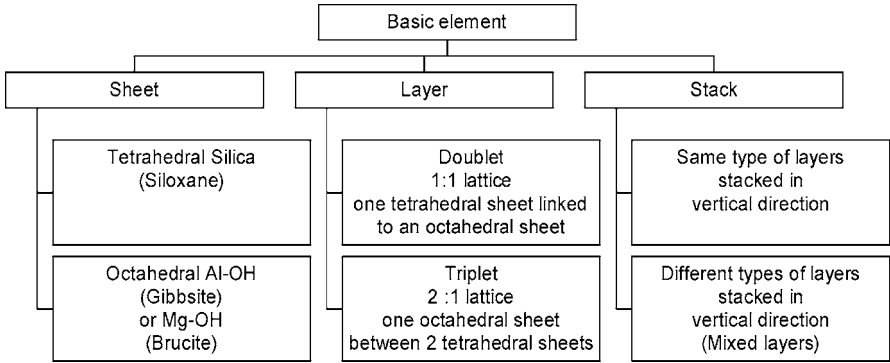


Fig. 2.9 Chart summarising the main basic structural elements of the clay minerals

Fig. 2.10 Structure of the kaolinite group

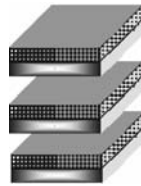


Fig. 2.11 Structure of the montmorillonite group

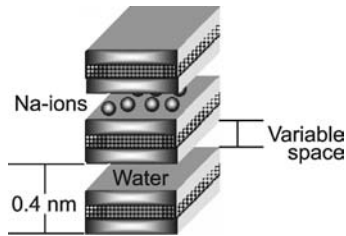
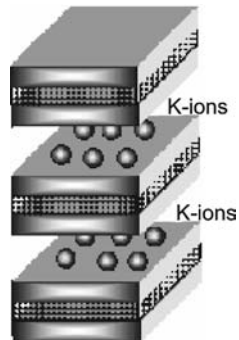


Fig. 2.12 Structure of the illite group



on each layer. This rest charge is balanced by accommodating K-ions in the interlayer space, making the interlayer bonding much stronger than the weaker ionic bonding in montmorillonite and rendering the illite lattice, unlike that of montmorillonite, non expandable.

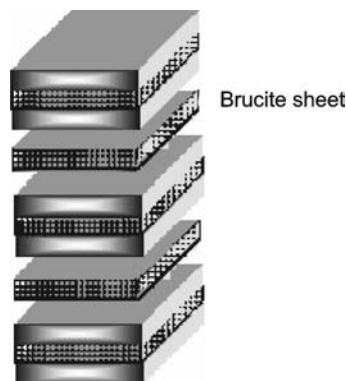
- *The chlorite group.* The chlorite group can be structurally viewed as being derived from montmorillonite by inserting a sheet of $\text{Mg}(\text{OH})_6$ (brucite) between each two adjacent montmorillonite layers (Fig. 2.13). This case, in which a single sheet functions by itself as a layer, is substantiated by the observation that montmorillonite is altered to chlorite in magnesium-rich seawater, that can provide the magnesium ions required to produce brucite sheets.
- *Mixed layer clays.* This group has a structure resulting from ordered or random stacking of the basic clay mineral groups in a vertical direction. It might be alternation between stacks of doublets with stacks of triplets (e.g. kaolinite-illite), or, as it is the case in chlorite, just a regular alternation of triplets with a single brucite or gibbsite sheets or even an alternation between stacks of chlorite and illite. The alternations may be regular, following a fixed rhythm like in chlorite or irregular like in some minor soil constituents

Factors Controlling the Formation and Alteration of Clay Minerals

The principal factors, controlling formation and alteration of clay minerals, are the chemical composition of the parent material and the physicochemical environment in which the process takes place. Kaolinite for instance, having only Al and Si as cations, will be formed in an environment where bases are continuously removed from the solution, giving rise to a residue with high Al/Si-ratios (kaolinite has the highest Al/Si-ratio among the clay minerals). Such an environment as here described, should be acidic and having a very active percolation of fluids to provide the effective removal of the bases. Therefore, kaolinite develops much more readily in relatively humid climates with free drainage and an enhanced percolation of groundwater.

Contrary to kaolinite, formation of members of the montmorillonite group (of low Al/Si-ratio about 0.5:1 and high content of iron, manganese, sodium, calcium, magnesium, and potassium), warrants the retaining of the bases. This can readily occur in a

Fig. 2.13 Structure of the chlorite group



neutral or a slightly alkaline environment of impeded drainage or high evaporation rates. Accordingly, montmorillonite is considered as a typical product of weathering in water logged terrain or semi-arid climates. The mere occurrence of montmorillonite in a landscape adds to the poor drainage character of the soil, due to its expandable lattice and its capacity to accommodate and retain water molecules.

2.1.4

Framework Silicates or Tectosilicates

In this category, complete sharing of all four oxygen atoms per SiO_4 tetrahedron is attained, giving rise to a framework structure. Minerals like quartz and the feldspars, which are very common in most soils, adopt this structure. Quartz is made up of Si-O tetrahedra linked through the O^{2-} ions, having the general formula $(\text{SiO}_2)_n$ or silicon dioxide. The name *quartz* stands actually for a mineral species under which about 300 varieties are included. The feldspars are far more important, as rock constituents, than any other group of minerals; in fact, they may be compared in igneous rocks to all other groups combined, since they constitute nearly 60% of such rocks and serve as the basis for their classification. They undergo *isomorphic substitution*, which is one of the fundamental properties of silicate minerals. In this process, an ion may be replaced by another ion in the silicate lattice, causing an imbalance in the electric charge of the crystal. To re-establish electric neutrality, extra ions or ionic species are incorporated or expelled from the crystal lattice. In feldspars a considerable part of the Si^{4+} ions are replaced by Al^{3+} ions with extra base cations like Ca^{2+} , Na^+ or K^+ to re-establish neutrality. The chief chemical types of feldspars are: KAlSi_3O_8 (orthoclase and microcline), $\text{NaAlSi}_3\text{O}_8$ (albite), and $\text{CaAl}_2\text{Si}_2\text{O}_8$ (anorthite). Natural crystals of microcline and of orthoclase contain 10 to 25% $\text{NaAlSi}_3\text{O}_8$. Albite and anorthite are completely miscible with each other and form mix-crystals (in all proportions), known as *plagioclase feldspars*, which are stable at any temperature. They normally contain 5 to 15% KAlSi_3O_8 .

Accessory soil minerals. Apart from silicate minerals, non-silicate minerals of minor occurrence may play an important role in the development of soil properties. Among those most widely distributed in soils (see Fig. 2.14) are the oxides of iron and aluminium, which are often lumped under the collective term *sesquioxides*. Limonite ($\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$), hematite (Fe_2O_3), goethite ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$), diaspore ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$), and gibbsite (Al_2O_3) best exemplify the sesquioxides.

Hydrous iron and aluminum oxides attain their highest concentrations in soils under humid tropical conditions. However, iron concentrations will principally depend on the *Eh* of the environment, such that, under oxidising conditions, iron that is not required for clay formation is precipitated as hydrated ferric oxide, while under reducing conditions ferrous iron is removed in solution. Other accessory minerals occurring in soils developed on recent volcanic deposits are anatase, TiO_2 , and amorphous silica.

