

### 3.5.3 *Flows of Energy and Material in Agroecosystems*

With regard to energy and material flows, intensively managed agroecosystems, in particular, have several characteristics distinct from those of natural ecosystems:

- Large proportions of the net primary productivity, i.e. the biomass of the crops, are removed from the system during harvest, which also results in a decline in the nutrient content of the soil.
- To compensate for these losses, fertilizers must be used (Sect. 2.3.3). Mineral fertilizers are imported into the agroecosystem from outside and must be produced and transported using energy, which in turn uses external resources, primarily fossil fuels.
- For the production of crops, further energy is required, specifically for soil cultivation, sowing, harvest, and possibly irrigation. This energy comes from manual labour, the use of animals or the application of machinery and is based on food, feed, or fuel, respectively. Usually, chemicals are also applied to control pests, weeds, and phytopathogens. These substances must also be produced, transported, and distributed. Their residues reach the food webs and ecosystems.
- Only a relatively small portion of the nutrients imported into an agroecosystem as fertilizers is taken up by the crop plants. For example, only approximately one third of the nitrogen applied to the soil in German agriculture is extracted via the plant and animal products. The rest is leached out or escapes as a gas into the atmosphere (Sect. 3.7.4.2). Sixty percent of the nitrogen input into the North and Baltic Seas originates from agriculture.
- Through global trade, agricultural products (e.g. cereals and soybean for animal production) reach other regions where they become a component of the material and energy flows of those ecosystems (e.g. in the form of animal excrement).

**Intensively cultivated agroecosystems in particular are characterized by high material and energy flows and to only a limited extent by internal cycles.**

## 3.6 Ecosystem Services

The present and future welfare of people, societies, and economies depend on the various goods and resources provided by nature. Beside the many kinds of plants and animals from agricultural and natural systems that sustain and benefit human life, this also includes a variety of services, often considered as granted and freely available. They are so-called public goods, which cannot be owned and have no markets and prices. Such services are based on natural ecosystem processes and functions, which result in the provision, regeneration, and long-term stability of

such resources as water, soil, nutrients, organisms and biomass. Their value is associated with a gain or loss to human welfare, which often is not obvious until a service becomes critically disturbed and leads to negative effects, for example water scarcity, flooding, soil erosion, or land degradation.

Together, the goods and services generated by ecological functions and processes that directly or indirectly affect human wellbeing are called **ecosystem services**. According to the Millennium Ecosystem Assessment (2005), they can be subdivided into four main categories:

- **Supporting services** are those that are necessary for the production of all other ecosystem services. They include the basic functions and outputs of ecosystems, for example photosynthesis, biomass production, soil formation and retention, nutrient and water cycling, and habitat structures.
- **Provisioning services** are services that can be extracted from natural and agricultural systems for direct use by humans. They refer to all products derived from cultivated systems (for example food, forage, biofuel, fibre, and other renewable resources), in addition to those which are exploited from unmanaged systems, for example firewood, timber, or seafood. They also include services such as the provision of genetic resources from biodiversity and the delivery of services from species, for example pollination and the natural control of pests and diseases.
- **Regulating services** can be defined as those services which are necessary for the sustainable delivery of other services by regulation and the support of ecosystem processes. They contribute to the buffering of environmental fluctuations and risks, and to the resilience of ecosystems against different types of disturbance. Regulating services include erosion and flood control, climate regulation through carbon storage, water filtration, and waste decomposition.
- **Cultural services** are those services that contribute to the maintenance of human health and well-being by providing recreation, spiritual and aesthetic values and education opportunities, and include the creativity born from interactions with nature (music, art, architecture). These services can be different in different local and national human societies but are mainly associated with the presence of close-to-nature systems (e.g. nature reserves) or the diversity of a cultivated landscape.

Ecosystem services can be regarded as the “natural capital” of human welfare that yields a flow of valuable ecosystem goods or services into the future. In practice, however, it is very difficult to assign a “value” in economic terms to natural services. There have been a variety of attempts to measure the economic or monetary value of ecosystem services. Costanza et al. (1997) attempted to put monetary value on 17 different ecosystem services and calculated the total value as being between 18 and 54 trillion US dollars per year, compared with a total global gross domestic product (GDP) of 18 trillion US dollars at that time. Indeed, this figure gives an idea of the dimension of these values, but it remains questionable whether it is an appropriate and feasible approach to express the value of specific ecosystem services in pure monetary terms, because the types of value can be manifold. This aspect is considered in the concept of **Total Economic Value**

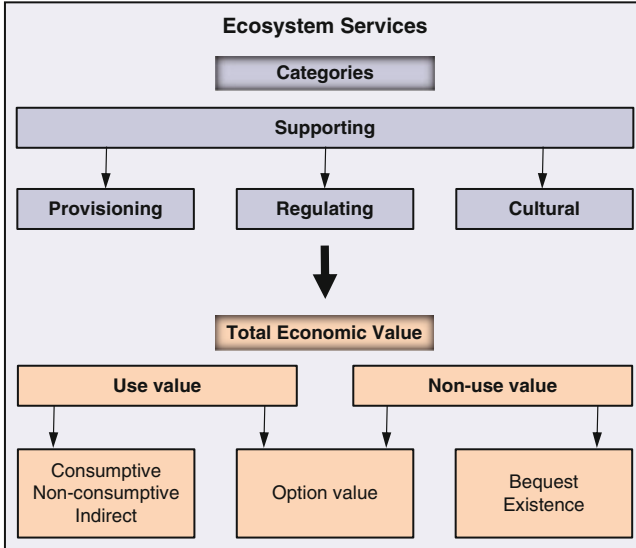


Fig. 3.12 Categories of ecosystem services and total economic values

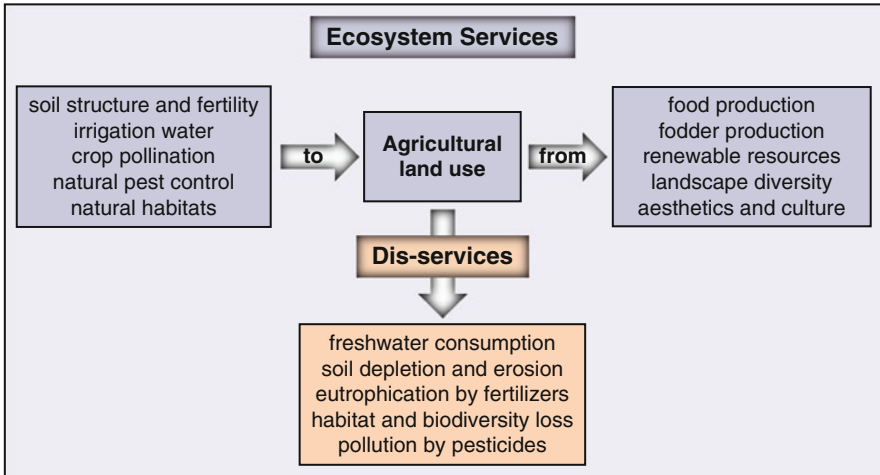
(TEV), a widely used framework for classification of the different ecosystem goods and services. It distinguishes between two main categories—use and non-use values—which are subdivided into further groups (Pearce and Warford 1993; Fig. 3.12):

**Use values** refer to the use of natural resources by humans for consumption or production purposes. These include

- consumptive use values, given by the extraction of natural outputs (e.g. by harvesting, hunting, or fishing);
- non-consumptive use values, given by activities that do not require extraction of products, for example recreation, sports, wildlife watching, and other touristic activities; and
- indirect use values, which are used as intermediate inputs for production of final goods and services for humans, for example water and nutrient supply, and for such non-consumptive values as clean air, clean water for swimming, and low health risks.

