1 Material Cycles

1.1 Geochemical cycles

1.1.1 Environmental areas

Our environment is divided into spheres. By 'biosphere', we mean all of the layers of the Earth inhabited by living organisms. We usually use the term 'ecosphere' today. The latter is in turn divided into different ecosystems. The atmosphere is the mass of air surrounding the earth with a fluid upper limit bordering on outer space. The ecosphere includes only inhabited space. Meteorologically the atmosphere is divided into troposphere and tropopause, stratosphere and stratopause, mesosphere and mesopause, and thermosphere, based on physical properties. The pedosphere represents the highest region of the soil which is inhabited by living organisms. It borders on the lithosphere, the outermost rock layer (geological foundation) down to a depth of some 100 km. The pedosphere is penetrated by the atmosphere and the hydrosphere (as groundwater in this case), i.e. by all other compartments (as individual parts of a complex ecosystem for the characterisation of material transformation and transport processes via interfaces) of terrestrial ecosystems.

1.1.2 Endogenous and exogenous material cycles

All geological processes on Earth can be summarily described as a cycle of the materials. Due to orogenesis or epeirogenesis, magma travels from the inner Earth up to the Earth's surface and hardens to form magmatic rock. Magma (Greek for 'kneaded mass, thick salve') is the name given to the glowing hot silicatic molten rock in the inner Earth. Orogenesis is a temporally and spatially limited mountainous formation process (also called tectogenesis). Epeirogenesis describes reversible, wide-ranging lifting and sagging of parts of the Earth's crust over long periods of geological time.

Metamorphosis includes the transformation of rocks. It takes place in the pressure and temperature fields of the Earth's crust, whereby mineral reactions (e.g. recrystallisation) take place as a result of changes in the physicochemical equilibrium. Depending on the origin of the starting material, metamorphic rocks are called orthorocks (former magmatic rocks) or para-rocks (former sedimentary rocks).

The magmatic and metamorphic rock which is exposed due to lifting is acted upon by exogenous forces – i.e. gravity, temperature, effects of water, ice and wind – to produce weathering products in solid or soluble form as well as soils. Chemical and biological processes in particular play a role in the formation of soils. Soil is the term used for the uppermost, inhabited weathering layer of the Earth's crust (see pedosphere). Weathering products and soils are displaced and deposited in other locations in the form of clastic or (bio)chemical sediments. Clastic sedimentary rocks are the products of mechanical weathering of stone, and are also called debris. Sedimentary loose rock such as dust, sand, claywash, mud ooze and peat are formed. With chemical and physical effects, in the course of diagenesis new sedimentary solid rocks are formed, such as sand, dolomite and limestone, shale clays and lignite.

Humans interfere with these natural cycles, in particular via the 'anthropogenic exploitation of natural resources', i.e. by the mining of ores and rocks, and by the use of water. This involves especially the processes of weathering and erosion, natural soil erosion due to the effects of wind or water, and the transport and redistribution of rocks or soil.

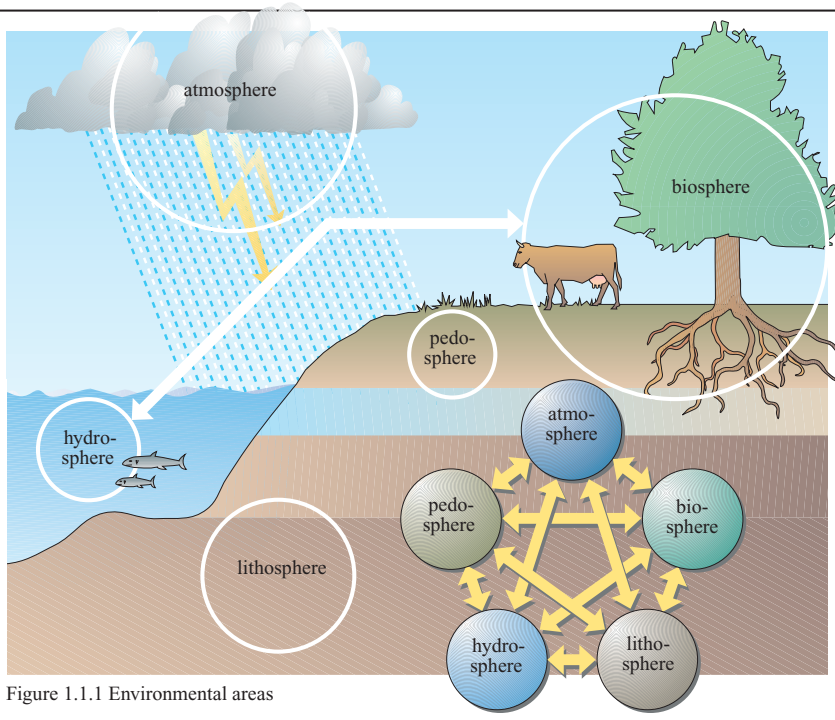

Figure 1.1.1 Environmental areas

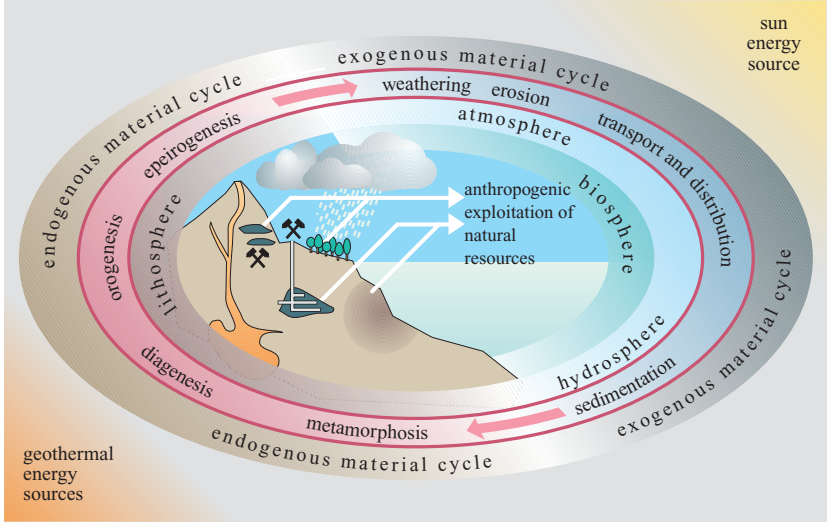

Figure 1.1.2 Endogenous and exogenous material cycles

1.1.3 The geological material cycle

For the geological material cycle, it is important that every transport of magma is based on a disturbance of the equilibrium from changes in the temperature and pressure ratios. Plutons are created when magma remains in the Earth's crust; in volcanoes, the magma finally reaches the Earth's surface. After the liquid magma phase, the actual hardening starts at about 1200 °C. The plutonic rocks are formed in the phases of early crystallisation (up to 900 °) and primary crystallisation (up to 600 °). They consist of silicates containing less silicic acid and the principal mass of lithogenous minerals.

In the geological cycle, new magmatic rocks can form via sinking to greater depths and the processes of metamorphosis, subsequent melting and re-solidifying upon being lifted up. On the other hand, sedimentary loose and solid rock can weather immediately after formation and again after being exposed, and it can be rearranged again. Para-rocks can also be created from solid rocks via metamorphosis, and they can come to the surface again even without melting. Finally, magmatic rock can also be converted to metamorphic orthorock even before it is made to stand out, and then enter again into the exogenous cycle.

1.1.4 The 'crust–ocean machine'

The 'geological mixer', or 'crust–ocean machine' of Garrels and Mackenzie (1971), starts with the energy centres: with the build-up of heat in the Earth's crust, caused by the decay of radioactive elements such as uranium and thorium, and with the radiation of heat via the nuclear processes taking place on the Sun. The endogenous processes are supplied with energy from the radioactive decay in the Earth's core. Gases and steam cause the weathering of the primary magmatic rocks. The sedimentary rocks and oceans of our Earth are the results of these processes in the form of a geological long-term effect.

The oceans represent a gigantic 'settling and evaporation vessel'. Due to the effects of gravity, the sedimentary rocks sink to greater depths, carried on by convection currents. At first they form wedges and prisms, but at these depths they are folded and/or broken and, depending on the depth, they undergo processes of diagenesis (solidification), metamorphosis (transformation) or melting (anatexis) – recycled rocks are produced. (Recycled) gases and water that are released during metamorphosis likewise return back to the weathering cycle on the Earth's surface.

In the course of the Earth's development during a period of 4000 million years, different spheres were formed (Section 1.1.1). First, the Earth's core was created out of iron-nickel. In the process, the primeval atmosphere of noble gases, ammonia, methane and hydrogen dissipated. This was followed by the creation of the three shells: core, mantle, and crust. The oxygen-free atmosphere contained gaseous materials from the inner Earth (water condensation, carbon dioxide, sulphur dioxide, hydrogen chloride). In the next developmental step, with the condensation of water and the formation of the oceans (as a result of cooling), the Earth's crust also changed its composition in the areas of the oceans and continents. The appearance of oxygen is linked with the higher development of life.

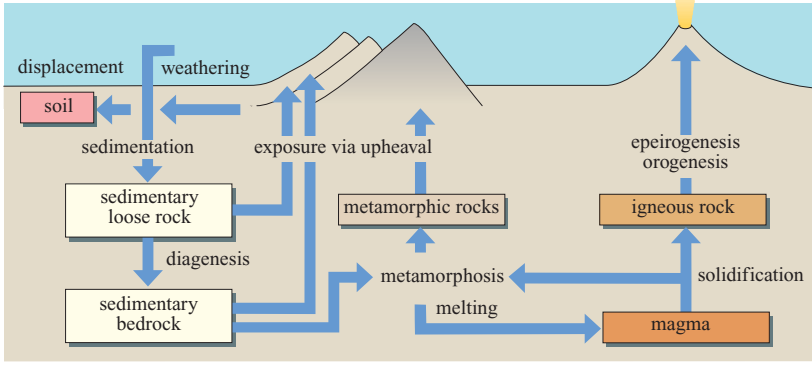

Figure 1.1.3 The geological material cycle

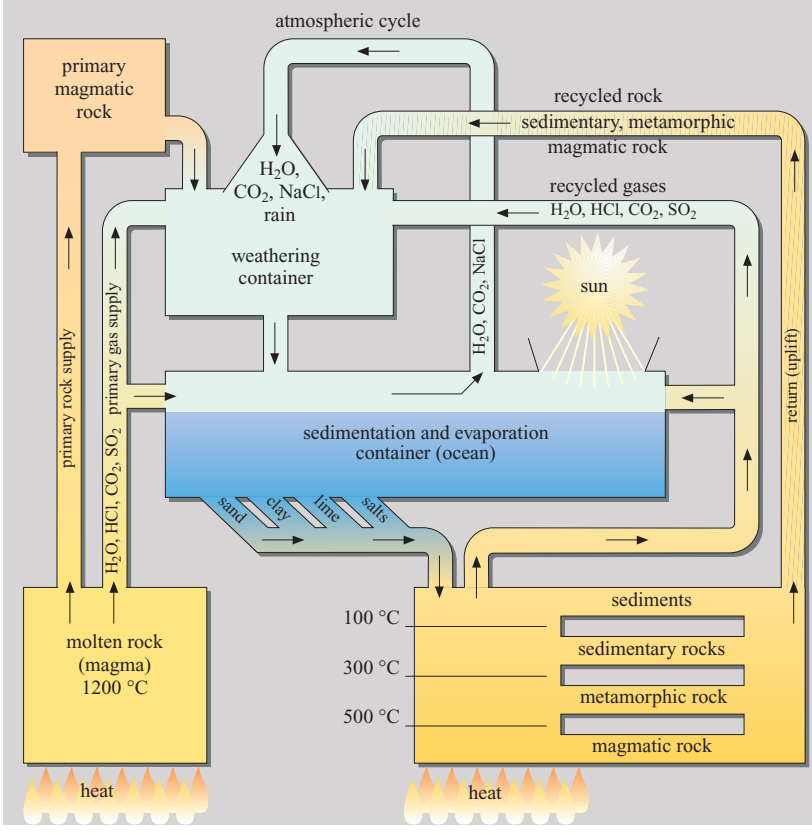

Figure 1.1.4 The 'crust-ocean machine'

