Biogeochemical cycles are involved in the interactions between vertical organisms. Biogeochemical cycles of terrestrial and aquatic organisms. interactions macrophytes in the Corrego do Geraldo, Aquatic Carlos Botelho reservoir (Lobo/Broa). UHE Carlos Botelho Photo: J. G.Tundisi.

10 Biogeochemical cycles

SUMMARY

The cycles of chemical elements and substances are interrelated with biological, geochemical and physical processes. The distribution and concentration of elements and substances in water depend on 'fixation' and the active concentration of macronutrients (carbon, hydrogen, nitrogen, phosphorus and sulphur) and micronutrients (magnesium, iron, copper and zinc). Macronutrients and micronutrients alike are found in living organic matter, particulate matter, decomposing matter, or dissolved in water. The nutrient recycling rate depends on the interactions between vertical and horizontal mixing and the activity and biomass of aquatic organisms.

The vertical distribution of nutrients is affected by the vertical circulation in lakes or reservoirs and depends on the type of circulation and its frequency. Bacteria with varying physiological and biochemical characteristics play a key role in biogeochemical cycles. Bottom sediment in rivers, lakes, reservoirs, estuaries and interstitial waters provide important quantitative and qualitative nutrient reserves. The availability of nutrients in sediment and interstitial waters depends on oxido-reductive processes and the anoxic or oxic layers of the sediment.

10.1 THE DYNAMICS OF BIOGEOCHEMICAL CYCLES

As shown in Chapter 5, the composition of natural waters largely depends on the geochemistry of the water basin and the main characteristics and processes in the basin: **soil types**, uses and agricultural practices. In inland waters, the distribution of nutrients is also influenced by **regenerative processes** in the lake's deepest layers and the sediment-water interface.

The principal nutrients are those that are important for all plants; these include carbon, nitrogen, and phosphorus. In combination with hydrogen and oxygen in various different configurations, these elements form the basis of metabolic processes and cell structure. Sulphur and silicon can also be added to this list, as silicon is found in the frustules of diatoms, and sulphur is an essential component in many proteins. These elements are called macronutrients since relatively high levels are needed for growth. Micro-nutrients, which are needed only in relatively low concentrations, include manganese, zinc, iron and copper. Their absence can restrict growth, but at higher concentrations these metals can be toxic.

The chemical composition of inland waters, when comparing data from many lakes, shows significant correlations between total dissolved solids (TDS) and HCO_3^-, and between Ca^{2+} and TDS (see Chapter 5).

Aquatic plants actively concentrate carbon, hydrogen, nitrogen, phosphorus and sulphur along with other micronutrients. The fixation of these elements occurs physio-logically. In general, average C:N:P levels by atoms occur stoichiometrically as 106C:16N:1P. This ratio is called the **Redfield Ratio** (Redfield, 1958). The cycles of these elements in inland waters are thus related to the biological processes in aquatic systems, and stoichiometric ratios in part reflect the way in which nutrients are found in water.

In general, **macronutrients** and trace elements are found in living organic matter, in dead and decomposing particulate matter, or dissolved in water. The amounts found in each of these compartments in the aquatic system are important and essential for understanding biogeochemical cycles. Therefore, the distribution and concentration of a specific nutritional element in a mass of water is a function of biological, geochemical and physical processes.

The nutrient recycling rate depends on the interactions between horizontal and vertical mixings (which determine temporal and spatial distributions), and also on the activity and biomass of the organisms present. Significant variables in these processes include the retention time of the water mass, the rates of transfer of elements between masses of water, and the recycling rates of the elements among the various compartments. A common distinction used in nutrient cycles is between a conservative vs. non-conservative substance. A **conservative substance** has a much longer retention time than the total mixing time of the lake and thus a more homogeneous distribution. The retention time of a non-conservative substance is much shorter than the total mixing time of the water mass and thus presents heterogeneous distributions through space and time.