**Non-use values** arise for ecosystem goods or services that people value for their existence, even though they may never make use of that resource or service (for example, the enjoyment of watching wildlife and landscape reports on television). Non-use values can be substantial for human wellbeing, but are difficult to quantify. This category includes:

- bequest values, which are values that people place on knowing that other people, including future generations, will have the option to enjoy the same goods and services, and



**Fig. 3.13** Ecosystem services and disservices related to agriculture

- existence values, which relate to the satisfaction to humans from knowing that ecosystems or wildlife species, for example whales or elephants, continue to exist, based on the feeling that nature has an intrinsic value.

**Option values** cover both use and non-use values and refer to goods and services that are not used at present but may become important in the future. These especially include the value of biodiversity, for example the genetic diversity of varieties and breeds of domesticated species, and natural species diversity, which may provide important pharmaceutical resources.

### 3.6.1 *Ecosystem Services Associated with Agriculture*

Human activities increasingly modify natural ecosystem functions and processes and, consequently, ecosystem services. Ecosystem changes that have contributed substantial net gains to human well-being and economic development via agricultural production have been achieved at the growing cost of the degradation of other services. Approximately 60% of essential ecosystem services are being degraded or used unsustainably, increasing the likelihood of potentially abrupt changes that will seriously affect human wellbeing (Millennium Assessment 2005).

Agricultural production systems are involved in all categories of ecosystem services in three ways: they provide services, demand services, and affect other services (Fig. 3.13).

**Ecosystem services from agriculture** primarily include the provision of food crops, livestock products, fibres, biofuel and other plant resources, for example rubber. Provision of additional services is highly dependent on the type of land use

and on management practices. Some agricultural landscapes provide cultural benefits because of their aesthetic values for recreation and tourism. These are often related to traditional land-use practices and/or the diversity of a cultivated landscape, but large monocultures in uniform landscapes have the opposite effect. Similarly, appropriate land use and management practices can improve soil properties or support biodiversity, but often affect such features negatively.

**Ecosystem services to agriculture** include several supporting and regulation services. Agriculture requires most of the global renewable water resources used for human activities (Sect. 3.7.1). Natural soil structure and fertility are of crucial importance in determining where different kinds of agriculture are conducted, and the productivity of the systems. Important provisioning services to agriculture include insect pollination of many crops (Sect. 4.5.3) and biological pest control provided by natural enemies, which depend on the availability of suitable habitats and other resources (Sect. 5.2.4).

**Ecosystem disservices from agriculture** are unwanted effects of agricultural production on other ecosystem services and the environment. These include a number of effects of global concern and are mainly related to agricultural intensification and land-use change. The main aspects are further discussed in other chapters and include

- irrigation of croplands, leading to depletion of freshwater resources;
- soil and land degradation by wind and water erosion;
- eutrophication of terrestrial and aquatic ecosystems as a result of excessive use of fertilizers;
- effects of pesticides on biodiversity and human health;
- expansion of production areas, leading to the loss of natural ecosystems; and
- emission of greenhouse gases from land-use change and livestock production.

Overall, ecosystem services associated with agriculture are closely interlinked and not independent of each other. This situation often requires ecological and economic tradeoffs in agricultural practice and management. Mitigation options should be considered on different spatial and temporal scales, including field, farm, landscape, or watershed, taking into account the lateral flows of ecosystem services.

Field measurements to reduce disservices may include selection of crops and land-use types adapted to the location (soil type, relief), use of cover crops and minimum tillage to reduce soil losses, and use of suitable intercrop and rotation practices to preserve soil fertility. At the farm scale, integration of crop and livestock production creates synergies by using crops and crop residues for livestock feed while capturing nutrients from livestock wastes for crop production.

The delivery and the provision of ecosystem services to and from agriculture is highly dependent on the structure of the landscape in which the agroecosystems are embedded. Production sites rely on services provided by nearby natural or semi-natural habitats, which may act as reservoirs for beneficial species and as buffers to reduce or regulate the escape of water and nutrients. This requires the maintenance of the integrity of multi-functional landscapes and is especially important in watersheds, where soil and water runoff brings the risk of landslides, floods, and

sedimentation, which affect downstream ecosystems including coastal areas. Therefore, watershed management is necessary and must include the preservation of natural systems, for example hillside forests and riparian vegetation.

### 3.7 Global Material Cycles

For their metabolism, living organisms require not only organic carbon and oxygen, which are primarily made available through photosynthesis, but also a series of additional elements or compounds, for example nitrogen, phosphorus and water. These substances are part of biogeochemical cycles, which means they proceed through various living and non-living compartments in the bio, litho, pedo, hydro, and atmosphere. In contrast with energy, these materials are available to organisms again after passing through their respective cycles. The most important global material cycles are discussed in the following sections.

#### 3.7.1 Water ( $H_2O$ )

The total quantity of water on earth can be regarded as constant and is estimated to be approximately 1.4 billion  $km^3$ . Approximately 71% of the Earth's surface is covered by the water of the oceans, which amount to more than 97% of the total water reserve. Less than 3% is fresh water. Most of the latter is not available to organisms because it is bound in the ice and snow of the polar regions and in glaciers, or is found in groundwater partly at inaccessible depths. Only approximately 0.6% of fresh water occurs as surface water, where it is also an important resource for humans and the landscapes dominated by humans (Fig. 3.14).

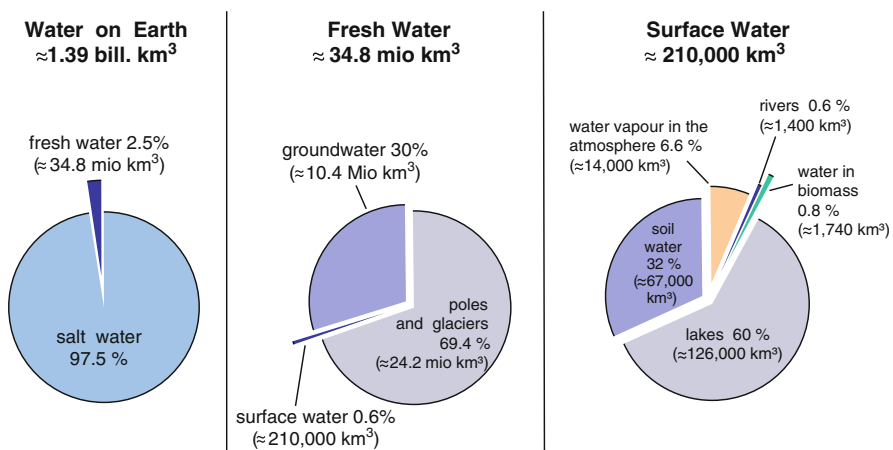


Fig. 3.14 Global water resources (Based on Wetzel 2001; Shiklomanov 1999)