2.2

Organic Matter and Soil Organisms

A major agent determining the character of the entire soil profile is humus, which is generally concentrated in the upper horizons. Brady (1974) has defined humus as:

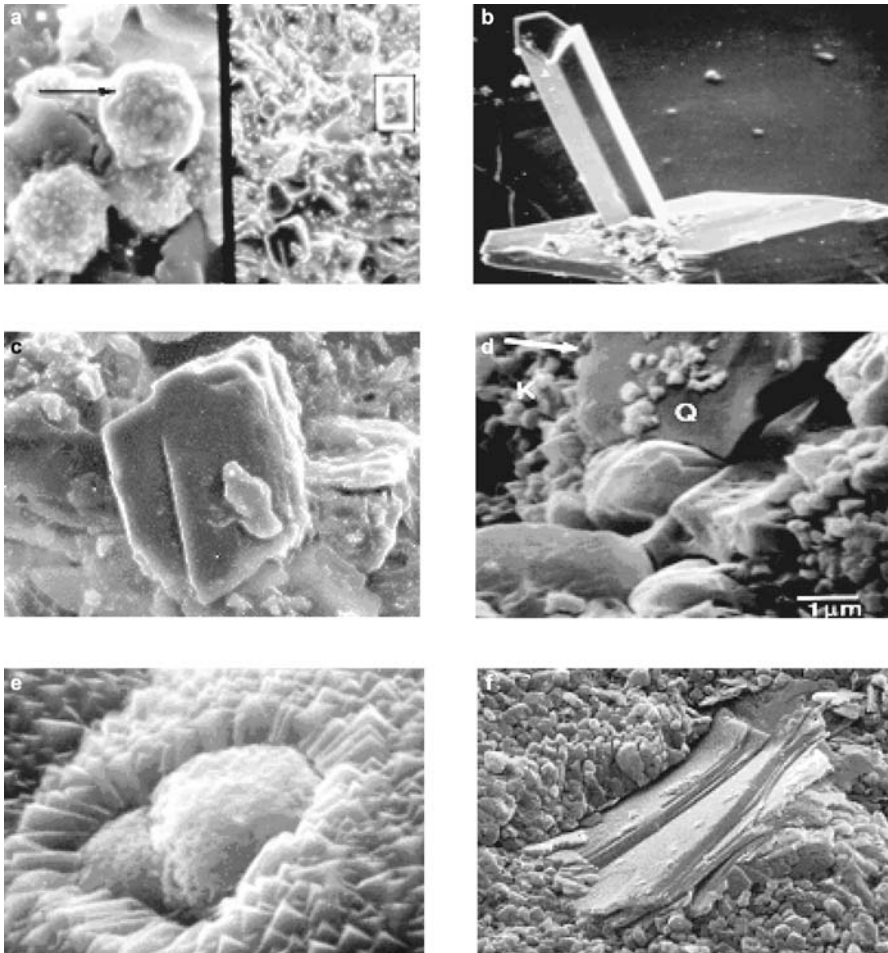


Fig. 2.14 **a** Raspberry shaped pyrite grains (*arrow*) close up from the right hand side of the picture (*rectangle*); **b** gypsum crystals (swallow tail-grain); **c** corroded dolomite crystal; **d** quartz grains (*arrow*); **e** calcite crystals encrusting a grain; **f** detrital mica plates (scanning electron photomicrographs)

“A complex and rather resistant mixture of brown or dark brown amorphous and colloidal substances modified from the original plant tissues or synthesised by various soil organisms.”

It is principally the product of decay of surfacial organic debris (litter), together with the decomposition products of roots within the uppermost soil horizons. In average soils, humus contains 4–6% organic substances, which, in turn, are made of 85% dead matter, 8.5% living roots and rootlets and about 6.5% soil organisms.

2.2.1 Soil Organisms

These are generally classified according to their biological activities in soils into producers, consumers, and decomposers. Decomposers form the basis of the nutritive chain among the three groups. They produce, by degradation of organic litter, the primary resources (CO_2 , N_2 , O_2 , etc.) used by the producers to synthesise complex nutritive material, which in turn will be consumed by the group of consumers. All three groups work hand in hand to change and continuously develop the soil profile. Soil organisms may also be classified according to their size into microfauna ($<200\ \mu\text{m}$), mesofauna ($200\text{--}1\,000\ \mu\text{m}$), and macrofauna ($>1\,000\ \mu\text{m}$). Table 2.1 illustrates the approximate distribution in volume % of soil organisms in the organic fraction of an average European soil.

Macrofauna

Macrofauna living on and in the soil includes large molluscs, beetles, large insect larvae, as well as vertebrates like moles, rabbits, foxes, and badgers. These normally bury deep in the soil and feed on other smaller organisms. Moles in particular consume a great deal of smaller soil dwellers.

Mesofauna

Soil dwellers of this category belong to four main groups – *nematodes*, *arthropods*, *annelids* and *molluscs* (see Fig. 2.15). Nematodes, the unsegmented roundworms (also called eelworms) are about 0.5 to 1 mm in length. They are considered to be the smallest soil fauna next to protozoa. In a soil block of $1\ \text{m}^2$ surface area and 30 cm depth, $10^6\text{--}2\times 10^7$ individuals of these worms, with a total weight between 1 and 20 g may be present. They feed on plant debris, bacteria and in some cases on protozoans.

- *Arthropods*, as shown by Table 2.2, comprise of various categories. To these, we count acari (mites), colembola (springtails), myriapods (centipedes and millipedes), isopods (wood lice), beetles, insect larvae, and termites. Among these categories, the

Table 2.1 Distribution of soil organisms in average European soils

Class of organisms	Vol% in humus of an average European soil
Bacteria and actinomycetes	50
Fungi	25
Lumbricid worms	14
Macrofauna	5
Mesofauna	2.5
Microfauna	3.5

Fig. 2.15 Some of the common mesofauna in European soils (based on Ellis and Mellor 1995)

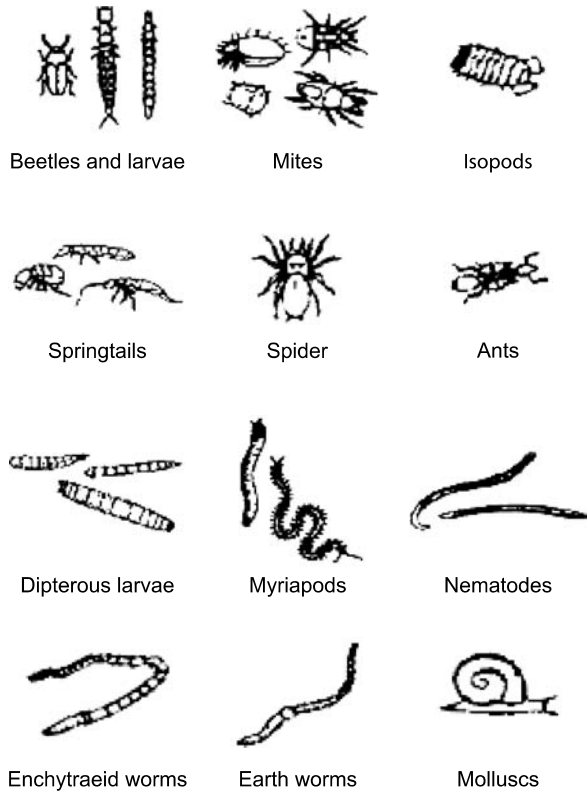


Table 2.2 Some data on small arthropods in soils

Group	Number of individuals	Total weight (g)	Characteristics
Mites	10^5 – 4×10^5	1 – 10	Common in acidic litter
Spring tails	5×10^4 – 4×10^5	0.6 – 10	Abundant with mites
Centipedes (chilopods)	50 – 300	0.4 – 2	Carnivorous
Millipedes (diplopods)	100 – 2000	0.05 – 1	Herbivorous
Isopods (wood lice)	50 – 200	0.5 – 1.5	Typical decomposers

Table 2.3 Number of individuals and total weight of microorganisms in a soil block of 1 m^2 surface area and 30 cm depth (after Klötzli 1993)

Group	Number (individuals m^{-2})	Total weight (g)
Bacteria	10^{12} – 10^{15}	50 – 500
Fungi	10^{10} – 10^{12}	100 – 1000
Algae	10^6 – 10^{10}	1 – 15

mites and springtails are the most abundant, especially in acidic litter, where they may form 80% of the soil organisms. Both mites and springtails feed on plant debris, bacteria and fungi. Ants and termites are most abundant in tropical soils, they are very active soil mixers. Earth pillars heaped by termites (termintaria) may reach several metres in height. Table 2.3 summarises some information on selected soil arthropods. The numbers are based on a soil block of 1 m² surface area and 30 cm depth.