1.1.5 The Earth as a biogeochemical factory

A view that is similar to the 'crust–ocean machine' is the analogy of a chemical factory that is reduced to a few processes (Sievers, 1974). Energy receives the heat machine from the Sun and in the inner Earth by means of the previously mentioned processes (Section 1.1.4). All of the processes are distributed to individual reactors. The heat generator drives the winds, ocean currents and the cycles of the water and the rock. Water is viewed as a means of transportation and as a chemical reagent. Over long periods of time, the reactions of the volcanic emissions (acids) with the basic rocks led to a constant composition of the oceans and to an atmosphere with a constant carbon dioxide level. Eruptive rock became soils, sediments and sedimentary rocks. After photosynthesis had become possible in the course of the Earth's development, and with the development of life, the biosphere became an 'entropy pump': due to the continuously radiating sunlight which was converted into thermal energy, the biosphere drove the biological and material cycles.

The oceans symbolise the central (main) reactor, which is connected to all other reactors. Mechanical erosion is depicted as the 'powder mill', the liquid extractor representing the chemical processes of weathering. The third reactor encompasses biological processes, which regulate the carbon dioxide and oxygen levels. If one views the Earth's core as the 'furnace', its energy induces the lifting of crystalline rocks and of sediments and leads to volcanic emissions. Components of all three secondary reactors feed into the main reactor. Detritus (from the Latin, meaning 'rubbed or ground off') is used in geology to indicate the rock debris created by weathering, and in biology to indicate finely dispersed materials – suspended and settling substances in waters – derived from the natural decay of dead plants and animals. These in turn contain organic residues such as lignin, cellulose and chitin, and they serve as food for the 'detritus-eaters'. The consumers are those organisms that feed on biomass, dead organisms, refuse such as foliage and excrement, as well as the accompanying microorganisms, and that then digest or mineralise these materials.

Dissolving processes take place in the liquid extractor, where the connection to the gas containers with oxygen and carbon dioxide emphasises their influence on the solubility of inorganic (e.g. calcium carbonate by CO_2) and organic (by O_2) substances. The water cycle is depicted by the distillation system, going from the oceans and to condensation in the liquid extractor. In this representation of the Earth as a chemical factory, in addition to the reactors we also differentiate among the following phases: gaseous, liquid, geologically sedimentary and crystalline.

All the processes which take place in the biogeochemical factory can be divided into biological/biochemical and geochemical/geophysical processes. The first group includes all metabolic processes (especially in the bioreactor). Geophysical/geochemical processes and hydrological processes, as well as erosion, sedimentation, geological metamorphosis and transport processes induced by winds, are principally those of melting and dissolving.

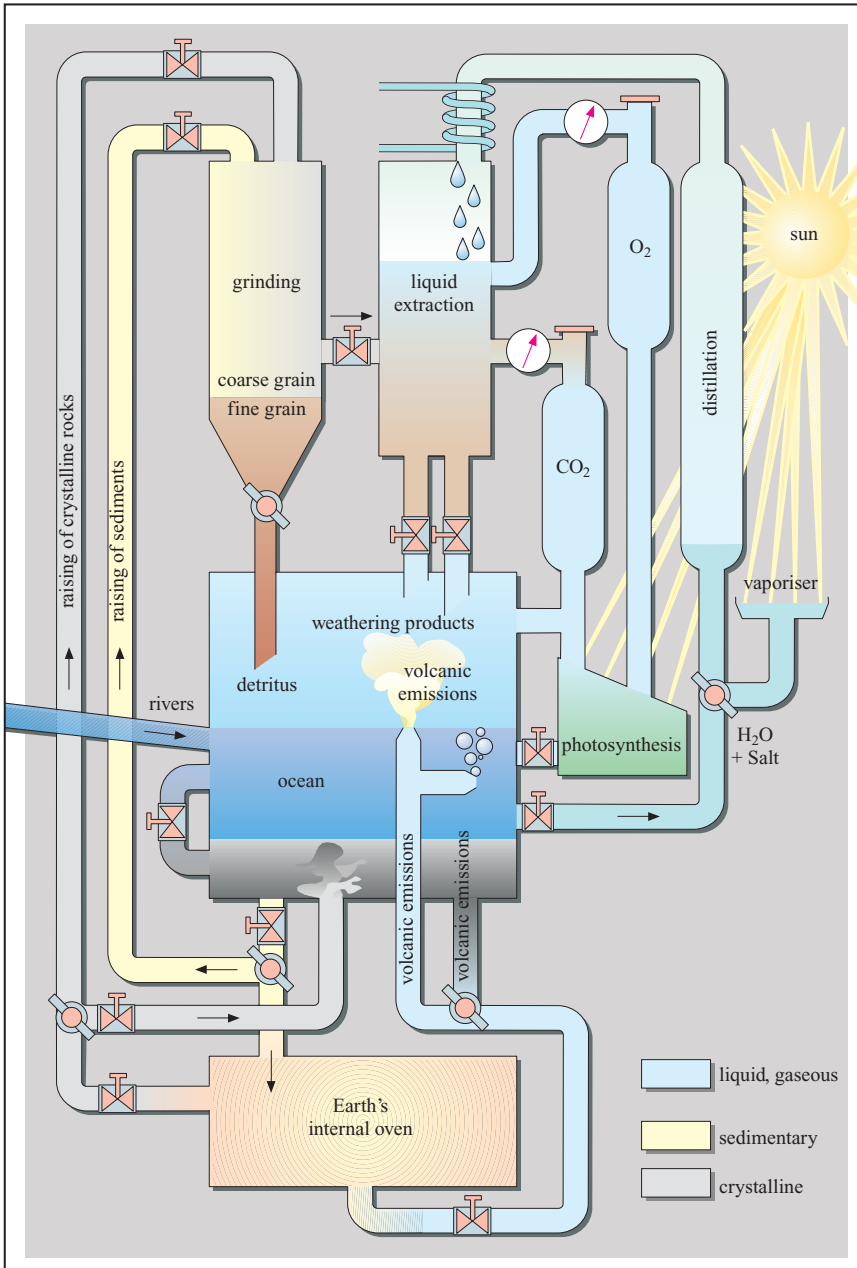

Figure 1.1.5 The Earth as a biogeochemical factory

1.2 The carbon cycle

1.2.1 Mineralisation and biosynthesis

The greatest portion of carbon in the form of carbon dioxide is stored in the oceans (3.8×10^{16} kg C) and in the atmosphere (7.2×10^{14} kg C). Approximately 15% of the CO_2 in the atmosphere is converted via photosynthesis in plants (see below). Half of this is used by the plants to produce biomass; the other half – starting from glucose – is used for acquiring energy and respiring back as CO_2 (respiration). Thus, the carbon cycle is directly linked to the oxygen cycle. Carbon reservoirs form carbonates in the hydrosphere (see inorganic forms of carbon), the biosphere (mussel shells, bones) and the lithosphere (lime, coral reefs in the hydrosphere boundary with 6×10^{15} kg C plus fossil fuels such as petroleum, natural gas, hard coal and lignite, and peat with 1.2×10^{15} kg C). Humans interfere with the carbon cycle through burning and the use of biomass. From the living and dead biomass, 6×10^{12} kg C (also as CO_2) is released into the atmosphere annually due to decomposition (mineralisation via microbial metabolism). The storage of biomass in the sediments (as fossilisation under the exclusion of air) removes carbon from the cycle (approximately 10^{11} kg C yr^{-1}). Another carbon cycle takes place between the atmosphere and the water: approximately 10^{14} kg C are exchanged between these compartments as CO_2 annually. Photosynthesis (by marine plankton with 65% of the total C taken up by the plant world) and the CO_2 uptake in the oceans represent sinks for the carbon. Currently approximately 4% of the CO_2 emitted into the atmosphere annually is of anthropogenic origin (combustion of fossil and non-fossil fuels, by the destruction of forests and soils and their outcomes). Compared to the amount of carbon that is taken out of the cycle by means of settling in oceanic sediment, the anthropogenic emission is greater by a factor of 50.

The equation

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$$

as the result of photosynthesis describes a complex chain of reactions. It takes place as two largely independent partial reactions, the light-dependent primary reaction (photochemical reaction in the light absorbing pigments, chlorophyll) and the light-independent secondary reaction (dark reaction). The dark reaction takes place in the stroma (framework) of the chloroplasts and requires $NADPH/H^+$ and ATP from the light reaction. CO_2 reacts with ribulose diphosphate with the formation of two molecules of phosphoglycerate (with three C atoms, a characteristic of C_3 plants), whereby CO_2 is reduced to a carbohydrate precursor and is fixed in the process. The photosynthesis system is disturbed by environmental toxins and specifically by herbicides.

The processes of mineralisation are in contrast to those of photosynthesis. Anaerobic decomposition processes, such as in a landfill (in compost in this case), generate CO_2 plus methane, and acids such as acetic acid and propionic acid. An aerobic phase (utilisation of atmospheric oxygen) shortly after the sedimentation is followed by three phases of anaerobic decomposition processes. An acidic fermentation is followed by the unstable and stable methane phase (methanogenesis). By photooxidation, carbon dioxide can be generated again for photosynthesis from methane via formaldehyde and carbon monoxide.