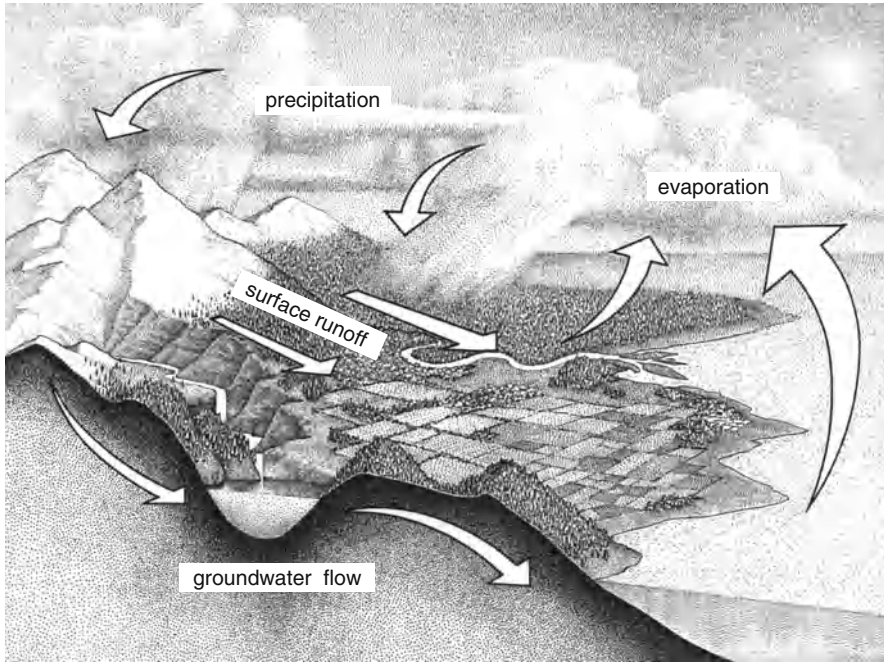
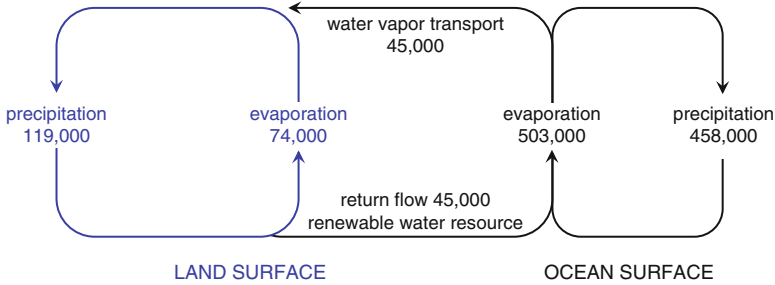


Fig. 3.15 The global water cycle

In most terrestrial ecosystems, water arrives primarily by precipitation. Because the average annual temperature decreases from the equator to the poles, this precipitation falls as snow for increasingly longer periods along this gradient. Precipitation is an essential factor in the definition of the different climate zones of the Earth (Chap. 6). In some deserts, rain only occurs at unpredictable intervals of several years. In contrast, the humid tropics usually receive more than 100 mm of rain every month. In the wet–dry tropics, more or less pronounced dry periods occur.

**Not only the quantity of precipitation but also its temporal distribution have a substantial effect on the living conditions of organisms.**

Water that reaches the soil surface can take a variety of pathways. Depending on the quantity of water, the topography of the site, and soil conditions, a larger or smaller portion of the water runs off over the surface. A further portion penetrates the soil and eventually reaches the groundwater by infiltration. Variable amounts of this water feed rivers and thereby reach the oceans. At the soil and water surface, evaporation also occurs. Solar energy is responsible for the transition from liquid to vapour, which also determines the quantity of evaporated water. The vaporized water reaches the atmosphere and condenses to form clouds, from which precipitation falls again (Fig. 3.15).



**Fig. 3.16** Quantitative data for the global water cycle ( $\text{km}^3 \text{ year}^{-1}$ ; based on Shiklomanov 1999)

Approximately  $503,000 \text{ km}^3$  of water evaporate from the ocean surfaces per year and an additional  $74,000 \text{ km}^3$  from land areas; this is then returned to the Earth by precipitation (about  $458,000 \text{ km}^3 \text{ year}^{-1}$  over the oceans and  $119,000 \text{ km}^3$  over land; Fig. 3.16). The difference between the precipitation and evaporation over land ( $119,000 - 74,000 = 45,000 \text{ km}^3 \text{ year}^{-1}$ ) forms the **renewable water resources**. More precisely, this is the quantity of water that is transported by rivers and reaches lakes and groundwater.

Currently, approximately 8.5% of the global renewable water resource is used by humans. Approximately 66% of that is used in agriculture (primarily in irrigation) whereas 34% is used in industry and households. The total demand increased by approximately 2% annually during the twentieth century (Fig. 3.17).

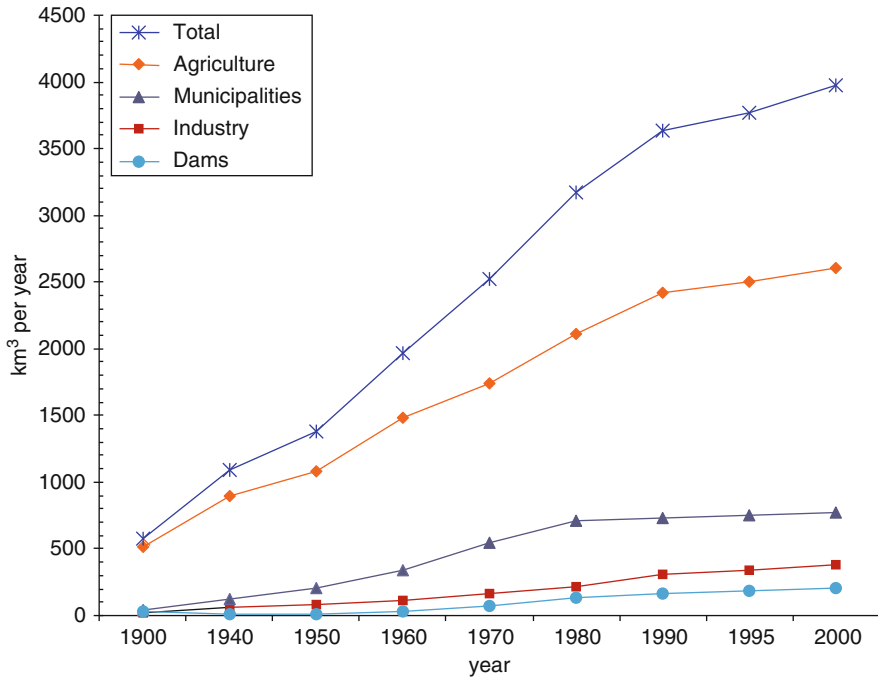
### 3.7.2 Carbon (C)

At the global level, the carbon cycle consists of five large carbon stores, among which exchange of a variety of C compounds occurs. In decreasing order of carbon stored, these are the lithosphere (the rocky shell of the Earth), the oceans, the soil, the atmosphere, and the living biomass of terrestrial ecosystems. Biotic processes in the oceans and of terrestrial vegetation make up the largest portions of natural emission and absorption of **carbon dioxide** ( $\text{CO}_2$ ).

The biological carbon cycle is closely linked to the energy flow of biological communities (Sect. 3.5.1). Figure 3.18 shows the pathways of carbon in natural terrestrial ecosystems.