- *Annelida* (ringed worms) is the name of the phylum to which the segmented earthworm, the leech, and the nereis belong. The Lumbricid worms (the earthworms) represent the first class of soil annelids. These occur in countless numbers in moist soils all over the world, emerging only at night and retreating under ground in the morning. Darwin made their activities the object of a careful study and concluded: “it may be doubted if there are any other animals which have played such an important part in the history of the world as these lowly organised creatures.” Indeed, the quantity of earth burrowed, mixed and brought up from below and deposited on the surface by these worms has been estimated to be as high as 18 tons per acre per year, or, if spread out uniformly, about 3 cm in 10 years. The effects of worms on the soil include (beside bringing out deeper parts of the soil to the surface and exposing them to the air) improving the drainage through the intricate net of burrows and adding, in the form of excretory waste, a great deal of organic material to the soil. Their numbers in European soils are estimated to be between 80 and 800, with a total weight of 40 to 400 grams per square metre. Some giant earthworms are found in tropical regions, especially in Australia. *Megascolecides australis* may be 3 m in length; it lives in burrows with volcano-shaped openings. The *enchytraeid*, or potworms, are the second class of soil annelids. They are smaller than the earthworms (0.1–5.0 cm) and have a thread-like appearance. Potworms feed on algae, fungi, bacteria, and other soil organic materials. They may attain numbers as high as 200 000 individuals per square metre.
- *Mesofaunal molluscs* (2–20 mm), found in soils, include slugs and snails. Their numbers per square metre may range between 50 and 1 000. They feed on plants, fungi, and faecal remains.

Microorganisms (Microfauna and Microflora)

These are mainly represented by four groups: *bacteria*, *fungi*, *algae* and *protozoa*. All four groups occur in great numbers in soils (see Table 2.3).

- *Bacteria*. These are normally unicellular organisms with cellular sizes between 0.0001 and 0.02 mm, being the smallest organisms visible under the light microscope. They occur, due to their tremendous reproduction rates, in very high numbers (about 10¹²–10¹⁵ m⁻²) mostly in water films surrounding the soil particles. According to their morphology, bacteria are classified into three main classes:
 - *Eubacteria*. This is the most representative class of bacteria and can be further subdivided into spherical bacteria (*cocci*) and rod-shaped (*bacilli*) bacteria. Prominent examples of this group are the bacteria responsible for nitrogen fixation in the soil – *Nitrobacter*.

- *Chlamydo bacteria* (*thread-shaped bacteri*). In this class the bacterial cells are attached together by a filament (*filamenatum*) into a linear chain similar to bead strings. Iron bacteria, playing a very important role in weathering and diagenesis of sediments, belong to this class.
- *Actinomycetes*. In this class, rod-like cells are united to form stellar forms of bacteria, which in their vegetative stage of reproduction, resemble fungi, consisting of fine branching filaments (about 1 μm in diameter). These morphological peculiarities make it difficult to determine the real systematic position of these organisms, yet Actinomycetes are considered as an independent class of the Bacteriophyta.

Another method of classification of bacteria is their susceptibility to staining by the so-called *Gram solution* (after the Danish bacteriologist H. C. J. Gram, 1853–1938). Bacterial cells, stained by this solution, are called *gram-positive*; others are collectively termed *gram-negative*.

The effects of bacteria on the soil are numerous. They decompose a wide range of materials under various conditions; examples of these range from oxidation of Fe^{2+} and reduced sulphur compounds, under catalytic action of *Thiobacillus ferrooxidans*, to the formation of nitrogen-fixing nodules on the roots of leguminous plants by *Rhizobium* sp. Some bacteria are also capable of metabolising a wide range of chemicals, for instance *Pseudomonas*, a species capable of metabolising pesticides.

- *Fungi*. Mycophyta or Fungi are, like the bacteriophyta, in their overwhelming majority, parasitic; their carbon needs are dependent on nutritive material synthesised by other organisms. They are characterised by filamentous structures (hyphae), which are about 0.5–10 μm in diameter and which grow into a dense network called *mycelium*. Fungi live mostly in the surface layers of the soil, preferring acidic conditions, yet some of them live symbiotically in plant tissues. They may, under favourable (acidic) conditions, be responsible for the decomposition of up to 80% of the soil organic matter.
- *Algae*. These are photosynthetic organisms confined largely to the upper surface of the soil. They include Cyanophyceae (blue-green algae) and Chlorophyceae (green algae). Blue-green algae regulate the nitrogen cycle in the soil.
- *Protozoa*. A variety of protozoa, like rhizopoda, ciliates, and flagellates live in water films surrounding the soil particles. They control the numbers of bacteria and fungi on which they live. Table 2.4 shows the numbers and total weights of some protozoa in a soil block of 1 m^2 surface area and 30 cm depth.

2.2.2

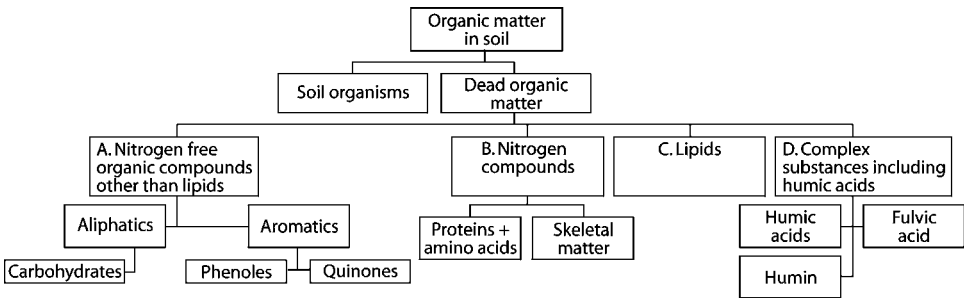
Dead Organic Matter

Soil organic matter formed by metabolic action of the soil organisms, as well as by the break down of pre-existing organic material, can be classified into four main classes:

- Organic compounds free from nitrogen (other than lipids)
- Nitrogen compounds
- Lipids
- Complex substances including humic acids

Table 2.4 Some data on soil protozoa

Group	Number (individuals m ⁻²)	Total weight (g)
Flagellates	$5 \times 10^{11} - 10^{12}$	10–100
Rhizopoda	$10^{11} - 5 \times 10^{11}$	10–100
Ciliates	$10^6 - 10^8$	10–100

**Fig. 2.16** Classification of soil organic matter

Each of these categories can be further subdivided as shown in the organisation chart in Fig. 2.16.

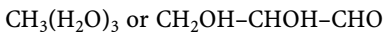
2.2.2.1

Organic Compounds Free from Nitrogen

Nitrogen Free Aliphatic Compounds

Carbohydrates are the most important representatives of this class of soil organic substances. Plants and soil organisms depend upon them for their structural material, which eventually ends up as important soil constituents. It is estimated that about 5–30% of the soil carbon exists as carbohydrates. They are so called because many of them (but by no means all) have a molecular formula which may be summarised by: $C_x(H_2O)_y$, where x and y can be equal or different numbers (see glycerinaldehyde formula below).

Carbohydrates are *polyhydroxyaldehydes* or *polyhydroxyketones*. On hydrolysis, they again give only substances, which are either polyhydroxyketones or polyhydroxyaldehydes. The simplest molecule that fulfils this definition, besides displaying optical activity, which is one of the basic properties of carbohydrates, is glycerinaldehyde (a polyhydroxyaldehyde). It has the formula:



Classification of Carbohydrates

A key reaction of carbohydrates that may be used as a basis for a general classification of the group is hydrolysis. Carbohydrates on hydrolysis, as it was mentioned before, dissociate to simpler molecules having the same nature of being polyhydroxyketones or

polyhydroxyaldehydes. So if a carbohydrate does not hydrolyse to simpler molecules of the said nature, it would be called a *monosaccharide*; so, glyceraldehyde is a monosaccharide, as is glucose, fructose, ribose, etc.

The ending “-ose” is commonly used to indicate a carbohydrate. Structural formulae of some monosaccharides are given in Fig. 2.17.

A carbohydrate that hydrolyses to two monosaccharide molecules is by analogy called a *disaccharide*. Thus sucrose, lactose and maltose are disaccharides (see Fig. 2.18).

Similarly carbohydrates that hydrolyse to a large number of monosaccharides may be termed *polysaccharides*. An example is given here by starch, having the formula $(C_6H_{10}O_5)_n$. It hydrolyses to (n) monosaccharide molecules according to the equation shown in Fig. 2.19

Another way of classifying carbohydrates may be based on whether a carbohydrate has an aldehyde or a ketone group. In the former case, the carbohydrate may be called an *aldose*, while in the latter case the carbohydrate is called a *ketose*. The two groups resulting from this classification are corresponding isomeric groups having the same composition but different structures. Examples are:

- $CH_2OH-CHOH-CHO$ (glyceraldehyde)
- $CH_2OH-CO-CH_2OH$ (dihydroxyacetone)
- $CH_2OH(CHOH)_3CHOH-CHO$ (glucose)
- $CH_2OH(CHOH)_3CO-CH_2OH$ (fructose)

As a matter of fact monosaccharides form rings, the skeletons of which may be as shown for glucose in Fig. 2.20.