The fixation of nutrients by aquatic plants always occurs through soluble and diffuse sources in such a way that nutrients must pass through a semi-permeable membrane into the cell (Reynolds, 1984). The nutrient levels, however, are always much lower in the liquid medium than the levels occurring in cells. Passive diffusion is rare and a transport system (**ion pump**) is needed, creating by enzymes located close to the cell surface (cell wall).

10.2 CARBON CYCLE

Some of the factors involved in the availability of carbon in natural waters were already discussed in Chapter 5. The balance of carbonate (CO_3^{2-}), bicarbonate (HCO_3^-) and CO_2 determines the **acidity** or **alkalinity** in natural water. Carbon is an element consumed in large amounts by photosynthetic organisms and is thus one of the essential elements in the biogeochemical cycle in natural waters. The photosynthetic activity of aquatic plants removes carbon from surface waters. Rapid sedimentation occurs after the death of organisms, such that sedimentation of organic matter plays an important role in the **carbon cycle**. Due to the equilibrium system between dissolved CO_2 (and its diverse chemical forms) in the water and atmospheric CO_2, carbon is always available to **photosynthetic organisms,** so the main theories concerning the limitations of photosynthetic growth processes do not include carbon as a limiting factor (Goldman *et al.*, 1972). However, in conditions of high pH due to photosynthesis, carbon may limit the process in surface waters, with a shift in equilibrium toward **bicarbonate** and **carbonate.** In waters with high **nitrogen** and **phosphorus** levels, the ability to fix bicarbonate or carbonate gives an additional competitive advantage to some phytoplanktonic or aquatic plant species (Harris, 1978). Some phytoplanktonic species can maintain a high intracellular CO_2 level because of a '**bicarbonate pump**' in the cellular membrane, which, along with the activity of a carbonic unit, physiologically operates this system. The fixation mechanisms of carbon and its transport in aquatic plants continually interact with the chemical compounds of inorganic carbon dissolved in water, which has enormous implications for methods (experiments to measure photosynthesis), physiology (respiration, consumption of energy, photosynthesis, excretion) and ecology (control of chemical conditions by aquatic plants, interactions with the seasonal cycle, and the processes of decomposition and recycling).

The biochemical differences among different species greatly affect the interrelations between the seasonal cycle of aquatic plants and their succession in time and space, as was demonstrated for several phytoplanktonic species (Harris, 1980). In general, the flow of carbon into cells occurs photo-autotrophically, although in some cases, 'fixing' carbon in the dark can become important. Figure 10.1 illustrates the carbon cycle in natural waters.

10.3 THE PHOSPHORUS CYCLE

Phosphorus, as a component of nucleic acids and adenosine triphosphate, is an essential element in the internal processes and growth of aquatic plants. The **flow of phosphorus** into inland waters depends on the geochemical processes in a water basin. The most common forms of organic phosphorus are generally of biological origin. Dissolved phosphates are derived from the **leaching** of minerals, such as the apatite present in rocks. Phosphorus can also be found in different-sized particles, even in colloidal form. Sedimentation of particles and excretion from planktonic or benthic organisms contribute to the accumulation of sediment, forming an important reservoir of phosphorus. It accumulates also in the **interstitial water**, and depends, in great part, on the processes of circulation and oxido-reduction at the **sediment-water interface.**
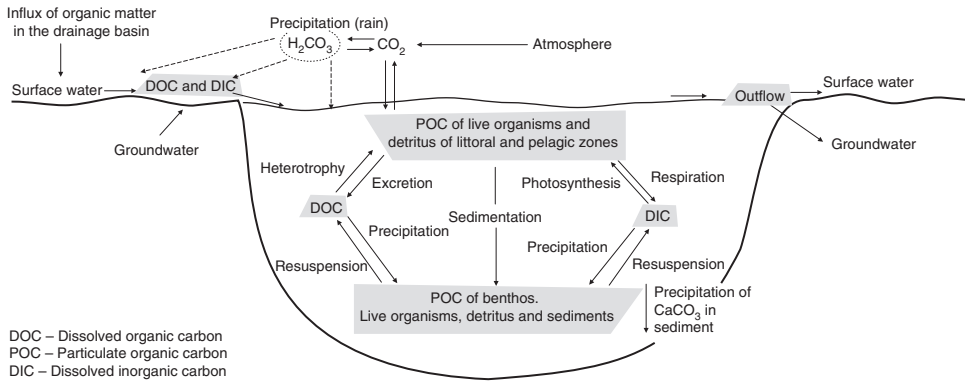
Figure 10.1 Generalized and simplified carbon cycle for a lake. In reservoirs with many compartments and shallow areas, the cycle can be more complex.