The carbon source for producers is the atmosphere. It currently contains approximately 380 ppm (parts per million;  $1 \text{ ppm} = 1 \times 10^{-6}$ ), or 0.038%  $\text{CO}_2$  gas, which plants use and reduce to other carbon compounds via photosynthesis. These compounds are used in the production of structural substances (primarily lignin and cellulose) and as components of additional metabolic products, for example fats, amino acids, and proteins, and specific plant products. On the other hand, producers require organic compounds for respiration, as do consumers and





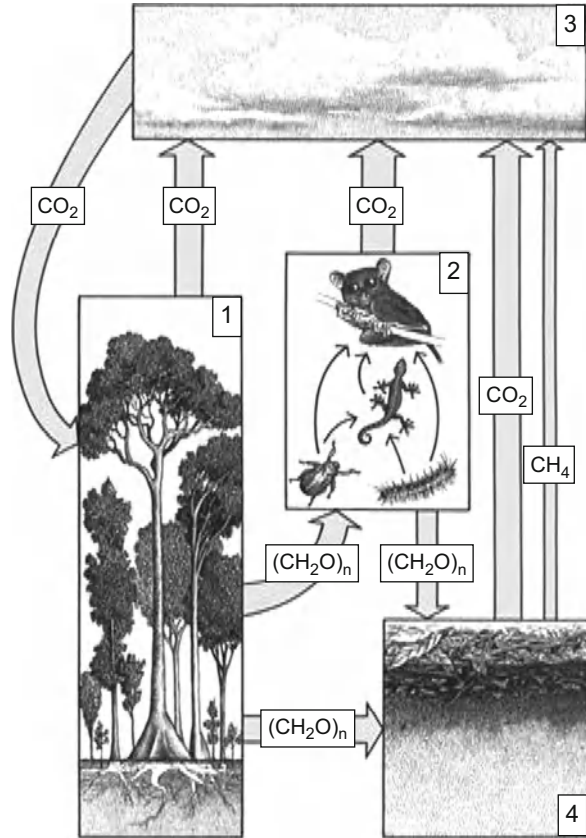
**Fig. 3.17** Anthropogenic use of global renewable water resources in the course of the twentieth century (Based on Shiklomanov 1999)

detritivores, whereby not only the stored energy but also the bound  $\text{CO}_2$  is released. For this reverse process of photosynthesis, most organisms use oxygen ( $\text{O}_2$ ). Some bacteria can also utilize nitrate, methane, or hydrogen sulfide.

In plants, the ratio of photosynthetically fixed carbon to the carbon released through respiration is, on average, 2:1; but for younger individuals in the process of growing, the proportion of carbon fixed as biomass is substantially higher. The carbon compounds found in dead, predominantly plant, biomass in terrestrial ecosystems is decomposed in the soil by organisms, whereby  $\text{CO}_2$  is released to the atmosphere (Sect. 4.3.5.1).

Theoretically, the  $\text{CO}_2$  budget of undisturbed ecosystems is balanced, which means that the quantity of carbon fixed in net primary production is respired by heterotrophic organisms (e.g. microbial decomposition of organic substances and the respiration of animals) and released into the atmosphere. **Net ecosystem production (NEP)**, i.e. NPP minus the heterotrophic respiration, would thus be zero. However, in this balance, spatial and temporal variations may occur. During the succession of a system, the NEP is usually positive and approaches zero during the climax stage. As a result of removal of parts of the NPP during harvest, the NEP in agroecosystems becomes negative if no organic fertilizers are applied.

**Fig. 3.18** The biological carbon cycle of natural terrestrial ecosystems (using the Philippine rain forest as an example). **1** = producers, **2** = first and second-order consumers, **3** = atmosphere, **4** = soil with decomposers



The activity of soil organisms, i.e. the rate of decomposition of carbon compounds in the soil and thus also the NEP, is highly affected by abiotic factors. These include temperature, water balance, availability of oxygen, and pH (Sect. 4.3.5.2). Microbial activity is primarily dependent on temperature and thus the rate of decomposition of carbon materials in the soil of the arctic tundra is approximately a factor of 20 lower than that in a tropical rain forest. The wet soils of swamps, rice fields, and other wetlands are generally anaerobic (i.e. free from oxygen). There, the carbon is predominantly released to the atmosphere in the form of **methane** ( $\text{CH}_4$ ). However, the rate decomposition by anaerobic methane-producing bacteria is lower than that by aerobic microorganisms and can result in an accumulation of organic matter (peat). Anaerobic conditions were also the precondition for the development of **fossil fuels** (oil, gas, brown and hard coal) from dead marine organisms and land and/or wetland plants in a variety of geological eras. Soil cultivation is an anthropogenic factor affecting microbial decomposition of biomass. As a result, transformation of forests, grasslands, and wetlands into agricultural fields can lead to a substantial decline in the carbon content of the soil.

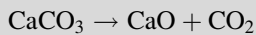
### 3.7.2.1 Anthropogenic Effects on the CO<sub>2</sub> Budget

The CO<sub>2</sub> content of the atmosphere has been subject to both small and large variations in the course of the Earth's history (Sect. 8.1.3.1). At the height of the last Ice Age approximately 21,000 years ago, the content was approximately 200 ppm and subsequently increased with increasing temperature. After the end of the Ice Age, approximately 10,000 years ago, 260 ppm had been reached and a slight increase led to approximately 280 ppm by 1800. Since the beginning of the Industrial Revolution, however, a substantial increase has been observed, and will probably continue beyond the current value of 380 ppm (Sect. 8.1.3.2).

Anthropogenic emissions, almost exclusively, can be regarded as the driver of the increase of more than 30% in CO<sub>2</sub> within the past 200 years. Specifically, the following human activities are known to have changed the natural carbon cycle:

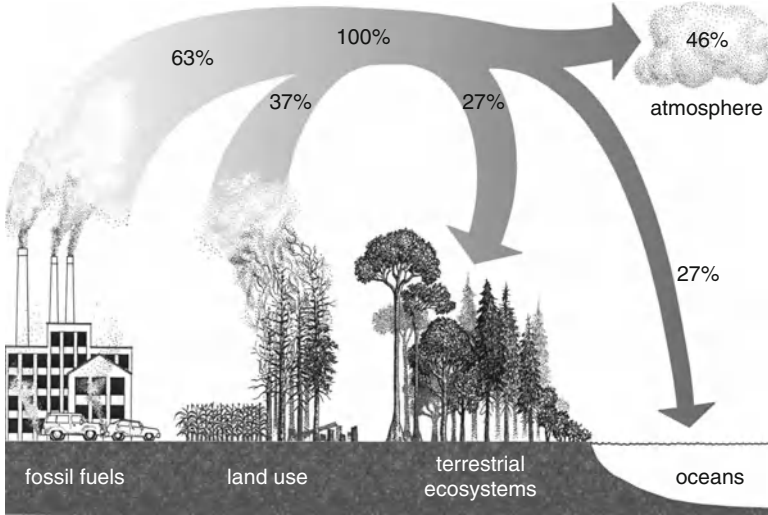
- release of CO<sub>2</sub> by **burning of fossil fuels** (coal, oil, natural gas), which were previously not incorporated in the carbon cycle but were instead, so to speak, sealed in the lithosphere;
- **land use change**, which includes clearing of forests, burning of biomass, and release of CO<sub>2</sub> from organic soil stores as a result of agricultural practices; and
- **production of quicklime or burnt lime** (CaO), primarily used for production of concrete and fertilizers, by heating of limestone (CaCO<sub>3</sub>), which results in release of CO<sub>2</sub>.

Formation of quicklime at temperatures of approximately 1,000 °C:



Through these processes, CO<sub>2</sub> sources are created that did not previously exist or that did not exist to the current extent. Approximately 88% (the average for the years 2000–2009) of annual anthropogenic CO<sub>2</sub> emissions originate from fossil fuels and the production of cement. Approximately 12% originate from land use change. Of the total quantity, only 46% remains in the atmosphere. A further 27% is absorbed by terrestrial ecosystems and the same proportion (27%) by the oceans (Fig. 3.19). Table 3.3 shows the values of these data in comparison with the period 1980–1989.