Such rings may be attached together by a process called *condensation*, taking place between the hydroxyl groups, giving rise to polysaccharides. Condensation may occur between similar molecules or by acting on other substances containing -OH groups. In this case the products are known as *glycosides*. These are often named after the sugars they contain e.g. *glucosides*, formed by reaction of glucose with methyl alcohol and hydrogen chloride.

The arrangement of the H's and OH's on the rings determines the chemical character of the substance formed, and that is why there might be several sugars of different chemical properties having the same formula of glucose, for instance α -glucose and β -glucose (see Fig. 2.21).

Nitrogen Free Aromatic Compounds

It is known that numerous low molecular weight *phenols* and *quinones* are liberated from dead vegetable matter. These may be utilised by fungi in building molecules with greater number of aromatic rings. It is also known that fungi (during the decomposition of lignin) produce extracellular phenol oxidases (enzymes, Sect. 9.4), which catalyse the introduction of hydroxyl groups into the phenol rings, giving rise to some aromatic soil constituents.

Phenols

Phenols form a class of aromatic compounds, the name of which is derived from “phen” – an old name of benzene. In this class one or more OH-groups are directly linked to

Fig. 2.17 Structural formulae of some monosaccharides

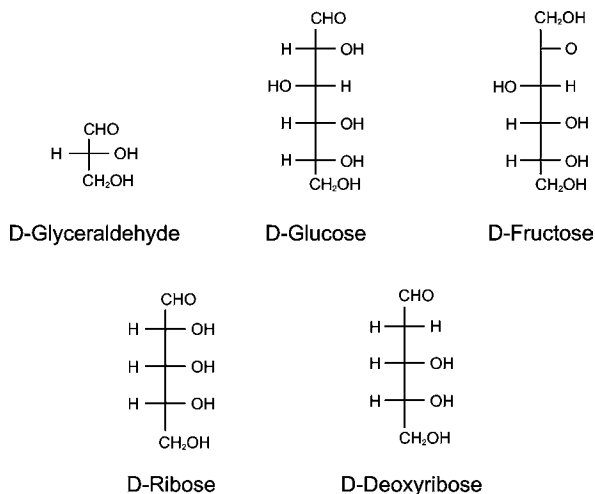


Fig. 2.18 Hydrolysis of sucrose

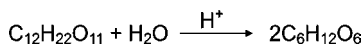


Fig. 2.19 Hydrolysis of a polysaccharide

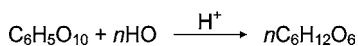


Fig. 2.20 Skeleton of glucose ring. The carbon atom outside the ring is the end carbon atom in the open chain formula

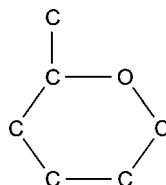
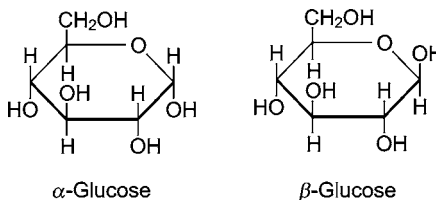


Fig. 2.21 Different arrangements in α - and β -glucose



the benzene nucleus. Accordingly there may be mono-, di-, or tri-hydric phenols depending on the number of hydroxyl groups in the molecule (see Fig. 2.22).

Quinones – The Colour Dispensers

“Hail you O’ land of Egypt, tell me O charming brunette where have you got this beautiful tan”. This song of an Egyptian peasant praising the dark colour of his field re-

veals how the enigma of soil colour has always kindled the imagination of people, living on the banks of rivers where cultural centres first appeared. The name *Egypt* itself is derived from a Greek word meaning black or dark brown soil. It is perhaps not by accident that Egyptians have always made parallels between the colour of soil and the “beautiful” dark tan of *Henna* or *Egyptian privet*, which is used in the East, since ancient times, as a drug and cosmetic as well as a dye for leather and skin. The colour producing pigment in henna is a substance known as *lawsone*. It has the structure shown in Fig. 2.23, and is a member of a class of compounds known as the *quinones*.

Quinones, known since early times in history as dyes, are responsible for many characteristic colours in the plant kingdom. They often occur in the bark and roots of plants. Some fungi also owe their brilliant colours to the presence of quinones in their tissues. Such colourations are by no means limited to plants; quinones are also responsible for most of the dark colour pigmentation of animals. For example, the natural colouring of sea urchins is due largely to naphthaquinones (see formula, Fig. 2.24). Dark colourations of humus are, as it will be explained below, largely due to reactions of quinones and their derivatives in soil.

Quinones have a conjugated structure (see Figs. 2.23 and 2.24) and are reactive substances that often give hydroxy derivatives: *o*-quinone, benzoquinone, naphthaquinone, anthraquinone.

Fig. 2.22 Phenols classified according to the number of hydroxyl groups; **a** monohydric phenol (hydroxybenzene); **b** dihydric phenols: catechol (*left*), resorcinol (*middle*), hydroquinone (*right*); **c** trihydric phenols (trihydroxybenzenes): pyrogallol (*left*), phloroglucinol (*middle*), hydroxyhydroquinone (*right*)

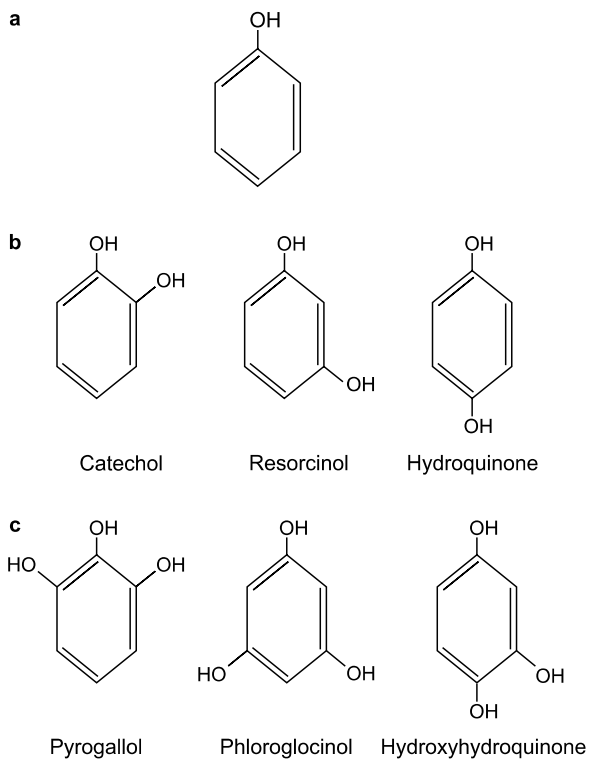


Fig. 2.23 Structure of Lowsone

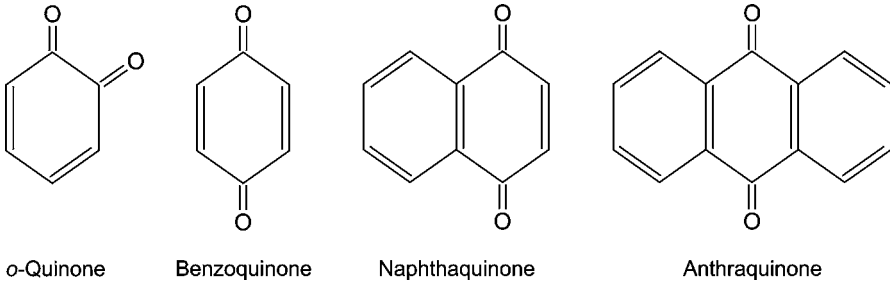
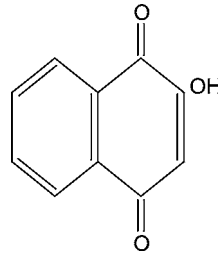


Fig. 2.24 Structure of different quinones

2.2.2.2

Nitrogenous Organic Compounds

Proteins and Amino Acids

The most important nitrogenous organic compounds, found in soils, are proteins and amino acids. It is estimated that about 20–50% of organic nitrogen in soils exists as amino acids. These are compounds that contain carboxyl, $-\text{COOH}$ and amino group, $-\text{NH}_2$. Thus many of them are neutral, but can react as acids or bases according to the prevailing conditions. Polymerisation of amino acids produce chain polymers known as *polypeptides*; very long chains of polypeptides are known as *proteins*. Both proteins and amino acids persist in the soil by being absorbed on the surfaces of clay minerals or being incorporated into other organic material. Proteins in soils ultimately break down, through bacterial or fungal action, into methane, CH_4 ; amines (compounds similar to ammonia, NH_3 , in which a part or all the hydrogen has been replaced by organic groups); urea, $\text{NH}_2-\text{CO}-\text{NH}_2$; carbon dioxide or water. Figure 2.25 summarises the breakdown series of the proteins.