Hutchinson (1957) distinguishes the differences between **dissolved phosphate, sestonic phosphate** dissolved in **acid** (mainly ferric phosphate or calcium phosphate), **dissolved organic phosphorus** (colloidal) and **sestonic organic phosphorus**.

Of these various forms, **dissolved orthophosphate** is clearly the main source of phosphorus for aquatic plants, especially for phytoplankton. The use by phytoplankton of dissolved organic phosphate through the production of alkaline phosphatase has also been reported by Nalewajko and Lean (1980) and Reynolds (1984).

Undisturbed terrestrial systems retain **phosphorus,** while deforested **water basins** generally lose phosphorus. Moss (1980) recorded the following typical levels of phosphorus in inland waters:

▶ 1 μg P/litre – natural pristine lakes in high-altitude regions;
▶ 10 μg P/litre – natural lakes in forested lowlands;
▶ 20 μg P/litre –lakes in early stages of eutrophication in agricultural or deforested regions;
▶ 100 μg P/litre – eutrophic lakes in highly populated urban areas with sewer discharge;
▶ 1000 μg P/litre to 10,000 μg P/litre – stabilization ponds, highly fertilized fish-production ponds; endorheic lakes.

An important component of the **phosphorus cycle** in inland aquatic systems is in the sediments. A portion of the phosphorus undergoes a complexation process during periods of intense oxygenation in the sediment, thus periodically becoming unavailable. The cycles of phosphorus, iron, and the **oxido-reduction potential** in water and sediment are thus closely correlated.

Since phosphorus does not have a common gaseous phase, its availability depends on phosphated rocks and on the internal cycle of lakes, in which decomposition and excretion play an important role. Phosphorus plays a key role in regulatory and recycling processes in lakes. In stratified lakes, an important part of the phosphorus cycle can also occur in the metalimnion, where the regenerative process occurs through the
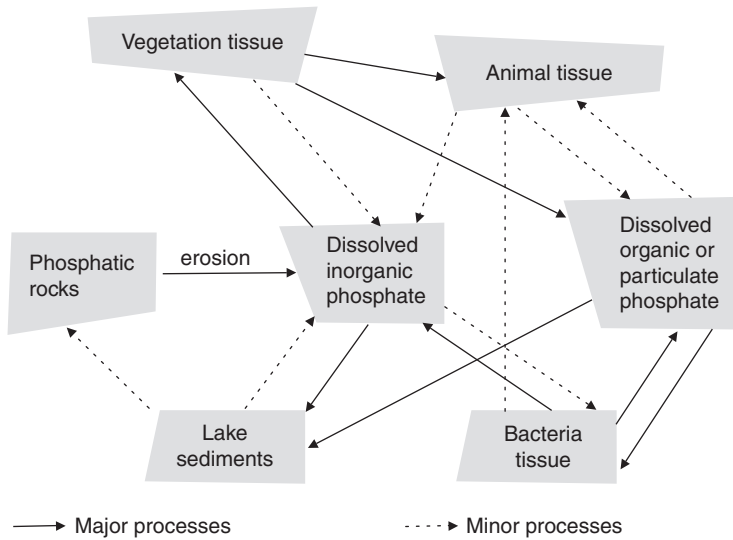
Figure 10.2   The phosphate cycle in aquatic ecosystems.
Source: Modified from Welch (1980).

reduction that occurs in metalimnetic layers with low oxygen levels (Gliwicz, 1979). Figure 10.2 illustrates the phosphorus cycle in aquatic ecosystems.