Currently, the highest terrestrial absorption of CO<sub>2</sub> is probably occurring in the ecosystems of the temperate latitudes of North America, Asia, and Europe, which are, therefore, an important CO<sub>2</sub> sink. The main reasons for this could be changes in land use. These include reforestation, transformation of agricultural land into fallow and grasslands, and agricultural production processes that lead to an



**Fig. 3.19** Global proportions of anthropogenic CO<sub>2</sub> sources and their fate (annual averages for the years 2000–2009; data based on Global Carbon Project 2010)

**Table 3.3** Global sources and sinks of CO<sub>2</sub> in the 1980s and 2000–2009

	Period	
	1980–1989	2000–2009
<i>Sources</i>		
Fossil fuels + cement	5.5	7.7
Land use	1.4	1.0
<i>Sinks</i>		
Atmosphere	3.4	4.0
Oceans	2.0	2.3
Terrestrial ecosystems	1.5	2.3

Values are gigatonnes (Gt) of carbon per year (1 Gt = 1 billion = 10<sup>9</sup> tonnes)  
(Data from Global Carbon Project 2010)

increase in organic soil biomass. It is also possible there are already effects that can be traced back to the increased CO<sub>2</sub> content of the atmosphere and increased global temperatures, which lead to an increased biomass production by plants (Sect. 8.1.3).

### 3.7.3 Oxygen (O)

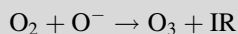
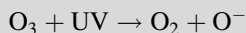
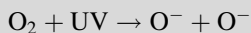
Oxygen is the most common element in the Earth’s crust, and with a content of 21% in the form of O<sub>2</sub>, is the second most common element in the atmosphere. Before the emergence of life there was almost no oxygen in the atmosphere. Only with the

start of photosynthesis by cyanobacteria and, later, primarily by plants, did the O<sub>2</sub> concentration gradually increase to its current value (Sect. 8.1.3.1). Biological oxygen metabolism is closely related with carbon metabolism and proceeds in the quasi opposite direction: in photosynthesis, O<sub>2</sub> is formed that is required by plants, animals, and most microorganisms for aerobic respiration. Furthermore, oxygen is consumed in natural and anthropogenic burning of organic substances, in some land use changes by promotion of aerobic processes (e.g. draining of wetlands), and by non-biological oxidation. However, a decline in atmospheric O<sub>2</sub> concentrations as a consequence of human activity is currently not expected.

Another compound of oxygen is **ozone** (O<sub>3</sub>), which is naturally concentrated 20–30 km above the Earth's surface in the stratosphere. Despite the relatively small concentration of, at most, 10 ppm, ozone fulfils a function of existential importance to life on Earth—up to 90% of solar UV-B rays are absorbed by the ozone layer. O<sub>3</sub> molecules are continuously created and destroyed by UV radiation, whereby the quantity of O<sub>3</sub> remains constant. The following reactions take place in this process:

1. splitting of O<sub>2</sub> by UV rays into free oxygen atoms, which bind with O<sub>2</sub> to create O<sub>3</sub>; and
2. splitting of the O<sub>3</sub> molecules by UV rays into O<sub>2</sub> and free oxygen, from which O<sub>3</sub> is again created with release of heat (i.e. infrared radiation, IR). Overall, the UV-B radiation is thus transformed into harmless forms of energy.

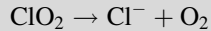
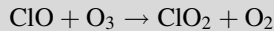
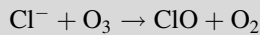
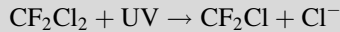
Absorption of UV radiation in the stratosphere:



However, these stratospheric processes are affected by anthropogenic activity, and specifically by release of halogenated hydrocarbons, for example Freon (dichlorodifluoromethane; CF<sub>2</sub>Cl<sub>2</sub>). Such compounds were and are used in various ways in industry (as coolants in refrigerators and air conditioners, in synthetic materials, as cleaning products, in fire extinguishers, and as propellants in spray cans). In the stratosphere these compounds lose halogen atoms (e.g. chlorine), because of the action of UV radiation, which react with ozone with formation of O<sub>2</sub> and halogenated monoxides. The latter combine with free oxygen atoms,

whereby  $O_2$  is formed and the halogen atoms are again released. This is a catalytic process that repeatedly causes the destruction of  $O_3$  molecules. This chain reaction leads to a decline in the concentration of ozone in the stratosphere and is also believed to be responsible for the annual emergence of the “ozone hole” over the Antarctic.

Splitting of halogenated hydrocarbons (e.g. Freon) and reaction of halogens in the stratosphere:



Ozone can also be formed close to the ground (low-level ozone). There, it does not occur here as a result of the splitting of  $O_2$ , because the radiation energy is too low. Instead, nitrogen dioxide ( $NO_2$ ) for which the available light energy is sufficient to drive photolysis, serves as the supplier of oxygen atoms. By reaction of the free oxygen atoms with  $O_2$ , ozone is formed.

In nature, this reversible process is of little importance, because nitrogen dioxide is only available in small quantities. Under specific conditions, however, high ozone concentrations can form close to ground level, particularly in cities with heavy traffic in association with intense sunlight during the summer. Oxides of nitrogen, primarily nitric oxide ( $NO$ ), are released as vehicle emissions. Another precondition for formation of low level ozone is the presence of light and volatile hydrocarbon compounds (e.g. exhaust, solvents), as a result of which, in a series of reactions, oxidation of  $NO$  to  $NO_2$  occurs. This leads to a high concentration of  $NO_2$ , so ozone can be continuously formed in sunlight. In the dark, no ozone formation occurs, because the balance of the chain reaction shifts toward ozone degradation (oxidation of  $NO$  by  $O_3$ ). The same effect can be achieved during the day if emission of nitrogen oxides or hydrocarbons is consistently reduced. As a result of wind drift, it is possible that increased ozone concentrations are also found outside the areas in which they are produced. In rural areas there are fewer sources of nitrogen oxides, which means that the nightly decomposition of ozone is significantly reduced. As a result, there is also the threat of damage to plants, primarily of the leaf surfaces. Reduced growth and increased susceptibility to pests and diseases can be related to this.

Formation of low-level ozone:

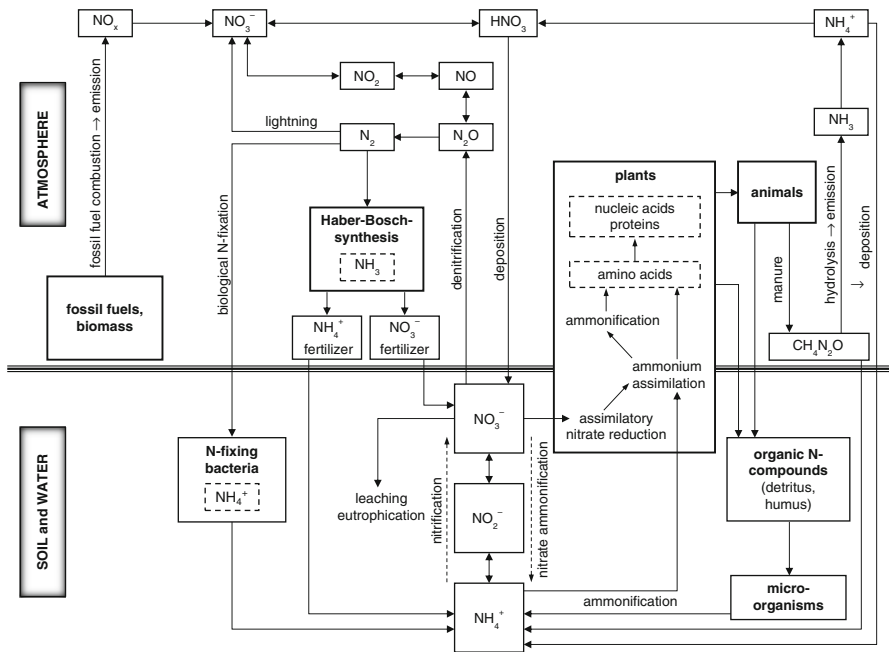


Fig. 3.20 The nitrogen cycle

### 3.7.4 Nitrogen (N)

Nitrogen, in the form of N<sub>2</sub>, is the most common compound in the atmosphere, the proportion being 79%. This element is a component of a variety of organic compounds, for example amino acids, proteins, and nucleic acids, and is thus essential for all organisms.