We should, however, bear in mind that not only decomposition takes place; in some cases, bacteria may resynthesize the simple molecules generated by protein decomposition.

In addition to the above-mentioned groups, nitrogenous organic compounds in soils may exist as *amino sugars*, nucleic acids or any other biological compounds.

Amino sugars are derived from sugars by substitution of one of the $-\text{OH}$ groups by an amino group $-\text{NH}_2$. D-glucosamine (Fig. 2.26), formed from glucose, serves as an example.

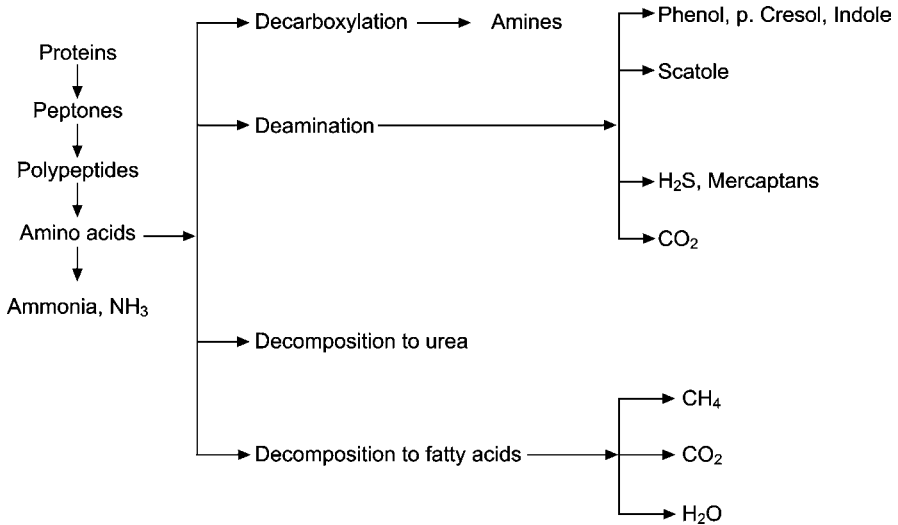
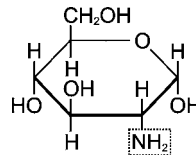


Fig. 2.25 Breakdown series of the proteins

Fig. 2.26 D-glucosamine (after Stevenson 1994)



Nucleic acid is the name given to a substance found in all living cells. It may also occur in soil as a complex high molecular weight biopolymer, the monomers of which are known as *nucleotides*. Each of these nucleotides consists of three components: a nitrogenous heterocyclic base (either a purine or a pyrimidine), a pentose sugar and a phosphate group. According to the pentose sugar in the chain forming the single nucleotide, two types of nucleic acid are known. If the sugar was ribose (see Fig. 2.27) the acid would be called *ribonucleic acid* (RNA). In case of deoxyribose (see Fig. 2.27), the acid formed would be a *deoxyribonucleic acid* (DNA).

Skeletal Nitrogen Substances

These include cartilage of vertebrates and chitin of invertebrates. They are unlikely to decompose and persist in an almost unchanged state in the soil. Cartilage is largely made of a hardened mucous substance known as *mucoprotein* or *glycoprotein*. This is a covalently linked conjugate of a protein and a polysaccharide, whereby the latter forms about 4 to 30% of the whole compound. Another mucoprotein that may form a gel in soil at a low pH comes from mammalian urine, where it is most abundant.

Chitin (the name is derived from the same Greek word meaning *tunic*, referring to hardness) is a polymer made of a chain of an indefinite number of N-acetyl glucosamine groups (see Fig. 2.28). It is one of the main components in the cell walls of fungi, the exoskeletons of insects and skeletal parts of other arthropods.

Fig. 2.27 Structures of ribose (left) and deoxyribose (right)

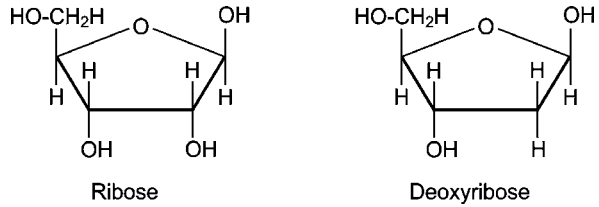
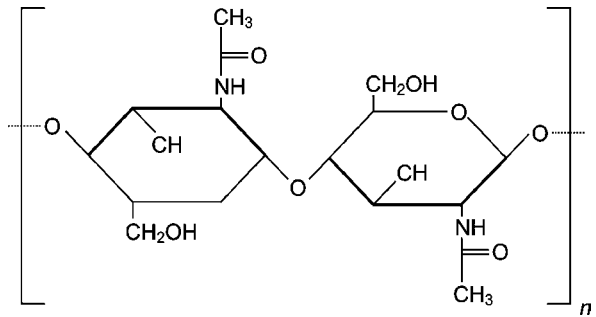


Fig. 2.28 Structural model of chitin



2.2.2.3

Lipids

Lipids are esters of fatty acids with glycerol:



Animals and plant waxes are esters of higher acids with other higher alcohols. Other lipids are compounds containing phosphorus or nitrogen or both. On hydrolysis, they yield the parent acids with glycerol, aliphatic alcohols, carbohydrates, nitrogenous bases, or sterols. Lipids are resistant to decomposition, but they are soluble in ordinary “fat” solvents such as ether and chloroform

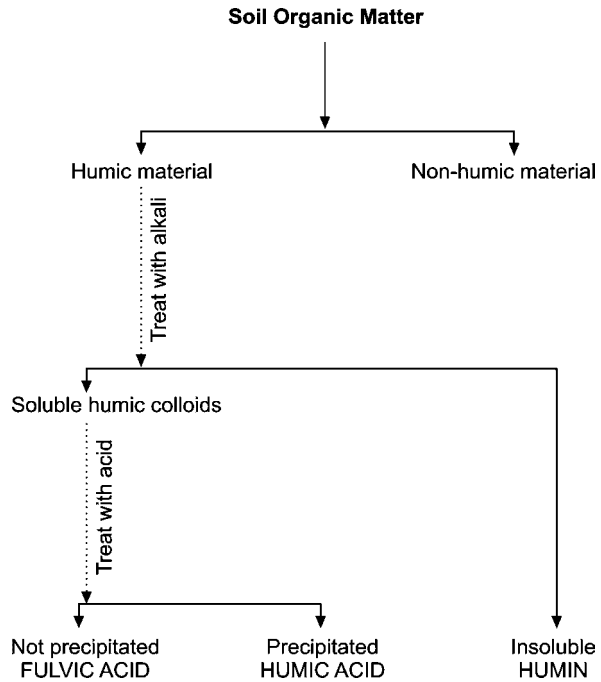
2.2.2.4

Complex Substances Including Humic Acids

Humic substances are generally defined as natural organic substances, which are normally rich in nitrogen and may result from bacterial decay of plant and animal remains. They include a complex of poorly understood compounds, having different shades of brown and yellow colours.

It has been shown by many authors, that they comprise of three main fractions (*humic acids, fulvic acids and humin*), having molecules of 6–50 nm of no single structural formula and characterised by high molecular weights (1 500–30 000) and a large specific surface area. The three fractions are differentiated according to their solubility in water at different pH-values – a method that is normally used for their laboratory fractionation (see Fig. 2.29).

Fig. 2.29 Fractionation of humic substances (according to Ross 1989)



Humic Acid

This is the fraction soluble in water at a pH-value lower than 2, indicating that humic acid is only soluble under alkaline conditions (Stevenson 1994). It is of brown to grey black colours and may be extracted from soil using aqueous alkaline solvents. Humic acids were first reported by Achard in 1786, who extracted them from peat bogs near Berlin, Germany, and spent later a long time studying their properties and trying to decipher their origin and mode of formation. These studies led him to the conclusion that humic acids were derived from simple sugars. He then formulated this in the *sugar-amine condensation theory*, which was held, for a long time, as an explanation for the origin of humic material.