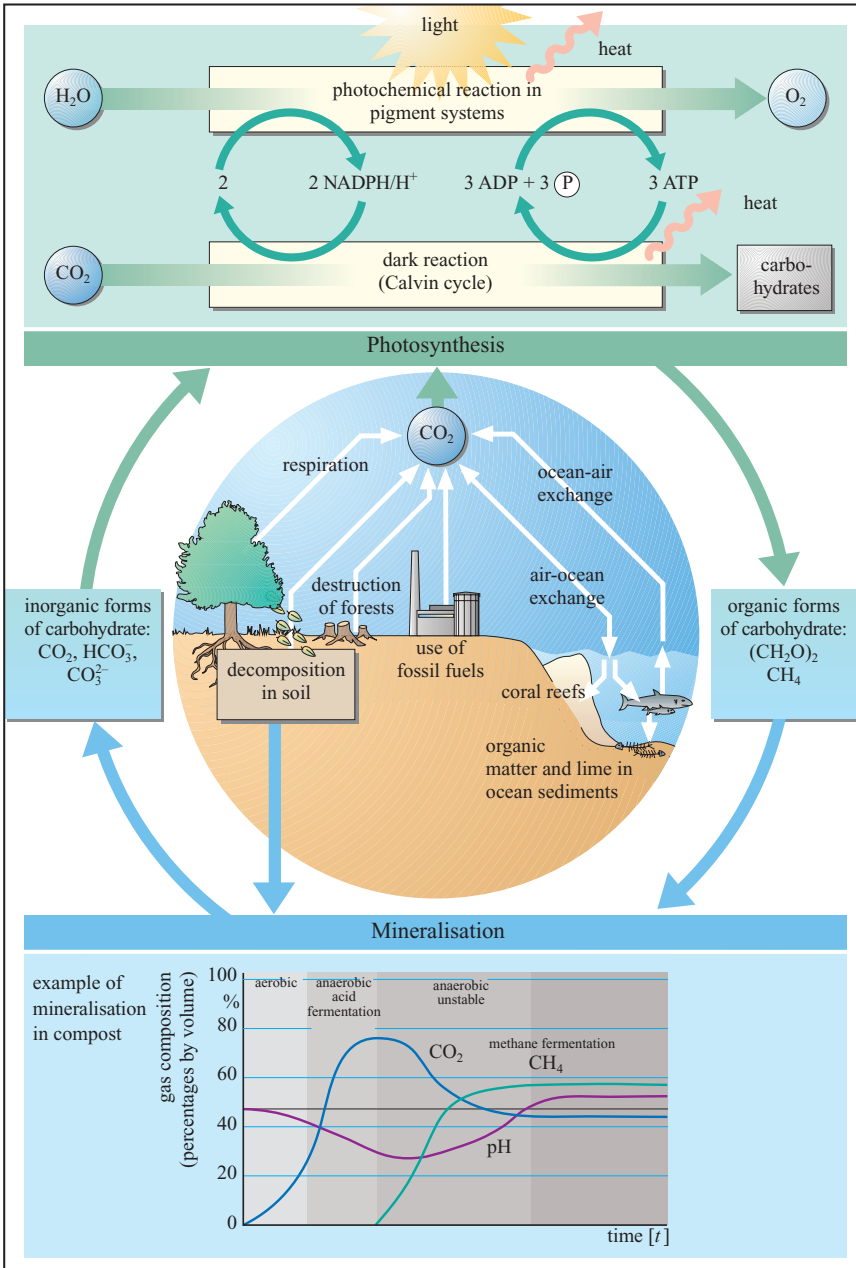

Figure 1.2.1 Mineralisation and biosynthesis

1.3 The nitrogen cycle

1.3.1 The global nitrogen cycle

The global nitrogen cycle is characterised by its numerous oxidation states between –3 and +5. Some 80% of the atmosphere consists of elemental nitrogen (oxidation number 0). Other species of the element nitrogen are organic compounds such as amino acids, proteins, amino sugars, amides and urea, and especially the inorganic substances NO_3^- (+5), NO_2^- (+3), NH_4^+ (–3) and nitrogen oxides NO (+2), NO_2 (+4), and N_2O (+1); see also Section 1.3.3. The biological nitrogen cycle is determined by nitrogen fixation, whereby atmospheric nitrogen enters into the hydrosphere and pedosphere and especially in biomass. Biological fixation is done by microorganisms and blue algae and in symbiosis of microorganisms with higher plants (e.g. rhizobia with legumes – legume bacteria) (nitrogen assimilation as a biocatalytic process). The oxides NO and NO_2 especially play a role in the atmospheric chemistry of nitrogen. Proteins can be formed from inorganic forms of nitrogen (ammonia assimilation). In the reverse process, organic nitrogen compounds can be converted back into ammonia by ammonification (by deaminating bacteria such as *Pseudomonas*). Microorganisms that cannot use light as an energy source use this to obtain the necessary energy: via oxidation, amino acids are converted into carbon dioxide, water, ammonia and energy; via nitrification (bacteria such as *Nitrosomonas* and *Nitrobacter*), they are converted into nitrite and nitrate. N_2O and N_2 are formed by denitrification, and they go into the atmosphere. Nitrates are easily washed out of soils, and by means of sediments they end up in the deep-sea floor or in the lithosphere. Volcanoes transport nitrogen into the atmosphere in the form of ammonia or nitrogen oxides. The lithosphere contains 0.2×10^{18} t N, the hydrosphere 23×10^{12} t, and the atmosphere 3.0×10^{15} t. Some 0.92×10^{12} t N are stored in biomass, 1.7×10^9 t in living biomass and 9×10^{11} t in dead biomass.

1.3.2 Anthropogenic effects

Nitrogen molecules are split in a natural manner in thunderstorms, and with atmospheric oxygen they form nitrogen oxides, which are a component of acid rain but which at the same time serve as nitrogen fertiliser. The growth of plants is limited by nitrogen, so humans disturb the equilibrium in the cycle with fertilisers (nitrate, ammonia and organic fertilisers). Using nitrogen fertilisers causes the same transformations as in the natural global nitrogen cycle: reactive nitrogen compounds from the atmosphere contribute to the destruction of ozone (see Section 2.2). Nitrogen oxides also enter into the atmosphere as a result of combustion processes. The intensification of the nitrogen cycle due to anthropogenic effects causes ecological problems such as the regionally increasing concentration of volatile nitrogen compounds (NO_x, N_2O, NH_3) in the troposphere and stratosphere, a greater exchange of nitrogen compounds between atmosphere and pedosphere, increasing concentrations of oxygen consuming nitrogen compounds such as urea $(NH_2)_2CO$, NH^+_4 and NO_2 in the hydrosphere, plus generally higher levels of nitrate in ground and surface waters. Under unfavourable conditions, carcinogenic nitrosamines can be produced from amines and nitrite.

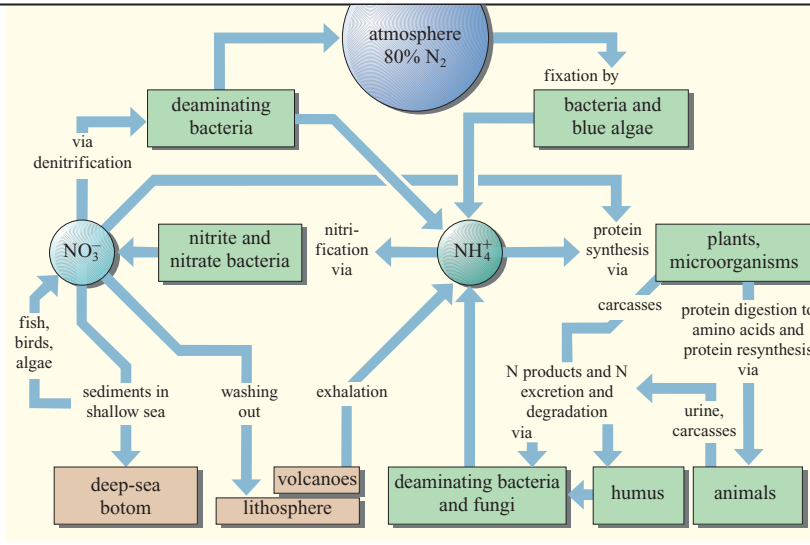

Figure 1.3.1 The global nitrogen cycle

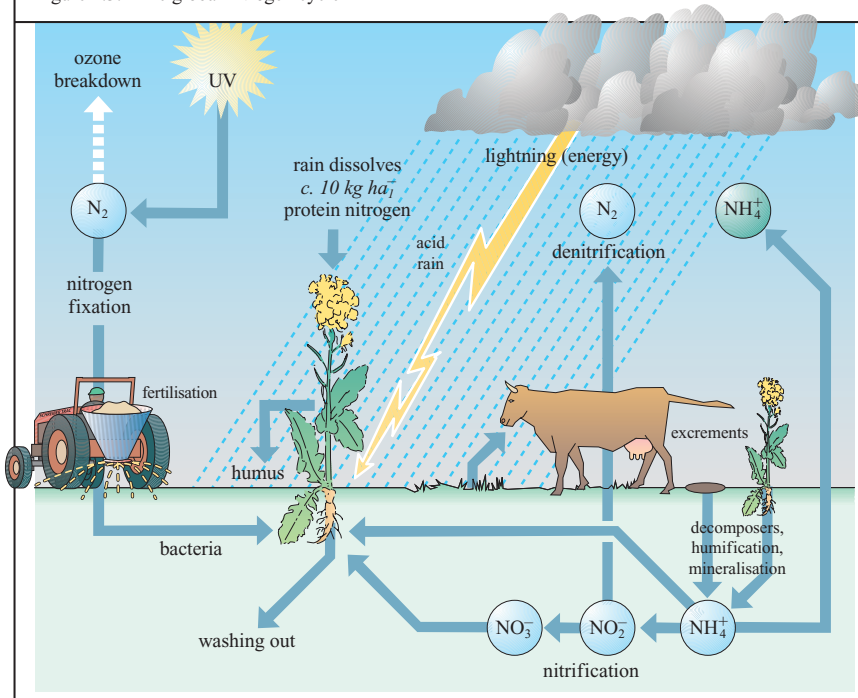

Figure 1.3.2 Anthropogenic effects

1.3.3 Ammonification, nitrification, denitrification

The increase in nitrogen concentration in surface waters can be traced back to a number of different water-soluble nitrogen compounds with differing oxidation numbers between –3 and +5: urea as a fertiliser component and a metabolic product of certain animals whose main end product of protein metabolism is urea, e.g. sharks, terrestrial amphibians, some turtles and all mammals. Ammonia and ammonium salts are derived from fertilisation, from putrefaction and biological food chains, and from waste water. Nitrates are components of fertilisers and an end product of nitrogen species with low oxidation numbers. The processes of the microbial nitrogen cycle include redox and acid–base reactions, plus reaction mechanisms that lead to the formation or splitting of C–N bonds.

In ammonification, owing to nitrogen fixation (Section 1.3.1), atmospheric nitrogen is incorporated into organic molecules (proteins). Because of metabolic processes by organisms, proteins or amino acids are converted into the excretion products urea $(NH_2)_2CO$ and ammonia, which exists as the ammonium ion in the presence of acids. Ammonia can go back into the cycle for the formation of proteins. According to the equation

$$(NH_2)_2CO + 2H_2O \leftrightarrows NH_4^+ + NH_3 + HCO_3^-$$

the hydrolysis of urea catalysed by the enzyme urease leads to ammonia or the ammonium ion (depending on pH conditions). In the environment, ammonium salts go into the water cycle or the soil.