#### 3.7.4.1 Processes in the Nitrogen Cycle

As N<sub>2</sub>, nitrogen is useful to neither plants nor animals. Thus, processes in which transformation of nitrogen compounds occurs are of central importance in the global nitrogen cycle (Fig. 3.20).

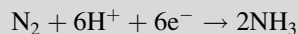
## Nitrogen Fixation

The term nitrogen fixation includes those processes that lead to the formation of N compounds from atmospheric N<sub>2</sub>. In nature, there are two ways in which this can occur:

1. **Lightning.** N<sub>2</sub> is a very inert gas. The energy that is released by lightning strikes leads to splitting of the nitrogen molecule. By way of various reactions with oxygen and water, nitrous acid (HNO<sub>2</sub>) and nitric acid (HNO<sub>3</sub>), or nitrite (NO<sub>2</sub><sup>-</sup>) and nitrate (NO<sub>3</sub><sup>-</sup>), are formed.
2. **Biological nitrogen fixation.** In contrast with plants and animals, some bacteria are capable of fixing atmospheric nitrogen, whereby N<sub>2</sub> is reduced to ammonia (NH<sub>3</sub>) and ammonium (NH<sub>4</sub><sup>+</sup>).

Among the nitrogen-fixing bacteria, free-living and symbiotic species can be distinguished. Representatives of different heterotrophic genera (e.g. *Azotobacter*, *Azospirillum*, *Klebsiella*, *Beijerinckia*) are found in the soil and can be concentrated in the vicinity of the rhizosphere of specific plants. This occurs, for example, with a variety of Poaceae, for example sugar cane, rice, maize, and other cereal species. The bacteria utilize organic compounds, which are released by the roots of these species as food sources. Cyanobacteria are another group that include nitrogen-fixers. Because they are autotrophs, they do not live in the soil but primarily in water and on moist surfaces and are of importance in agroecosystems, especially rice paddy fields.

Reduction of atmospheric nitrogen to ammonia:

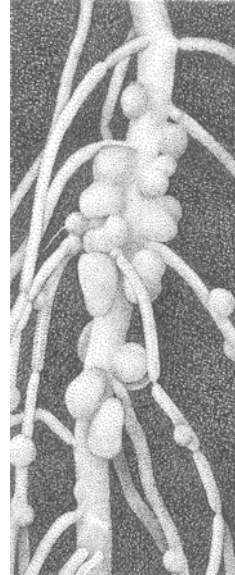


Symbiotic nitrogen-fixers live in mutualistic relationships with other organisms (plants and some corals). They receive carbon compounds from these organisms and the partner profits from delivery of fixed nitrogen. From an agroecological perspective, the following symbiotic relationships between bacteria and plants are of the greatest importance:

- **Root-nodule-forming bacteria and legumes.** Bacteria of the genera *Rhizobium* and *Bradyrhizobium* (**rhizobia**) are found in soil; they carry out aerobic metabolism, utilizing a variety of organic carbon compounds, and nitrate and ammonium as nitrogen sources. In the presence of legumes (Fabaceae) these bacteria change their life strategy. They enter the roots of the plants, reproduce by cell division and form a micro-colony, typically visible as root nodules (Fig. 3.21). There, the bacteria differentiate morphologically into the so-called bacterioids



**Fig. 3.21** Roots of a leguminous plant with typical root nodules



capable of fixing atmospheric nitrogen. The ammonium produced reaches the plant cells and is transported in the form of amino acids through a transport system that also supplies the nodule tissues with photosynthetic products. This  $N_2$  fixation is performed with the aid of the oxygen-sensitive nitrogenase enzyme system. Leghaemoglobin is responsible for maintenance of low  $O_2$  concentrations. This compound consists of a protein component (globin) that is delivered by the plant and a pigment component (protohaem) that originates from the bacteriod. Colonization of the plant also promotes reproduction of the rhizobia; i.e., after the death of the plant the number of bacteria in the soil increases. More than 90% of leguminous species are infected by nodule-forming bacteria; these include soybean, field beans, beans of the genus *Phaseolus*, pea, lentil, and peanut among the numerous agriculturally important crops. Important fodder plants include *Trifolium*, *Lotus*, and *Medicago* species.

- ***Azolla* and *Anabaena*.** The genus *Azolla* are aquatic floating ferns of the family Salviniaceae, of which six species are known worldwide. They have small, distichously arranged leaves divided into two lobes. In the upper lobe, photosynthesis occurs; the lower lobe is in contact with water. The plant hosts the cyanobacteria *Anabaena azollae* in hollows on the underside of the upper lobe. The cyanobacteria can be found there at all stages of the fern's development. Because *A. azollae* has highly specialized cells, called heterocysts, it is capable of fixing atmospheric nitrogen. The resulting ammonium is taken up by the fern, which in turn supplies the cyanobacteria with photosynthetic products (primarily sucrose). Similar to the legumes in terrestrial systems, the *Azolla* species, via symbiosis with nitrogen-fixing bacteria, also have the potential to improve the

supply of this nutrient to rice paddy fields and thus to increase rice yields. Use of such species (primarily *Azolla pinnata*) is of particular importance, with a long tradition, in southeast Asia.

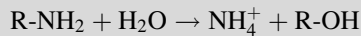
### Ammonium Assimilation

Uptake of ammonium ( $\text{NH}_4^+$ ) and its transfer in compounds produced by an organism is called ammonium assimilation. Plants that live in mutualistic relationships with nitrogen fixers receive these compounds from the respective bacterial species. However, ammonium can also be taken up by the plant directly via the roots. In the soil, however,  $\text{NH}_4^+$  is of quantitative importance only under acidic, moist, and oxygen-poor conditions. Generally, nitrate ( $\text{NO}_3^-$ ) in the soil is the most important source of nitrogen for plants.

### Ammonification

Separation of  $\text{NH}_4^+$  or amino groups ( $-\text{NH}_2$ ) from organic nitrogenous compounds is termed ammonification. This process occurs in plants and in ecosystems (in soils and water). In plants,  $\text{NH}_2$  groups are enzymatically removed (deamination) and transferred to other compounds (transamination).

Ammonification as the first step in N-mineralization in ecosystems:



In the soil, most of the nitrogen is present in the form of organic compounds (>95%), which primarily originate from dead organisms. Ammonification there is performed by a variety of bacteria and fungi and is the first step in nitrogen mineralization.