Amine-Sugar Condensation Theory

According to this theory, condensation reactions between reducing sugars (ketoses and aldoses) and amino compounds lead to the formation of an N-substituted glycosylamine. This is supposed to give, in the course of dehydration and fragmentation, the brown nitrogenous polymers forming the bulk of what is known as *humic acid*. This may be understood by considering the so-called *Maillard reaction* (the browning reaction), known from food chemistry, which was described by Luis Camille Maillard in the early 1920s. This reaction consists of, according to Lee and Nagy (1983) and Mauron (1981), three main stages:

1. *The initial stage (formation of glycoside)*. In this stage condensation between the carbonyl group of an aldose and the free amino group of an amino acid results in

the formation of an N-substituted glycosylamine according to the equation shown in Fig. 2.30.

The initial stage is made up of two partial steps; in the first partial step, condensation between the carbonyl group of the aldose and the amino group in the amino acid, results in a condensation product (right upper part of Fig. 2.30). As expected when primary amines undergo condensation with aldehydes, the condensation product, in the second partial step, rapidly loses water to form a dehydration product, known generally as a *Schiff's base* – a reaction that is reversible and acid-base catalysed. The Schiff's base subsequently changes into the cyclic compound aldossylamine (in this case D-glucosylamine). During the initial stage no browning occurs.

2. *The medium stage (formation of ketosamine)*. Fragmentation of the products formed in the initial stage produces charged species known as *immonium ions*. These are the charged ends resulting from the fragmentation of peptide chains. The immonium ions are rearranged, after their formation, by isomerism (see Fig. 2.31) and subsequently form a compound called *ketosamine*. This process is known as *the Amadori rearrangement*.
3. *The final stage (formation of reactive substances that polymerise to produce dark brown humic acids)*. In the final stage the ketosamines may undergo dehydration to form reductones (compounds containing a hydroxyl group on each of the carbon atoms of a C=C double bond; so called because of their reducing power, e.g. ascorbic acid: vitamin C) and dehydroreductones. Ketosamines may undergo fragmentation as well, forming compounds such as hydroxyacetone (*acetol*: $\text{CH}_3\text{-CO-CH}_2\text{-OH}$), or pyruvaldehyde (Fig. 2.32) which subsequently undergoes degradation to form the so-called *Strecker aldehyde*.

Fig. 2.30 Initial stage of the Maillard reaction

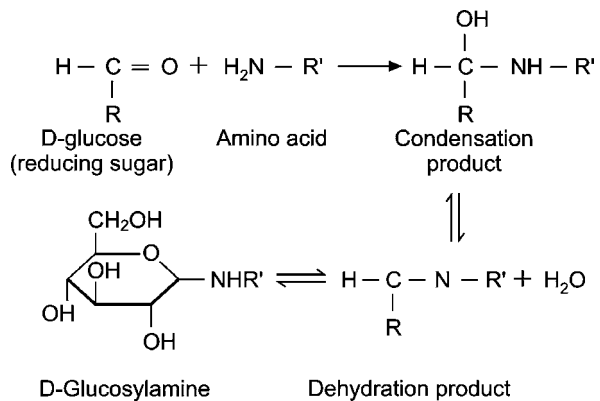


Fig. 2.31 Formation of the ketosamine (*Amadori rearrangement*)

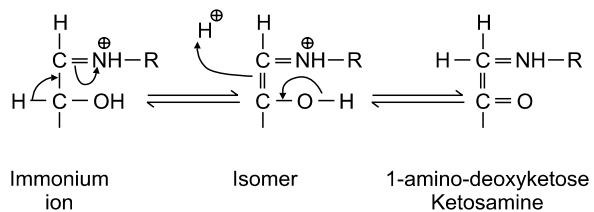
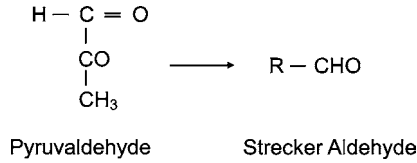


Fig. 2.32 Formation of Strecker aldehyde



These compounds are highly reactive. They eventually polymerise to form macromolecules of humic acids. A model of humic acid, according to Stevenson (1994), is shown in Fig. 2.33.

The model shows a macromolecule made of free and bound phenolic OH groups, quinone structures, nitrogen and oxygen as bridge units and COOH groups variously placed on aromatic rings.

It remains to say that the Maillard reaction, as known from food chemistry, is a temperature controlled reaction which works best at temperatures above 300 °C. Such temperatures are naturally not available at near surface sedimentary environments. That is why it is thought that microorganisms may be playing a key role in this process. Mineral catalysts such as clay minerals may also be supportive in overcoming the energetic barriers of the reaction. (Gonzales and Laird 2004)

However, due to the recognition that sugars were not the only possible precursors of humic acids, many authors challenged the amine-sugar condensation theory during the 1920s. In Germany, coal petrographers drew attention to the possibility that Lignin may be the parent material for humic acids, thus delivering the first arguments for what was later known as the *lignin theory*.

The Lignin Theory

Arguments delivered by coal petrographers that sugars in the natural environment were originally assimilated by microorganisms, and that they were not capable of persistence for a long time, paved the way for alternative notions considering lignin to be the parent material for humic acid (Waksman 1932). By the 1950s, the lignin origin theory seemed to be holding sway.

Lignin – a component in the cell walls of vascular plants – is a polymer with an aromatic structure, built up of phenyl propane monomers (see Fig. 2.34); it can be completely degraded by white rot fungi (Kirk and Farrell 1987). These fungi are capable of producing lignolytic enzymes that oxidatively cleave the phenylpropane monomers.

According to Waksman, fragmentation of lignin macromolecules is followed by elimination of methyl groups, oxidation and condensation with N-compounds, to give humic acids (see Fig. 2.35).

The lignin theory according to Waksman (1932) is supported by the following facts:

- The great majority of fungi and bacteria are capable of decomposing lignin and humic acids, albeit with considerable difficulty.
- Both polymers (lignin and humic acids) are soluble in alcohol and pyridine, hinting at a certain degree of kinship.
- Both are also soluble in alkali and precipitated by acids. They are both acidic in nature.
- Heating lignin with aqueous alkali gives methoxyl-containing humic acids.
- Humic acids and oxidised lignins have similar properties.

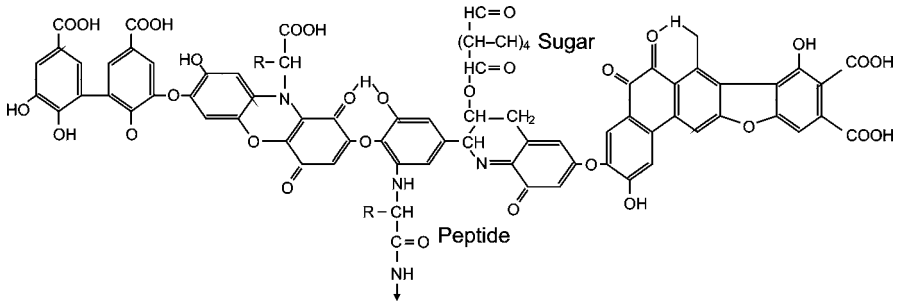


Fig. 2.33 A structural model of humic acid (after Stevenson 1994)

Fig. 2.34 Lignin monomer (according to Kirk and Farrell 1987)

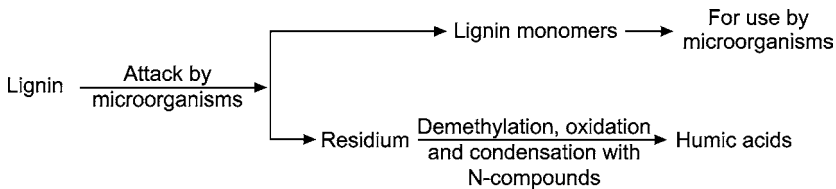
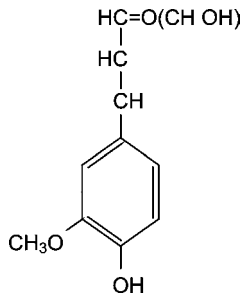


Fig. 2.35 The lignin theory according to Waksman (1932)

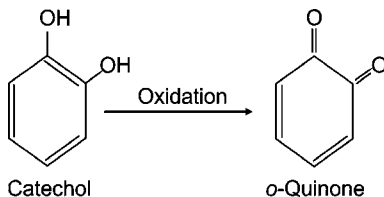
As a matter of fact, the lignin theory, as formulated by Waksman, is considered obsolete today. Yet lignin still plays a key role in the subsequent theories, which are supported by most authors at present. Among such modern theories the *polyphenols theory* holds a central position.