In nitrification, in aerobic zones a microbial oxidation of ammonium ions takes place where nitrite is converted to nitrate as processes of nitrification. Microorganisms of the *Nitrosomonas* genus oxidise ammonium ions to nitrite:

$$2NH_4^+ + 3O_2 + 2H_2O \rightarrow 2NO_2^- + 4H_3O^+$$

(molar reaction enthalpy: 260 kJ mol^{-1}). In the second stage, *Nitrobacter* species oxidise the nitrite to nitrate:

$$2NO_2^- + O_2 \rightarrow 2NO_3^-$$

(molar reaction enthalpy: 100 $kJmol^{-1}$). The overall equation for the nitrification processes is

$$NH_4^+ + 2O_2 + H_2O \rightarrow NO_3^- + 2H_3O^+$$

Denitrification, or the reduction of nitrate to atmospheric nitrogen, takes place in anoxic zones (anoxic = based on oxygen deficiency) due to metabolic processes by numerous facultative anaerobic, heterotrophic microorganisms. They use nitrate nitrogen as an electron acceptor for the oxidative breakdown of organic carbon compounds. Denitrification occurs in stages; {H} stands for H donors:

$$NO_3^- + 2\{H\} \rightarrow NO_2^- + H_2O$$
$$NO_2^- + 2\{H\} \rightarrow NO + H_2O$$
$$2NO + 2\{H\} \rightarrow N_2O + H_2O$$
$$N_2O + 2\{H\} \rightarrow N_2 + H_2O$$

The end product of nitrification is nitrogen; intermediates, which can end up in the environment if insufficient H donors (e.g. methanol or acetic acid from the carbon cycle) are available, also include the nitrogen oxides NO (nitrogen monoxide) and N_2O (dinitrogen monoxide). N_2O in particular enters the atmosphere from anthropogenic sources (as a result of fertilisation). In order for the nitrogen cycle to run as described in the soil, temperatures of 5–8 °C are necessary.

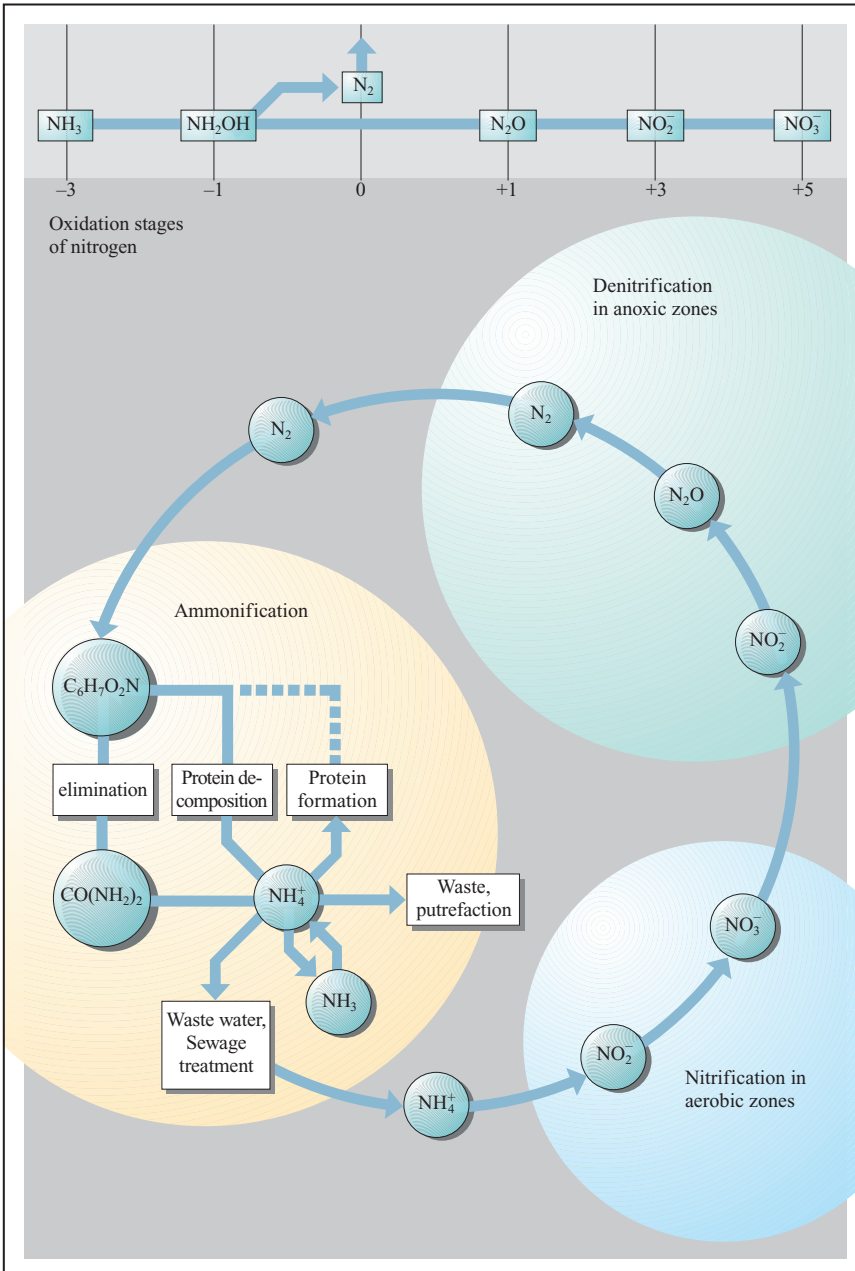

Figure 1.3.3 Ammonification, nitrification, denitrification

1.4 The sulphur cycle

1.4.1 The global sulphur cycle

The sulphur reservoirs in the lithosphere, pedosphere, hydrosphere and biosphere are estimated to be 12×10^{15}, 10^{13}, 1.3×10^{15}, and 6×10^{9} t S, respectively. Some 2 to 3 million tonnes are released annually (as SO_2 or H_2S) by volcanic eruptions. The anthropogenic sulphur emissions due to burning amount to some 75 to 80 million t yr^{-1} and therefore represent the dominant factor in the sulphur cycle, next to the biogenic S emissions (see below). As sulphuric acid (acid rain), they enter into the hydrosphere in the form of wet deposition (or adsorbed to particles as dry deposition). As a result of spray and evaporation, maritime sulphate aerosols (seasprays) are created from oceanic surface waters, of which 1.5 million t yr^{-1} (10% of the sprayed sulphur) reach the continents, and after an intermediate depositing in rivers they are transported once again to the oceans (average residence time approximately 1 year). In addition to hydrogen sulphide, gaseous sulphur compounds from the degradation of biological material include dimethyl sulphide, carbon disulphide, and carbonyl sulphide in small amounts. Altogether about 35 million t yr^{-1} of S each are released into the soil and the hydrosphere. On a percentage basis, the annual sulphur emissions worldwide into the atmosphere consist of 38% biogenic and 38% anthropogenic S emissions, 20% from sea spray, and 4% of volcanic origin.

1.4.2 The biochemical sulphur cycle

The main product of biogenic sulphur conversion in the coastal areas, marshes and moors is dimethyl sulphide $(CH_3)_2S$, with 40 million t S yr^{-1}. On the other hand, vegetation in inland soils produces mainly hydrogen sulphide H_2S, at the rate of 10 million t S yr^{-1} (all numerical data are from Kimmel and Papp, 1988). For example, sulphur is present in amino acids such as l-methionine and l-cysteine. Sulphur and sulphur compounds are very important to the energy metabolism of numerous strains of bacteria and some fungi. Under anaerobic conditions, sulphides can be oxidised to sulphates by thiobacteria. In deep waters, *Beggiatoa* strains oxidise H_2S to form elemental S, whereas *Thiobacillus* strains convert it into sulphate. In this way, the bacteria acquire chemoautotrophically via oxidation the energy needed for forming organic compounds (see Section 1.2 for the reduction of CO_2). In areas with shallow water, green and purple bacteria use light energy and H_2S in the role of an oxygen acceptor in order to convert CO_2 into carbohydrates via reduction. Green sulphur bacteria oxidise sulphides to form elemental sulphur, whereas red and purple and colourless bacteria form sulphate. Sulphate is formed from heavy metal sulphides such as iron sulphides (pyrite, FeS_2 – oxidation number of the sulphur +1) either chemically by oxygen oxidation or by special thiobacteria (aerobic sulphide oxidisers – *Thiobacilli*). Sulphate is reduced again to hydrogen sulphide via desulphurication by anaerobic bacteria of the *Desulfovibrio* group (e.g. by *Sporovibrio* species). Sulphur is fed back into the cycle as a result of protein degradation by bacteria and fungi. Aerobically, the decomposition of organic waste is accomplished by bacteria and fungi such as *Aspergillus* or *Neurospora*; anaerobically, the organic sulphur is reduced by bacteria of the *Escherichia* and *Proteus* genera. In the presence of heavy metal ions, sulphide is bound again at first as a slightly soluble heavy metal sulphide.

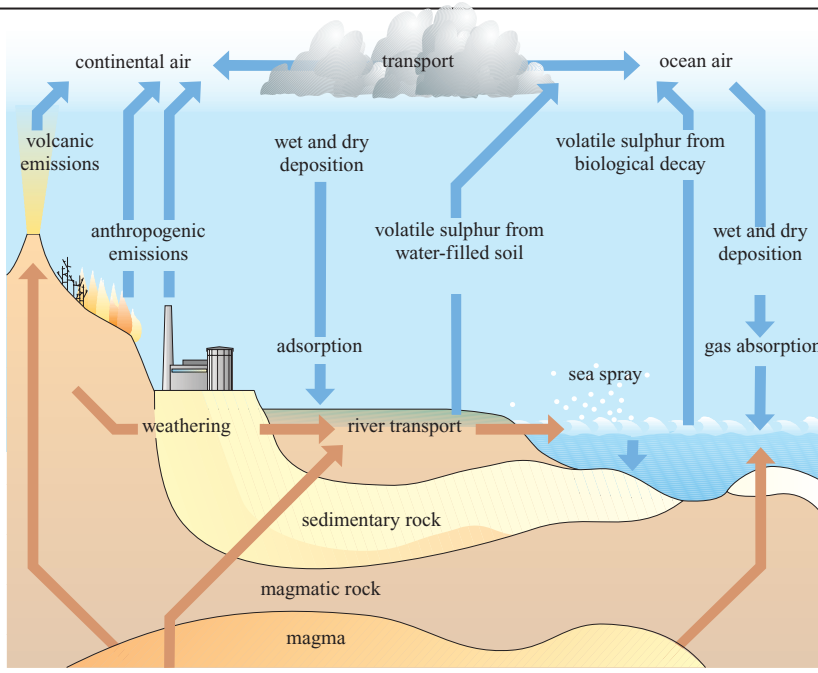

Figure 1.4.1 The global sulphur cycle

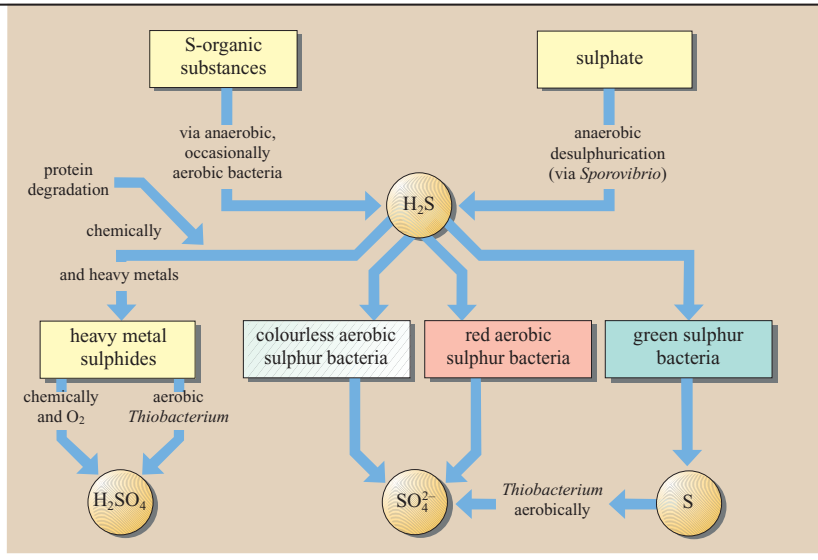

Figure 1.4.2 The biochemical sulphur cycle

1.4.3 Environmentally relevant sulphur compounds

Sulphur species in a reduced state are hydrogen sulphide (H_2S), dimethylsulphide ($(CH_3)_2S$) (and methylmercaptan, CH_3SH), carbon disulphide (CS_2) and carbonyl sulphide (COS). They come mostly from natural (geochemical or biological) sources. Sources for the relatively long-lived COS include volcanic activity and biological processes, in which oxidation of the carbon disulphide (CS_2) takes place, e.g. in forest fires. For the sulphur compounds mentioned, the primary sources are biological processes in anaerobic conditions, such as are found in swamps and in tidal lands. For example, dimethyl sulphide is made by algae.