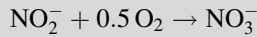
### Nitrification

$\text{NH}_4^+$  released in the soil by ammonification is oxidized by some microorganisms in the presence of oxygen. This first produces nitrite ( $\text{NO}_2^-$ ) and finally nitrate ( $\text{NO}_3^-$ ). These processes are two steps in the mineralization of nitrogen whereby the two products are produced by different chemoautotrophic bacteria that gain energy in the process. Nitrite is primarily released by members of the genus *Nitrosomonas* and is subsequently oxidized to nitrate by *Nitrobacter* bacteria.

Formation of nitrite by Nitrosomonas:



Formation of nitrate by Nitrobacter:



Under suitable conditions (neutral to slightly acidic soils, temperatures around 25 °C, moderately moist and sufficiently oxygenated), nitrification proceeds almost completely, which means that no significant amounts of ammonium or nitrite remain. Annual nitrification and mineralization of organic nitrogen compounds in soils range between approximately 1 and 5%.

### Nitrate Reduction

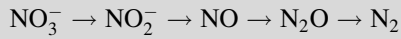
Transformation of nitrate into an organism's own organic nitrogenous compounds, i.e. the reverse of mineralization, is called the **assimilatory nitrate reduction** pathway. This process is performed by plants and a variety of microorganisms, but not by animals. The reduction proceeds in two main steps, from nitrate to nitrite and from nitrite to ammonium. Subsequently, assimilation of ammonium occurs, i.e., incorporation of  $\text{NH}_4^+$  into organic compounds, initially forming the amino acid glutamine.

In largely anaerobic, wet, and acid habitats, some bacteria can reduce nitrate to nitrite and further to ammonium. This pathway is called **nitrate ammonification** and might be regarded as a shortcut in the biological nitrogen cycle that formally combines denitrification and nitrogen fixation. In contrast with assimilatory nitrate reduction, this process does not include direct transformation of  $\text{NH}_4^+$  into an organic substance, i.e. the ammonium is present in the ecosystem and available to plants.

### Denitrification

Denitrification is another process in which nitrate is transformed into further compounds under anaerobic conditions. This is mostly by heterotrophic bacteria that can use the oxygen in nitrate and nitrite for respiration, instead of  $\text{O}_2$ . Reduction of nitrate occurs in several steps and the final product is molecular nitrogen ( $\text{N}_2$ ).

Reduction of nitrogen in denitrification:



Denitrification is also promoted by high availability of organic carbon, a high soil water content, and high temperatures, among other factors, and occurs primarily in neutral soils.

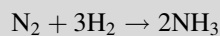
### 3.7.4.2 Anthropogenic Effects on the Nitrogen Cycle

Similar to the carbon cycle, global turnover of nitrogen compounds has substantial anthropogenic components. At present, more than half of the fixed nitrogen cycling through the atmosphere and back to terrestrial surfaces results from human activity (Table 3.4).

The most important contributions to the transformation of the natural nitrogen cycle are:

- Production and use of fertilizers: industrial nitrogen fixation, largely for production of nitrogen fertilizers, was made possible by the Haber–Bosch process patented in 1910, which produces ammonia ( $\text{NH}_3$ ) from atmospheric nitrogen ( $\text{N}_2$ ) and hydrogen ( $\text{H}_2$ ). The synthesis occurs under high pressures, at approximately  $500^\circ\text{C}$  and with the help of a catalyst based on iron. From the resulting ammonia, urea ( $\text{CH}_4\text{N}_2\text{O}$ ), and nitric acid and its salts (nitrates) can be produced and thus a variety of fertilizers can be manufactured. The quantity of industrial nitrogen fixation worldwide is estimated to be approximately 125 Teragrams (Tg) per year.

Reaction of the Haber–Bosch process:



- The production of some crop plants: by cultivation of legumes ( $\text{N}_2$  fixation by rhizobia) and establishment of rice paddies ( $\text{N}_2$  fixation by cyanobacteria), humans contribute to the annual amount of nitrogen fixed by approximately 20 Tg. In comparison, the quantity of atmospheric nitrogen fixed by natural, terrestrial ecosystems is estimated to be  $120 \text{ Tg year}^{-1}$  at most.
- Use of fossil fuels: mineral oil products and coal contain nitrogen compounds that are released in combustion, primarily in the form of nitrogen oxides ( $\text{NO}_x$ ).

**Table 3.4** Nitrogen budget for the global land surface

	Pre-industrial (natural)	Human-derived	Total
Biological nitrogen fixation	120	20	140
Industrial nitrogen fixation	0	125	125
Fossil fuel combustion	0	25	25
Lightning	5	0	5
<i>Totals</i>	<i>125</i>	<i>170</i>	<i>295</i>

Based on Schlesinger (2009). Values are Teragrams (Tg) nitrogen year<sup>-1</sup> (1 Tg = 10<sup>12</sup> g = 1 million = 10<sup>6</sup> metric tons)

At high temperatures, fixation of atmospheric nitrogen also occurs, as occurs naturally as a result of lightning. As a result of the use of fossil fuels, the natural nitrogen cycle receives an additional 25 Tg of fixed nitrogen per year.

These and other human activities, for example biomass burning and soil cultivation have far-reaching consequences in the atmosphere and biosphere. These are primarily related to the effects of nitrate, ammonia, dinitrogen oxide (laughing gas), and other oxides of nitrogen.

### Nitrate (NO<sub>3</sub><sup>-</sup>)

The only way to bind nitrate added to agroecosystems in the form of mineral fertilizers is uptake by organisms. Because soils have high adsorption capacity for cations only, excess nitrate (an anion) can easily end up in surface water and groundwater. The extent of such leaching depends largely on the quantity of fertilizer applied, the climate, the soil type, and the crop stand. At temperate latitudes, leaching is highest in the winter months, because of the reduced activity of plants and microorganisms. However, by cultivation of winter cover crops nitrate leaching can be reduced. Nitrate in groundwater and drinking water is problematic even though the compound itself is only toxic in high quantities. In the human body bacterial transformation of nitrate into nitrite occurs, which can lead to symptoms of poisoning, especially in infants. Nitrate reacts with amines and amides to form nitrosamine and nitrosamide, respectively, which are carcinogenic.

In surface waters, input of nitrogen and phosphorus can lead to **eutrophication**, i.e. increases in nutrient content. As a consequence of this, growth of algae increases, which can initially lead to an increase in oxygen content near the water surface. During decomposition of the dead biomass, this oxygen is consumed by detritivores. Further transformation of the organic matter then proceeds under anaerobic conditions, and such gases as hydrogen sulfide, methane, and ammonia are formed. The presence of organisms that require oxygen is, therefore, no longer

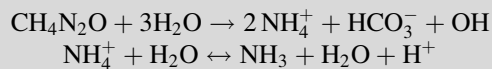
possible. Lower inputs of nutrients, which are not sufficient to cause algal blooms in waters, can still result in a decline in biodiversity. The reasons for this are the same as for nutrient inputs in terrestrial ecosystems (Sect. 3.3.1).

### Ammonia (NH<sub>3</sub>)

Human activities are responsible for approximately 70% of the ammonia released worldwide. The largest part originates from agriculture, with more than 80% coming from animal excreta in livestock production. There, the most important process is the hydrolysis of urea found in liquid and solid manure.

Formation of gaseous ammonia occurs in alkaline environments and is promoted by heat. Because ammonia is highly water soluble, it reacts rapidly in the atmosphere to form ammonium. This is returned to terrestrial and aquatic ecosystems, where it is transformed into nitrate.