The Polyphenols Theory

Polyphenols are chemical substances, principally found in plants, giving some flowers and vegetables their characteristic colours (see above). Chemically, they are phenolic compounds having more than one hydroxyl group. An example of these is Catechol (Fig. 2.36), which causes the dark colouration of some plants and vegetables when cut opened and exposed to air (apples, potatoes, etc.). The darkening occurs in this case due to the change of catechol into *o*-quinone by oxidation (see Fig. 2.36).

Quinones are capable of condensation with amino compounds (e.g. proteins and other macromolecules) to form strong dark coloured complexes of high molecular

Fig. 2.36 Formation of *o*-quinone from a polyphenol (catechol) by oxidation



weights similar to humic acids. For this reason, it is easy to imagine a similar process through which lignin, cellulose or any complexes of polysaccharides, could be attacked by microorganisms to yield phenolic aldehydes and acids, which in turn would produce polyphenols. The latter would eventually be oxidised with the help of phenoloxidase enzymes (microorganisms) to produce quinones (Marshall et al. 2000). This, on condensation with amino compounds, can change into humic macromolecules. The whole process can be summarized in the schematic representation shown in Fig. 2.37 (Stevenson 1994).

Inspection of the different theories about the origin of humic acids shows clearly that the whole controversy lies in one point: that is at which stage in the alteration of plant and animal material does the reaction heads towards the formation of humic macromolecules and what chemical mechanisms steer the reaction. Does the reaction start at the stage of simple sugars? Does it start directly at the moment when lignin or cellulose is attacked by microorganisms? This remains a matter of speculation. Yet one point remains clear: humic acids are produced as a result of decomposition of organic materials, especially of plant origin – a matter substantiated by observation. It is also needless to say that the decomposition of plant remains is one of the central processes that keep the bio-geochemical cycle going. Plant tissues are sinks for CO₂ and if they were not decomposed, releasing CO₂ back into the atmosphere, a depletion of the gas with all its consequences for the bio-geochemical cycle would occur. At present, however, many authors believe that all the above-mentioned mechanisms of humic acids formations work together, hand in hand, and that in one and the same place, all three mechanisms may be active, replacing each other at given interfaces according to the physical chemical conditions. Microorganisms mostly provide active biological matter that work as a catalyst.

Fulvic Acid

This is the fraction of humic substances that remains in solution on acidification of the alkaline extract (humic acid precipitates at a pH-value of less than 2).

Figure 2.38 illustrates a partial structure of fulvic acid according to the model proposed by Buffle (1988).

Fulvic acids are less intensively studied than humic acids. Similar to the latter, they are darkly coloured acidic substances lacking the specific chemical and physical characteristics of simple organic compounds. Buffle (1988) suggested a model for fulvic acids (see Fig. 2.38) containing both aromatic and aliphatic structures, extensively substituted with oxygen and characterised by a predominant occupation with –COOH

Fig. 2.37 The polyphenol theory (after Stevenson 1994)

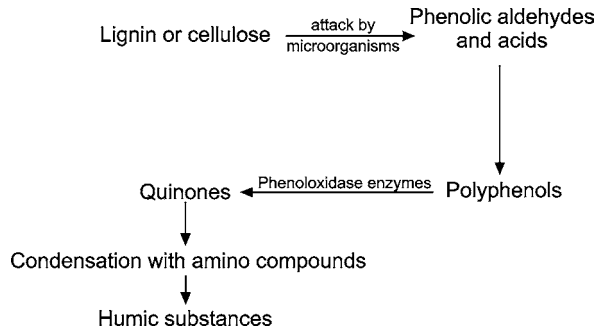
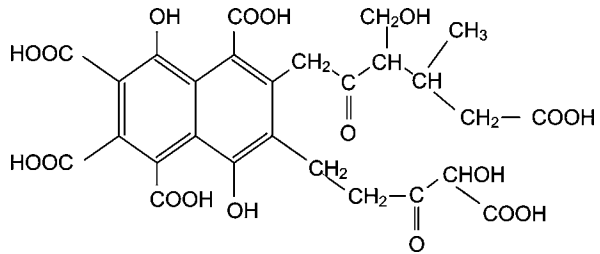


Fig. 2.38 A model for the structure of fulvic acid (according to J. Buffle 1988)



and –OH functional groups. These give them their acidic character and specific activity in adsorbing, complexing and chelating metals.

Fulvic acids modes of formation are similar to humic acids. According to Waksman, (1932 – *lignin theory*), they are formed by fragmentation of humic acids to smaller molecules. The polyphenol theory, however, suggests that they are directly formed from quinones parallel to humic acids. The ratio of humic acids to fulvic acids depends upon the type of soil, ranging from 0.3 in *tundra soils* to 2.0 or 2.5 in ordinary *chernozem soils* (Kononova 1966).

Humic

Humic is the stable fraction of humic materials, insoluble at all pH-values. It usually forms the predominant organic material in most soils and sediments (Kohl and Rice 1996). Its organic carbon represents more than 50% of the total organic carbon in soil. A considerable number of organic pollutants (e.g. pesticides, herbicides, polychlorinated biphenyls – PCBs) bind rapidly, and in many cases, irreversibly to it (*ibid*).

However, the insolubility of humin seems to have made it very difficult to understand its environmental as well as its analytical chemistry, and despite the great advances on the fields of analytical techniques, such as IR and GC, no generally accepted models of structure for all humic substances have been achieved.

Nevertheless, some authors have been trying to establish tentative models for humin (Rice and MacCarthy 1990; Lichtfouse 1999). The model of Lichtfouse (1999) is based on the assumption that humin is mainly formed of three components:

1. Resistant straight chain biopolymers, indicated by the presence of C_{11} – C_{24} compounds, which are typical breakdown products of these biopolymers, C_{27} – C_{33} linear alkanes and alkene doublets, having typical wax structure, encapsulated in the humin matrix.
2. Compounds bound to the humin bulk by chemical bonding (sterol and phytol), probably derived from chlorophyll and other plant material.
3. Despite the fact that no indications were shown for links between two or more molecules, the author suggested a tentative model, shown in Fig. 2.39 to approximately explain the structure of humin.

2.3

The Liquid Phase – Soil Water

Soil water is principally derived from two sources: precipitation and groundwater. Each contributes to the amount of moisture in the soil, within the regime of a sensitive dynamic equilibrium, depending mainly on the climate and the water balance between the atmosphere and the plant-soil system. The amount of water lost to the atmosphere comprises the sum of the water transferred by evaporation and of that transferred by plant transpiration, forming together the *evapotranspiration*. This depends directly on the climatic conditions as well as the properties of the plant-soil system. The evapotranspiration that would take place under optimum precipitation conditions and soil moisture capacity is known as the potential evapotranspiration, or, in short, *POTET*; it can be determined by empirical methods. Under ideal conditions, *POTET* will be equal to the actual amount of water transferred to the atmosphere by evapotranspiration in the region under consideration, which is known as *ACTET*. In other cases when

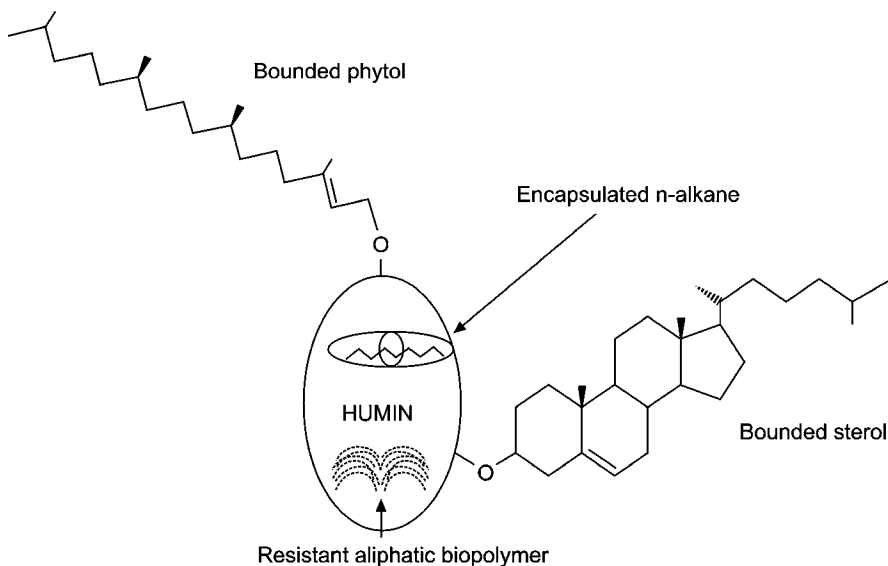


Fig. 2.39 The tentative model of humin suggested by Lichtfouse (1999)