In the atmosphere, sulphur species with an oxidation number of –2 are attacked largely by OH radicals and by oxygen atoms, and are converted via intermediate products to sulphur dioxide. Here are examples for possible reaction mechanisms for carbonoxisulphide (* radicals):

1. $COS + OH^* \rightarrow CO_2 + SH^*$

2. $COS + O \rightarrow CO + SO$

For dimethyl sulphide:

1. $(CH_3)_2S + OH^* \rightarrow CH_3OH + CH_3S^*$

2. $CH_3S^* + 3.5O_2 \rightarrow 2CH_2O + 2SO_2 + H_2O$

Carbon disulphide is oxidised first to CS and SO_2 at a wavelength below 280 nm, and in a second step to COS and atomic O. At wavelengths above 300 nm, first there is a splitting into CO and S, and then an oxidation to form CO and SO_2. The average atmospheric lifetime is 2–4 days for H_2S, 0.1–0.3 days for CH_3SH, 0.8–1.2 days for $(CH_3)_2S$, 10–40 days for CS_2 and more than 100 days for COS.

Due to the long residence times of CS_2 and COS, these sulphur species can diffuse into the stratosphere as source gases and can contribute to the formation of the sulphate layer there via oxidative degradation. The oxidation of sulphur dioxide can occur via oxidation of photoexcited singlet or triplet SO_2 molecules, as a result of oxidation by hydroxy or hydroxyperoxy radicals, or by nitrogen oxides or ozone. SO_2 or sulphuric acid arrives back on the Earth's surface as a wet deposit (dotted line in Figure 1.4.3) or as a dry deposit.

1.4.4 Emissions and transformations

Depending on the conditions, volcanic emissions produce SO_2, H_2S, and also elemental sulfur from the reaction of the two sulphur compounds. All combustion processes of sulphur-bearing fuels create other sources of SO_2 emissions. Sulphur dioxide or sulphurous acid, as well as sulphuric acid (Section 1.4.3), fall from the atmosphere back to the Earth's surface and serve as a contributing factor to deforestation. As a result of anaerobic processes, substances such as hydrogen sulphide are generated from organically bound sulphur. In the presence of sufficient oxygen, sulphates are formed from mineral sulphides such as sulphidic ores, lustre (*'glanz'*) and blende due to weathering processes and microbial processes (Section 1.4.2). These sulphates are largely washed out of soils and finally end up in the oceans. In watt, where reducing conditions predominate (the black colour of the watt comes from iron disulphide, or pyrite), the sulphate can be reduced again to sulphide. Under oxidising conditions, sulphate is formed again; likewise, inorganic sulphur species can be generated anew from organic sulphur compounds as a result of mineralisation. These partial cycles take place largely in soils and in the sediments of streams, rivers and lakes.

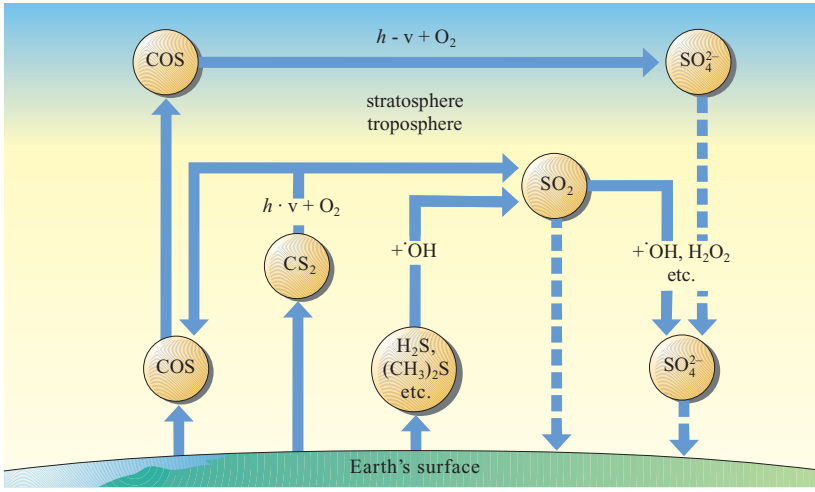

Figure 1.4.3 Environmentally relevant sulphur compounds

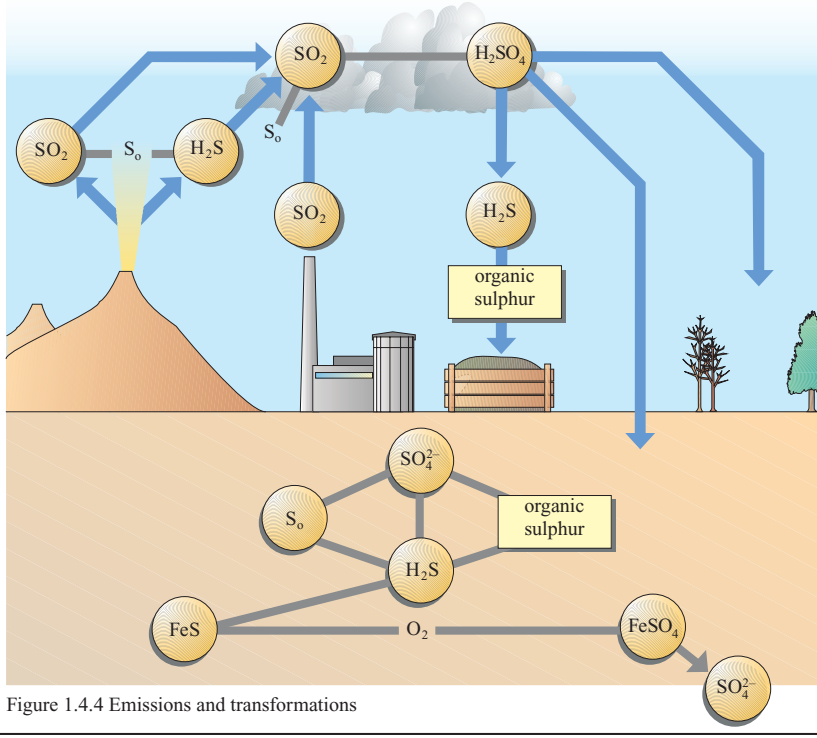

Figure 1.4.4 Emissions and transformations

1.5 The phosphorus cycle

1.5.1 The global phosphorus cycle

With respect to its abundance, phosphorus takes 11th place in the lithosphere (0.7% of the Earth's crust). It occurs with an oxidation number of +5 in phosphate rocks, such as the mineral apatite, $Ca_5[X(PO_4)_3]$, with X = F, Cl, OH. Phosphorus is the most important growth-limiting element in an ecosystem. Phosphate ores in the Earth's surface (as apatite, 32×10^9 t) are mostly of sedimentary, or more rarely volcanic, origin (P in the deep-sea sediments with 10^{12} t, in the hydrosphere with approximately 10^{11} t, and in the land biomass with 2×10^9 t). Phosphate-rich guano deposits can be found on Pacific islands. Guano consists of the excrement of cormorants and other seabirds, and contains calcium phosphate and other nitrogen-organic compounds. It also collects along the coasts of Peru and Chile due to its use as a fertiliser. Because they are only slightly soluble, numerous phosphates (Ca, Fe, Al) are removed from the cycle via sedimentation (13 million t yr^{-1}). In contrast to nitrogen, there is no phosphorus in the gas phase cycle. In the soil, 60% of the phosphorus is present as phosphate, and 40% is stored in the form of organic substances, such as that bound to humus. As soluble phosphate (only 5% of the soil phosphates), phosphorus enters into the food chain – in plants and animals to humans and via excrement back into the cycle. Phosphorus is stored particularly in the bones and teeth of animals and people. In the soil, microorganisms can dissolve the slightly soluble phosphates due to the production of acids such as citric acid and sulphuric acid. Phosphate ions from weathering processes are precipitated as calcium phosphate in alkaline soils and as iron or aluminium phosphate in acidic soils.

1.5.2 The biogeochemical phosphorus cycle

Phosphate-containing rocks reach the surface via diagenesis (Section 1.1), and they can be taken up by plants to a small degree (Section 1.5.1). Phosphorus is required by living organisms as a building block of nucleic acids and of phospholipids (in membranes), and it plays a significant role in energy metabolism as AMP, ADP and ATP (adenosine mono-, di- and triphosphate). The endogenous cycle of phosphorus in phytoplankton occurs very rapidly: phosphates are taken up in 5 minutes and excreted again after 3 days, or they are passed on to the zooplankton, which excretes as much phosphate daily as it takes up. The human organism (70 kg) contains some 700 g P, 600 g of it in the bones. Phosphates also enter into the atmosphere with dust particles due to erosion, and they return back to the Earth's surface via dry deposition. Farmers take up large amounts of phosphate during harvest operations in the fields. However, this phosphorus loss or removal can only be geochemically compensated for to a small degree by weathering, so phosphates must be used in fertilisers. The terrestrial (mineralisation of 0.2 million t yr^{-1}) and the aquatic phosphorus cycle (mineralization of 0.06 t yr^{-1}) are largely independent of one another: both insoluble inorganic phosphate and organic phosphorus-containing residues enter into the sediment. In the aquatic area, phosphates are part of the diet of phytoplankton. Overfertilisation has led to the well-known algal bloom which assimilates the dissolved oxygen with a subsequent decomposition of the biomass (eutrophication). Concentrations of 10 to 100 mg m^{-3} in rainwater come from dust and sea spray.