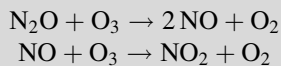
Hydrolysis of urea and formation of ammonium:



### Dinitrogen Oxide (N<sub>2</sub>O; Laughing Gas)

Under specific conditions, nitrate reduction in the soil does not proceed to completion; as a result, not only is N<sub>2</sub> produced as a final product but also other products, primarily laughing gas (dinitrogen oxide, N<sub>2</sub>O). Low temperatures, low availability of carbon compounds, high nitrate content (primarily as a result of fertilization) and acidic soils are some of the factors that promote this process. Laughing gas, similar to hydrocarbons, contributes to depletion of the ozone layer (Sect. 3.7.3) in the stratosphere and also acts as a greenhouse gas (Sect. 8.1.3.1).

Degradation of ozone by reaction with laughing gas:



### Nitrogen Oxides (NO<sub>x</sub>)

Use of fossil fuels makes the largest contribution to global production of NO<sub>x</sub> compounds (especially NO and NO<sub>2</sub>). These compounds not only contribute to the

ground level development of ozone (Sect. 3.7.3), but also to the development of acid rain. This happens via oxidation of NO and NO<sub>2</sub>, whereby nitric acid and nitrate are formed. Via a variety of processes, ammonia also contributes to acidification (see above). Another, sometimes larger, contribution to acid rain is that of sulfur dioxide (SO<sub>2</sub>) which, similar to nitrogen oxide, is primarily released during burning of oil and coal and forms sulfuric acid and sulfate (SO<sub>4</sub><sup>-</sup>) via oxidation.

Atmospheric deposition of nitrogen compounds in Central European ecosystems amounts to approximately 10–30 kg ha<sup>-1</sup> year<sup>-1</sup> and makes a significant contribution to eutrophication and acidification of soils and waters.

### 3.7.5 Phosphorus (P)

Phosphorus is similar to nitrogen in its importance as an essential nutrient for all living organisms. It is a crucial component of nucleic acids, cell membranes, and of the energy carrier adenosine triphosphate (ATP). In the form of phytic acid, phosphorus is found as an energy source and reserve in plant seeds. Calcium phosphate is a component of the bones and teeth of vertebrates.

The largest phosphorus reserves on Earth are found in marine sediments and the resulting rocks, in rocks of volcanic origin (basalts), and in soils. The approximately 200 known inorganic compounds in which phosphate is found are almost all derivatives of phosphoric acid (H<sub>3</sub>PO<sub>4</sub>). The most common are calcium phosphate (apatite), which is found in the form of fluorapatite (Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F), hydroxyapatite (Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH), and chlorapatite (Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>Cl). Gaseous compounds of phosphorus are not of importance. Unfertilized soil contains, depending on a variety of factors (e.g. parent material, extent of weathering, clay and humus content) between approximately 100 mg kg<sup>-1</sup> (sandy, strongly weathered soil) and 1,500 mg kg<sup>-1</sup> (soil on basaltic rock) of total phosphorus. Total phosphorus is made up of a variety of organic and inorganic compounds. The latter comprise stable phosphates, which are found as salts (mineral phosphate), and labile phosphate ions (HPO<sub>4</sub><sup>2-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>), which are attached to soil particles (primarily clay minerals). These forms make up the bound phosphate. Plants primarily take up phosphorus in the form of hydroxyphosphate (H<sub>2</sub>PO<sub>4</sub><sup>-</sup>), which is then incorporated into organic compounds. However, the quantities of phosphate present in solution in the soil and therefore available to plants are very limited and amount to only approximately 0.1% of the total phosphorus in the soil. To supply plants, phosphate must be delivered from the bound fraction, which only occurs when the concentration in the soil solution is low, i.e. when the soluble supplies have been taken up by the plants. In phosphorus-poor soils, mobilization of bound phosphate can proceed via organic acids, which are produced by free-living microorganisms, plant roots, or mycorrhizal fungi. Most phosphorus compounds introduced via litter and detritus,

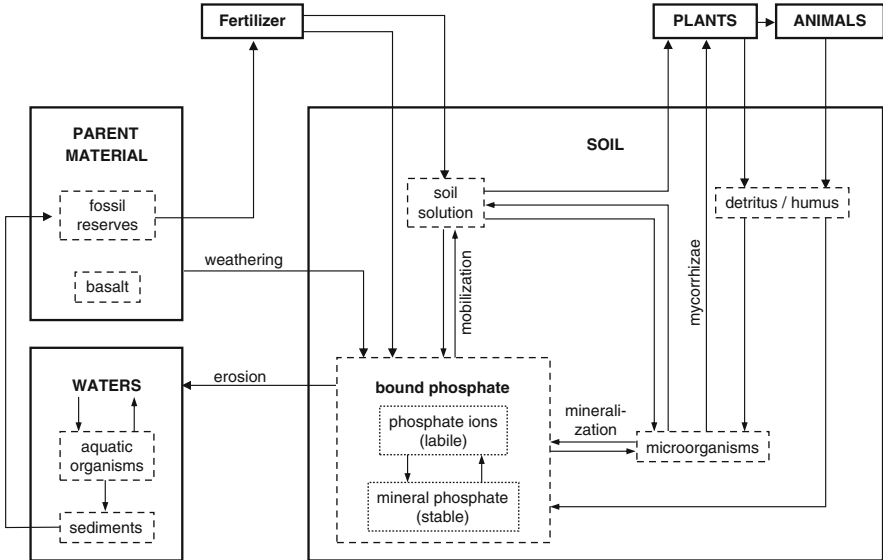


Fig. 3.22 The phosphorus cycle

which are rapidly decomposed by microorganisms, or are directly returned to the soil reserves via leaching (Fig. 3.22).

Phosphorus mineral fertilizers used to improve the phosphorus supply in agricultural soils primarily originate from rock reserves. However, these raw phosphates are usually poorly water soluble and must therefore first be modified. This is achieved by grinding or by treatment with sulfuric acid (in the production of superphosphate). Only a small proportion of the phosphate fertilizer applied to fields reaches the soil solution; most is transformed into bound phosphate. Over time, the phosphate content of many intensively used agricultural soils increases, because the bound phosphate is only subject to leaching to a limited extent, as a result of strong adsorption by mineral soils. For this reason, phosphate fertilization—in contrast with over-fertilization with nitrogen—has little effect on groundwater. As a result of erosion and runoff, however, phosphates reach rivers and lakes on soil particles, which, in association with nitrogen fertilization, leads to eutrophication of waters and to an increase in plant growth (Sect. 3.7.4.2). In Germany, approximately half of the phosphate that reaches flowing waters and, eventually, the ocean originates from agriculture.

In contrast with the situation in intensive agriculture at temperate latitudes, large areas of the tropics have a low soil phosphate content, which is a limiting factor in plant production. This is not only because of the insufficient availability and high cost of phosphate fertilizers but also the result of the high phosphate fixation of many soils (e.g. Ferralsols, Sect. 7.2.1) of these climate zones. This severely limits the continuous supply of phosphate to crops.



Modern agriculture is dependent on phosphorus derived from phosphate rock; this is a non-renewable resource and current global reserves may be depleted in 50–100 years. Although phosphorus demand is projected to increase, the expected global peak in phosphorus production is predicted to occur around 2030. Although the exact timing of peak phosphorus production might be disputed, it is widely acknowledged within the fertilizer industry that the quality of remaining phosphate rock is decreasing and production costs are increasing (Cordell et al. 2009).

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