POTET is not met by *ACTET*, the considered area will suffer a moisture shortage. The difference between *POTET* and *ACTET* in this case is known as the deficit or simply *DEFIC*. Still there may be another scenario when *POTET* is fully satisfied, yet the soil still receives water input, a situation will arise where water oversupply will lead to the formation of surface puddles and/or a recharge of the groundwater reservoir. This water surplus is shortly known as *SURPL*. To establish an account or water budget for a given region, all the foregoing quantitative factors are united in the following simple equation, known as *Thornthwaite's water-balance equation* (after C. W. Thornthwaite 1899–1963):

$$PRECIP = (POTET - DEFIC) + SURPL \pm \Delta STRG \times ACTET \quad (2.1)$$

where *PRECIP* stands for precipitation and $\Delta STRG$ for the soil moisture, storage or the amount of water that is stored in the soil and is accessible to plant roots. Indeed, not all water stored by the soil can be classified in this category, for there are two main types of soil moisture: the type available to plant roots, which is held in the soil by surface tension and cohesive forces and is known as *capillary water*; and the type inaccessible to plant roots, which is known as *hygroscopic water*. This is made up of thin films of water molecules held tightly to the surfaces of soil grains by hydrogen bonds. Soils containing predominantly hygroscopic water and none or very little amounts of capillary water are not in a position to support plant growth; they are said to be at *wilting point*. Whereas, soils having pores full of capillary water are generally said to be at *field capacity*. In the case of water oversupply to the soil, the amount of water percolating downward to join the groundwater reservoir will be termed *gravitational water*. A soil, in which all gravitational water is drained out, contains the maximum level of capillary water and is consequently at field capacity. Based on the principles of water balance, the U.S. Soil Conservation Service recognises the following five soil moisture regimes:

1. *Aquic*. This is the case, when the soil is constantly wet, like in bogs, marshes and swamps. An aquic environment is a reducing one, virtually without dissolved oxygen. It is characterised by perennial stagnant water.
2. *Aridic (Torric)*. This regime occurs mainly in arid or semiarid climates, where soils are dry more than half of the time. Soil temperatures at a depth of 50 cm lie above 5 °C. This regime is characterised by thin soils allowing high rates of evaporation and/or surfaces sealed by dryness, so that infiltration and recharge are inhibited.
3. *Udic*. The water balance in this regime is characterised by a moisture surplus at least during one season of the year. If the surplus exists throughout the year, the regime is called *perudic*. The soil is always in a position to support plants due to its rich reservoir of capillary water.
4. *Ustic*. This regime occurs in semiarid and tropical wet climates. It is between the aridic and udic regimes. The water balance reveals a prolonged deficit period following the growing season.
5. *Xeric*. This is the regime characterising the Mediterranean climate: dry and warm summer, rainy and cool winter. In every six out of ten years, there are (under this regime) at least 45 consecutive dry days during the four months following the summer solstice.

2.3.1

Composition of Soil Waters

Soil solutions contain a wide range of dissolved and/or suspended organic and mineral solid and gaseous substances (Fig. 2.40). Organic substances include all minor amounts of soluble and suspended organic compounds. These, together with minor amounts of dissolved silica and some pollutants, such as heavy metals (lead, zinc, cadmium, etc.), belong to the minor constituents of the soil water. The major constituents of soil water include dissolved salts in mobile ionic form, and gaseous compounds such as CO_2 . This may be derived from the atmosphere by being dissolved in precipitation, or from the soil air, as a product of the respiration of soil organisms. It also may be the product of internal chemical reactions (e.g. as a product in the protein decomposition series). Mobile ions resulting from the dissolution of mineral substance include basic cations such as Ca^{2+} , Na^+ , K^+ , NH_4^+ , and anions such as NO_3^- , PO_4^{3-} , Cl^- . These are provided by external sources as well as by internal chemical processes taking place within the soil (weathering, diagenesis, decomposition and synthesis of organic matter). Chloride ions, and to a lesser extent sulphate ions (SO_4^{2-}), may be provided by atmospheric sources including air borne marine salts and acid deposition. Under acidic conditions, cations of iron and aluminum may also constitute a considerable part of the active cations in soil water. The concentrations of ions in the soil solution, however, depend mainly on the soil-pH, its oxidation status and the affinity to processes such as adsorption, precipitation and desorption. Lower pH-values result in diminished metal adsorption capacities, which will in turn lead to higher metal concentrations in the solution. An important factor in determining the soil pH is the concentration of CO_2 in the soil solution. It provides the solution with H^+ through the reaction:



Soil water in equilibrium with CO_2 in soil air has pH-values often below five. This acidity arises mainly from the following main sources:

- Organic acids produced during degradation of organic matter;
- Nitrification processes, where NH_4^+ is converted into NO_3^- ;
- Release of H^+ by plants in exchange for nutritive base cations;
- Sulphide oxidation;
- Pollution through industrial and urban emissions.

2.4

The Gaseous Phase – Soil Air, Origin, Composition and Properties

Soil air, or soil atmosphere, is the characteristic name given to the mixtures of gases moving in the aerated zone above the water table (see Fig. 10.13 in Sect. 10.4) and filling the soil pores, where these are not already occupied by interstitial water. Mass flow of these gases in the aerated zone will be wholly controlled by atmospheric factors such as temperature, pressure, and moisture conditions. As far as major constituents are concerned, soil air has a composition slightly different from that of atmospheric

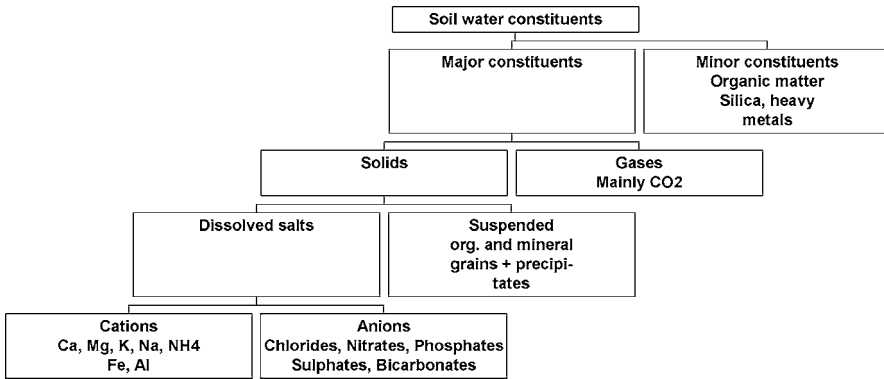


Fig. 2.40 Schematic diagram, showing the principal constituents of soil water

Table 2.5 Major constituents of soil air and atmospheric air in volume %

System	Composition (%)		
	Nitrogen	Oxygen	Carbon dioxide
Atmospheric air	78	21	0.03
Soil air	78	15–20	0.25–5.0

air (see Table 2.5). Although soil air contains 1–6% less oxygen by volume than atmospheric air, we find that it contains about 10 to 150 times more CO_2 .

These differences in the concentration of CO_2 and O_2 , between soil air and the atmosphere, result in partial pressure gradients between the two systems along which CO_2 moves from the soil to the atmosphere, while the oxygen flow takes place in the opposite direction. Gas exchange between soil air and the atmosphere occurs also along temperature gradients and in sites where rainwater introduces atmospheric gases into the soil. Beside the major constituents, minor or trace amounts of other gases may occur in the soil air, originating from deep-seated sources or as products of organic or mineral reactions in the soil environment. Examples of these are trace amounts of CO (carbon monoxide) and CS_2 (carbon disulphide), occurring in soils overlying geothermal sites in Utah (Hinkel et al. 1978). By contrast, light hydrocarbons such as methane (CH_4), H_2 , H_2S , CO , and water vapour, are mainly produced within the soil body as products of degradation of organic material (Schlegel 1974). Traces of the extremely toxic gas *dimethyl mercury*, generated by bacterial activities, may under extremely reducing conditions occur in the soil.