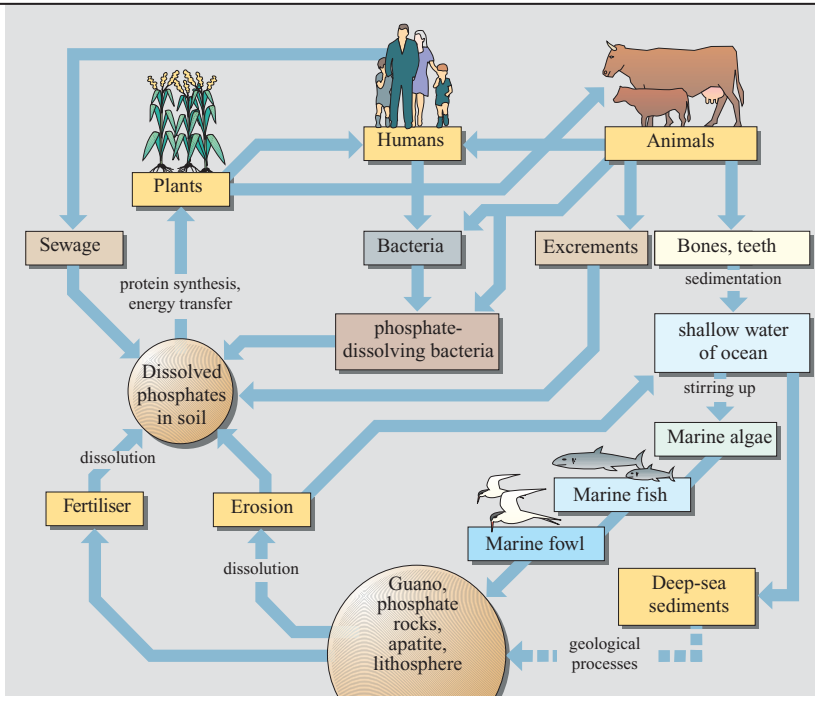

Figure 1.5.1 The global phosphorus cycle

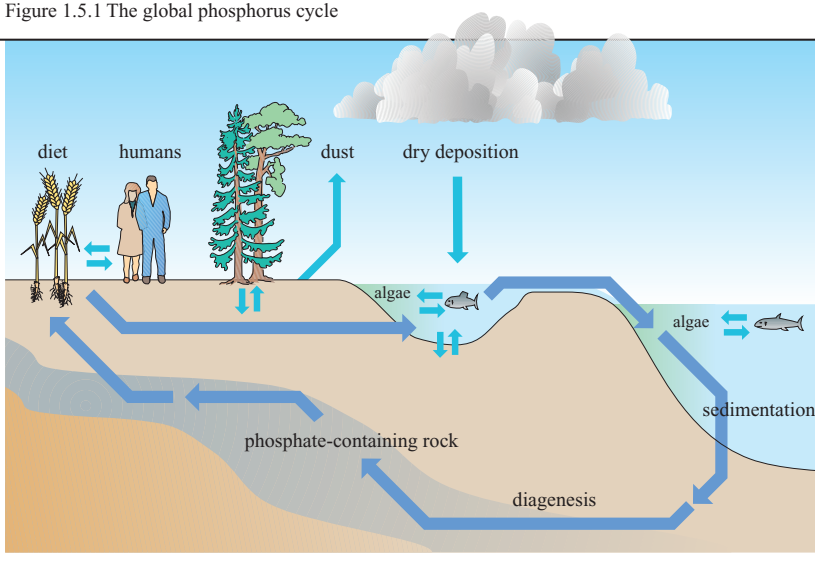

Figure 1.5.2 The biogeochemical phosphorus cycle

1.6 Metal cycles

1.6.1 The global anthropogenous cycle

Since the start of industrialisation in the nineteenth century, the material cycle amounts of heavy metals, which impact upon waters, soil, plants, animals and people, have increased considerably. Industry and trade – particularly the metal-processing operations and refineries – represent significant sources of heavy metal emissions. Special sources of emissions include cement works (thallium), battery manufacturers (lead) and electroplating operations (copper, nickel, chrome, zinc/cadmium, etc.). And through agro-chemicals, metals such as cadmium in phosphate-containing fertilisers can get into the soil. On the one hand, heavy metal emissions occur due to targeted production for particular commercial purposes; on the other hand, they are undesired emissions from coal and petroleum burning, trash burning, and cement and glass production. Through refuse, waste water or sludge and exhaust air (dust particles), they enter especially into or on soils and thereby into the food chain (plants→animals→humans). The degree of the anthropogenous effect of metal cycles can be represented as a global interference factor: it indicates the ratio of the anthropogenously induced amount of material to that of the natural (geochemical) material cycle.

1.6.2 The geochemical cycle

The geochemical cycle of metals begins with the plutonic rock, which then enters into the water and the atmosphere via the Earth's surface or the ocean floor due to volcanic activity. From the weathering of stones, metals are dissolved (chemical weathering) into the water cycle, or they are introduced into the cycle in the form of dust particles (physical weathering as clastation due to mechanical forces). Sedimentation represents the opposite process. Heavy metal compounds are removed from the cycle in this manner; however, they can be remobilised due to geochemical or anthropogenously induced changes (pH changes in the water, biogeochemical changes in the sediment, the effect of complexing agents from waste waters). The logarithm of the ratio of metal concentration in actual river sediments to that in prebiotic sediments is calculated as the geoaccumulation index. Processes in the geochemical cycle that are also common are the transitions of metal compounds in aerosols from the hydrosphere into the atmosphere and the return to the soil or the waters via precipitation. As gases, metals play only an insignificant role in the materials cycle (e.g. hydrides of As and Se or Hg in a gaseous state or volatile metallo-organic compounds such as methyl mercury). The ratio of the relative concentration of an element in the atmosphere to that in the Earth's crust (with Al as a standard) is known as the atmospheric accumulation factor.

1.6.3 The biogeochemical cycle

Finally, as part of the overall discussion of heavy metal cycles, we must consider the processes in the biosphere as well. The geochemical cycle (to the left in Figure 1.6.3) is connected via metabolic processes by microorganisms in the ocean floor, in sediments or sludge, or in water. Microorganisms, plants and small animals serve as food sources for fish. By means of plants and other animals, levels of heavy metals from waters and soils find their ways into our foods.

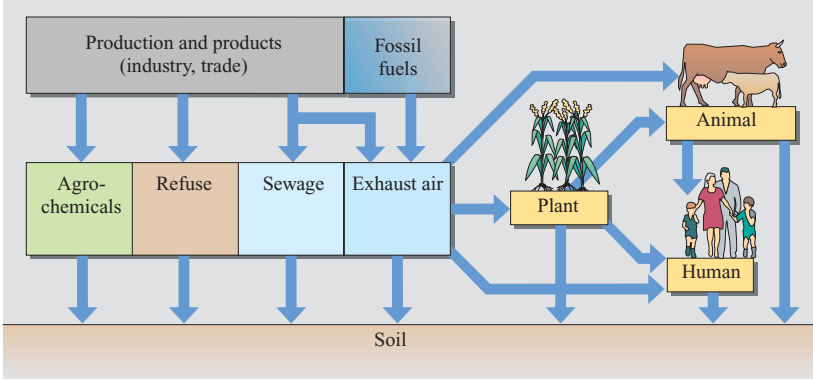

Figure 1.6.1 The global anthropogenous cycle

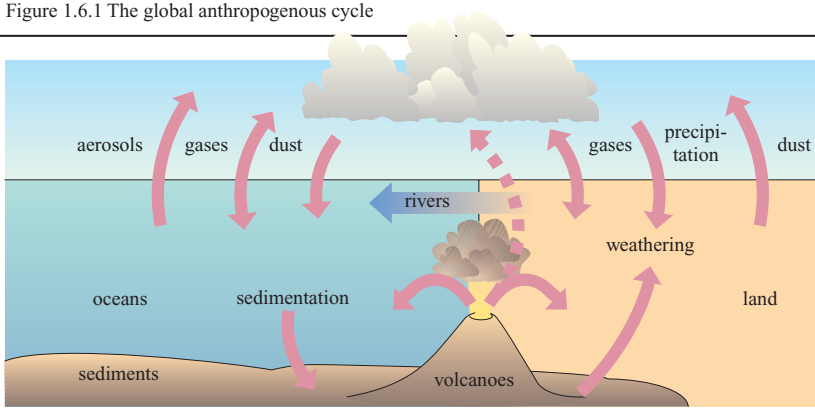

Figure 1.6.2 The geochemical cycle

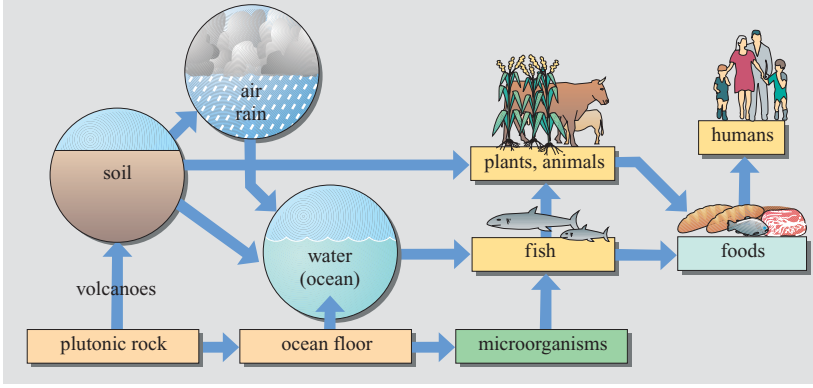

Figure 1.6.3 The biogeochemical cycle

1.7 Special cycles

1.7.1 Cycles of environmental chemicals

Environmental chemicals are those chemical substances that enter the ecosphere as a result of human activity (anthropogenously induced). As a rule, they occur in small amounts or concentrations, but on the other hand they often represent a potential risk. Based on a definition in the environmental programme of the Federal Republic of Germany of 1971, the term 'environmental chemicals' includes chemical elements, compounds of organic and inorganic nature, of synthetic or natural origin. Limiting the term to substances that can endanger living organisms is arbitrary, so that today, any substance introduced into the environment by people is labelled an environmental chemical. The term 'environmental chemical' is used in place of 'pollutant', even if not all of these substances have to be pollutants at the same time. Approximately 60 000 substances are produced world–wide. To protect people and the environment, chemical laws were passed in conjunction with the environmental laws.

Environmental chemicals in the water (Figure 1.7.1, 1) can be subjected to chemical and biological conversion reactions and/or decomposition reactions (e.g. as a result of hydrolysis) following vortexing and convection, which lead to a state of solution or suspension. From the decay of organic material, dead organisms provide the detritus as finely distributed suspended or deposited matter, to which water-insoluble heavy metal compounds (see Section 1.6.2), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) or other pollutants can be attached and settle. These deposited particles of biogenic origin (→ organic sedimentation) and suspended clay minerals (→ inorganic sedimentation) make possible the processes of adsorption and desorption, which can lead to an equilibrium in the water under constant chemical–physical conditions. The environmental chemicals that enter the waters can be taken up by organisms either directly or after transformation, and they can be excreted either in their original form or in a metabolised form. Biological effects of environmental chemicals can appear immediately or later, after bioaccumulation. We use 'bioaccumulation' to describe the ability of organisms to store substances in their own organism or to concentrate, or enrich, them in their environment (calculated as the bioaccumulation factor).

Environmental chemicals can get on and in soils (Figure 1.7.1, 2; see also Chapter 3) by means of either wet or dry deposition (sedimentation). Transformations on the surface occur due to phenomena such as photoreactions, which can also lead to the volatilisation of directly applied materials. The processes in the soil passage, which can lead to a separation of environmental chemicals after a time, play an important role in the soil itself. On account of the water content, the entrance of oxygen into the upper soil layers, and the presence of organisms, from soil bacteria to earthworms and moles, similar reactions and processes as occur in water can occur here. In addition, soil space filled with roots represents a special absorption pathway for environmental chemicals. Around tree roots, these chemicals can be decomposed and/or transformed to a higher degree due to the special flora and fauna. Finally, environmental chemicals can enter the groundwater after passing through the soil, either in a changed form or unchanged.

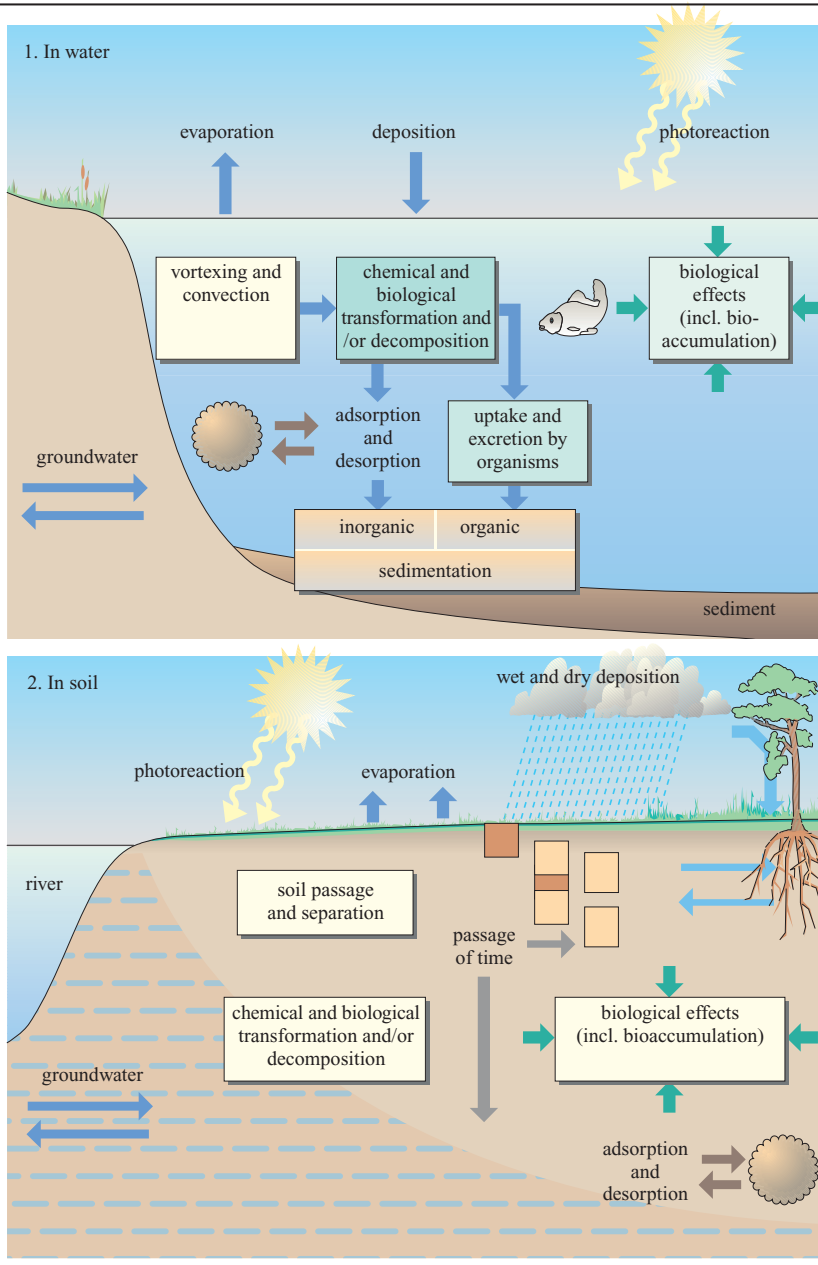

Figure 1.7.1 Cycles of environmental chemicals

1.7.2 Interrelationships among the C, S, P, N and O cycles

In order to decompose the body's own substances in large amounts, the living cell requires the principal elements C, H, O and N, and the macroelements P, S, Na, K, Mg, Ca, Fe, Si, Al and Cl. Although the entire biomass of the Earth has a mass fraction of only 0.1% in the crust, practically all of the chemical elements of the Earth's crust have participated in the decomposition during evolution. There are intensive interactions among the cycles of different elements, which can occur due to chemical and especially biochemical reactions.

Photosynthesis is characterised by the uptake of carbon dioxide and the release of oxidation via respiration in a living cell. At the same time as the CO_2 is being incorporated into organic material (shown here in general as CH_2O for carbohydrates), N, S and P are taken up as well for the building of amino acids, nucleic acids, etc. The organic material and oxygen are required in turn for the independent cycles of S, N and C, from which the participation of phosphorus (in the form of ADP) is derived. The C, N, P and S cycles that were previously described in detail are linked here with the oxygen cycle (P stands for the enzymatic energy-yielding processes via ADP). Over the long term, a change in one of the cycles has considerable impact on the four others.

1.7.3 Bacterial and biochemical cycles in the sedimentation of a lake

Anaerobic processes in the sediment of a lake lead to the reduction of sulphates to sulphide (Section 1.4.2). The number of sulphate-reducing bacteria reaches a maximum here depending on the depth of the layer of sediment. Biochemical (fermentation) processes take place in the upper region and lead to the formation of lactic acid and acetic acid. Both acids are products of anaerobic glycolysis, or the degradation of carbohydrates in cells that are poorly supplied with oxygen. Macromolecules (proteins, fats, carbohydrates) are first hydrolysed to form monomers in a fermentation and putrefaction process, or they are fermented to form different acids and ethanol (fermentation: decomposition of C compounds; putrefaction: decomposition of N compounds).

In light of the redox potential, the decomposition processes of biomass can be divided into a range from aerobic respiration to denitrification and desulphurication to methanogenesis. It has been observed that in lake sediments, sulphate-reducing bacteria in the uppermost 2-3 cm determine the biochemical events. It has also been determined that methane from a deeper layer in sediments with a high activity of sulphate-reducing microorganisms is consumed and is converted to CO_2 with the formation of hydrogen sulphide from the sulphates. The redox potentials for the processes of desulphurication (sulphate respiration) and methanogenesis are close to one another. Anaerobic methanogenic bacteria require acetic acid as a substrate. The processes in lake sediments described above were observed in Lake Vechten in the Netherlands. The spatial separation of sulphate-reducing and methane-producing microorganisms can be traced back to such factors as the inhibition of methanogenesis by sulphates in sediments. However, coexistence of these two groups of microorganisms has been proven as well.

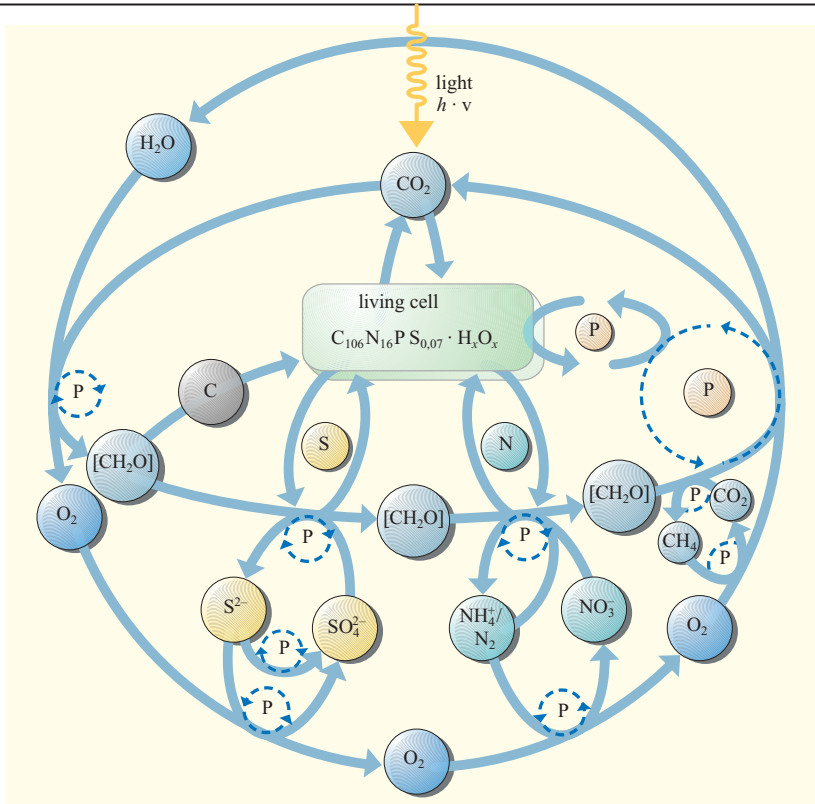

Figure 1.7.2 Interrelationships among the C, S, P, N and O cycles

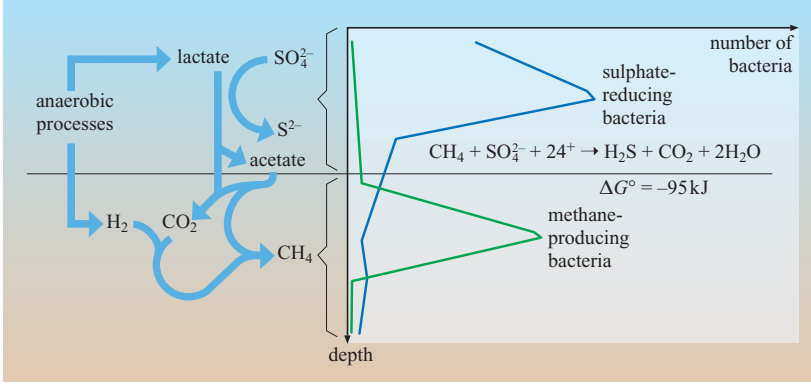

Figure 1.7.3 Bacterial and biochemical cycles in the sedimentation of a lake

1.7.4 Anthropogenously related surface material flow

Figure 1.7.4 shows anthropogenously induced flows of material (with units such as t yr^{-1}), in particular of solid materials that eventually end up on soils. Around 1990, 90% of the population in the old German *Bundesländer* were connected to sewage treatment plants. With a volume of some 8000 million m^3 per year (more than 3000 million m^3 of that as domestic sewage), about 10% of this is sludge, having a dry weight of 4 million tonnes. Sewage sludge has a high water content of 94–97% in raw sludge, which can be reduced to 55–70% by simple mechanical dehydration. Sludge from municipal treatment plants is viewed as part of urban refuse. Of the treated sludge, 45% ends up in landfills, 25% is used in agriculture, 15% is burned, and 0.5% is composted.

Of the 8-fold larger material flow for domestic refuse (about 32 million t), in 1987 some 66% went to a landfill, 2% was composted, and 26% was incinerated and thereby returned back to the soil in the form of exhaust gases (including water and carbon dioxide) and ash.

1.7.5 Material cycles with links to the environment

If one considers human activities, in the overall system of material cycles there are numerous possibilities – shown as paths – for transfer into the environment. Environmental chemicals can enter the natural cycles in this way. The most important pathways from industrial production are exhaust air, waste water and waste disposal. Even when transporting and storing materials there is a risk of transfer into the environment, especially if safety devices fail. Leachate collects in landfills; its path into the environment (especially into groundwater) is determined by the geological nature of the subsoil. Landfill gases are released owing to biological decomposition. Even the regulated use of plant protection agents, fertilisers and other everyday chemicals, which contain readily volatile solvents in particular, leads to material impact on the ecosphere. A portion of residual materials goes into the different environmental compartments following waste water treatment and incineration of waste, and even after the cleaning of exhaust air.

The overall goal of environmental protection technology is to keep the anthropogenously related cycles contained as much as possible, by preventing, reducing or reusing waste products. This requires special cycles of recycling and waste utilisation. Of domestic refuse, the following materials are recycled: glass (some 10% of the total domestic refuse), metals (3%) and paper and cardboard (about 16%). Recyclable plastics (5%) and the vegetable part (biological waste) of about 30% out of a refuse volume of 300–400 kg yr^{-1} per resident are collected separately. The object of waste containment, i.e. landfills in particular for residual materials which cannot be recycled for technical, economic or ecological reasons, is to reduce the pollutant pathways mentioned above to a minimum. It is the goal of all environmental protection methods especially to keep the industrial cycles as closed as possible.

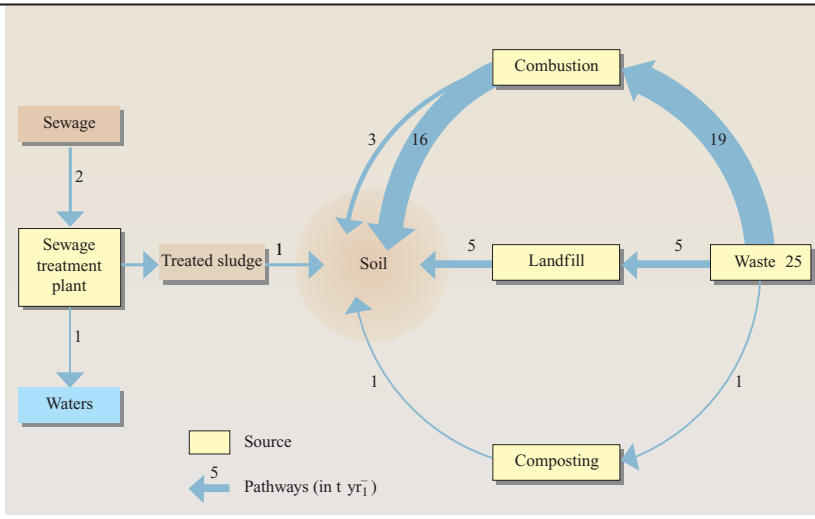

Figure 1.7.4 Anthropogenously related surface material flow

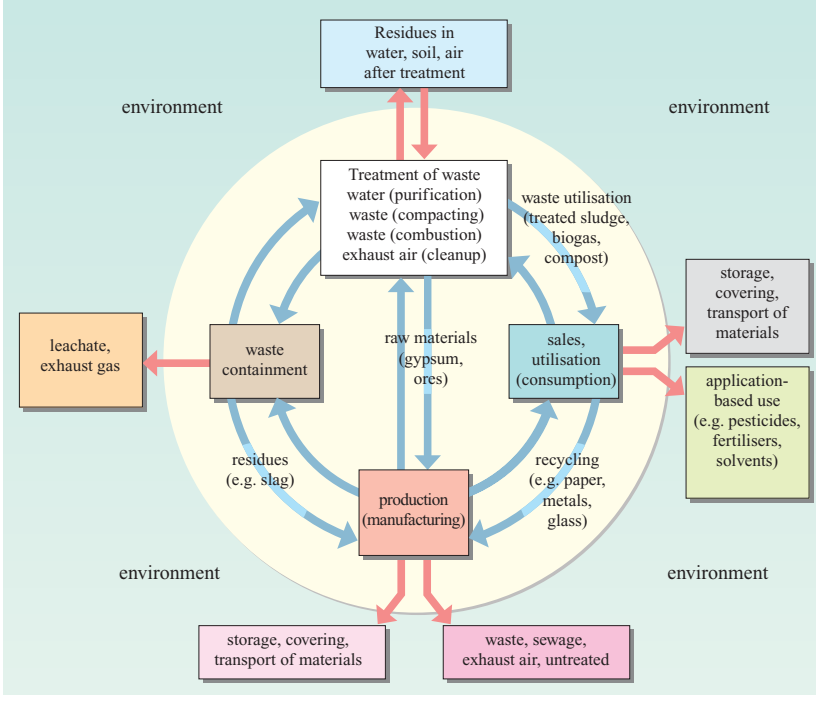

Figure 1.7.5 Material cycles with links to the environment

1.7.6 The ecologically oriented material cycle

The biogeochemical material cycles between atmosphere, water, soil, plants and animals are connected with the anthropogenous material cycles here. Since the start of the Industrial Revolution in the nineteenth century, humans have become the most significant factor in the ecosphere. Intervention into the energy and material reserves of the Earth has led to scientific, technical and social accomplishments in the development of civilisation on the one hand, but has also induced a substantial acceleration of the biogeochemical material cycles on the other. It is the task of an ecologically oriented material cycle to coordinate the effects of human activity on the system performance of the biosphere and ecosphere with its relationships, feedback and special means of functioning. We remove mineral and vegetable raw materials from the natural material cycle, and they are used directly in industrial production and processing. Agriculture and forestry avail themselves of natural resources in the area of flora and fauna, wherein animal husbandry represents a particularly intensive portion with a clear ecological impact.

The industrial production and processing of plant and mineral resources and animal husbandry give rise to intervention in the atmosphere. In turn, the ecologically oriented material cycle necessitates the cleaning of the exhaust gases and the recycling of the air if possible. Water pure enough for drinking or service use is needed by consumers and industry. The waste waters that accumulate have to be directed to a water treatment plant, and the purified waste water returns to the bodies of water, and after sufficient water conditioning can be fed back into the cycles of drinking water and process water. Add to this household refuse from the consumer area, and waste water treatment produces sludge. Both of these must be processed as refuse, i.e., they must be separated into usable and residual materials. Usable materials, those recyclable materials in the refuse area, include humus, which returns nutrients to the soil. Non-reusable residual materials from waste processing end up in landfills.

The ecologically oriented material cycle depicts the interactions between the extraction of raw materials, including energy production, and environmental changes. It must be the goal of environmental protection technology to minimise human disturbance of the natural cycles – using the approach of avoid, reduce and utilise. Some 10^5 million t yr^{-1} of natural resources that cannot be regenerated in the short term are removed from the biogeochemical material cycle of the ecosphere. Of the total by-products that are not immediately reusable products from the technical transformation and processing of natural resources, at the top are pollution gases, agricultural wastes, residues from incineration and smelting, and faecal matter.

As a subfield of the economic sciences, the environmental economy provides ecological viewpoints with its theories, analyses and cost calculations. It is a strategic goal of waste product treatment to avoid or reuse waste products and to put them in landfills only when those two options are not technologically and economically viable. The progressive political environmental economy already uses a substantial portion of waste products as secondary raw materials and strives for the recycling of materials and especially for closed industrial material cycles.

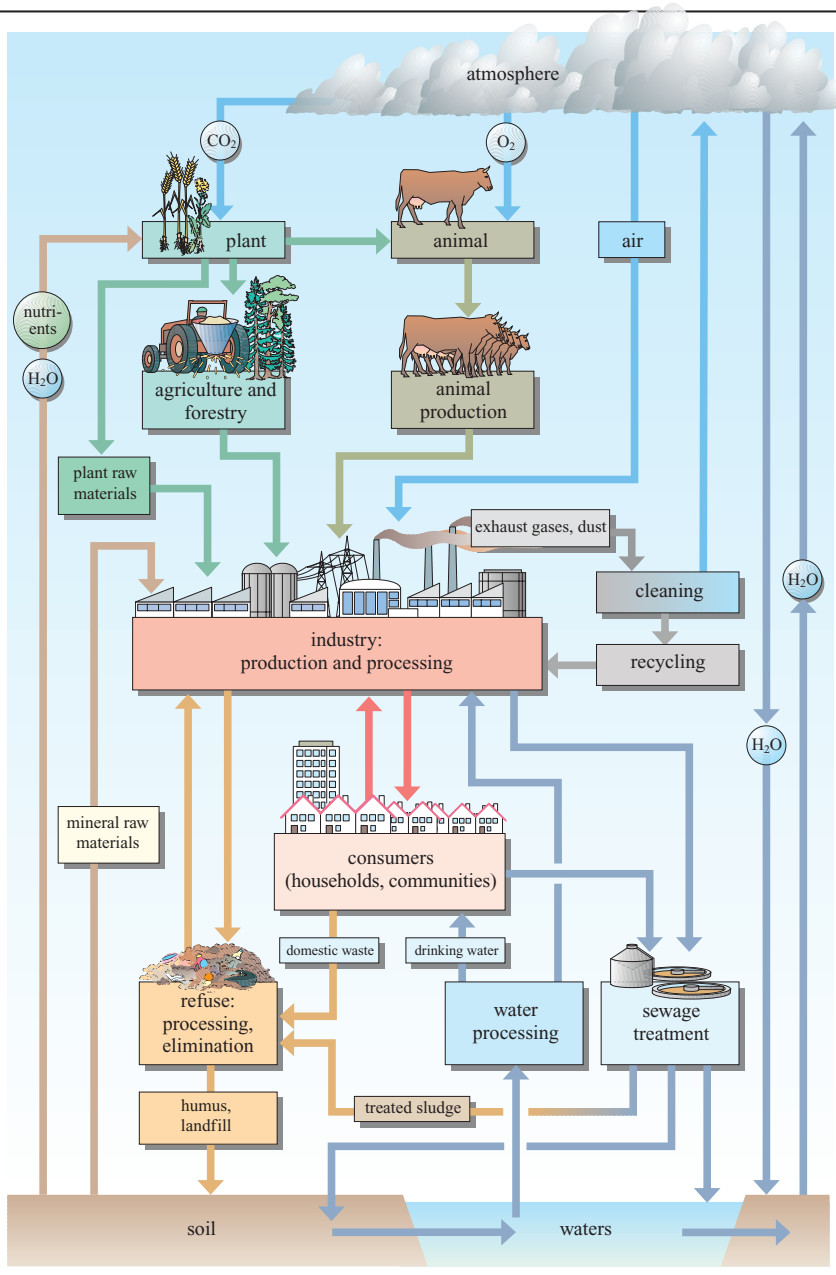

Figure 1.7.6 The ecologically orientated material cycle