10.4 THE NITROGEN CYCLE

Aquatic plants use nitrogen mainly to synthesize **proteins** and **amino acids**. The primary sources of nitrogen are nitrate, nitrite, ammonium, and dissolved nitrogen compounds, such as urea, and free amino acids and peptides. **Atmospheric nitrogen** dissolved in the water can be 'fixed' by some species of cyanobacteria.

Inorganic nitrate is highly soluble and abundant in water with high nitrogen levels, often due to the discharge of household sewage or agricultural activity. High nitrate levels are found, for example, in the Bonita Barra reservoir in the state of São Paulo ($1–2\,mg\ N\text{-}NO_3^-\cdot L^{-1}$), due to the discharge of domestic sewage and the drainage of fertilized agricultural soils (Tundisi and Matsumura Tundisi, 1990).

Tropical lakes and reservoirs generally present low nitrate levels, the result of the drainage from forests or savannas with nitrogen-poor soils. Stratified lakes may present low nitrate levels in the epilimnion (Tundisi, 1983).

In natural conditions, the ammonium level is also relatively low in epilimnion waters ($<100\,\mu g\ N\text{-}NH_4\cdot L^{-1}$). In stratified lakes, ammonium levels can be higher, principally in anoxic conditions, where nitrate is reduced to ammonium ($1–2\,mg\ N\text{-}NH_4\cdot L^{-1}$). In eutrophic lakes, in the metalimnion and hypolimnion, ammonium levels can oscillate due to excretion and decomposition by organisms. In the epilimnion of tropical lakes, nitrogen may be regenerated through the excretion of ammonium by zooplankton or decomposition of organic matter by bacteria (Tundisi, 1983; McCarthy, 1980).
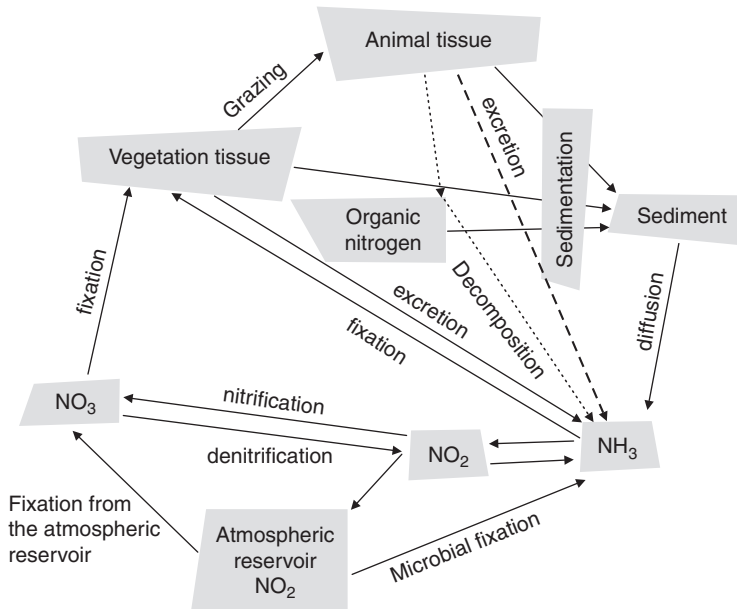
Figure 10.3 Simplified nitrogen cycle in inland aquatic ecosystems.
*Source*: Modified from Welch (1980).

The nitrite level is consistently low ($<60\,\mu g$ N-N$_3\cdot$L^{-1}) since this ion can be reduced chemically or by bacterial activity that reduces nitrate or oxidizes ammonium. In tropical waters, nitrate levels are generally extremely low, frequently below the limit of detection. Nitrite occasionally accumulates in bubbles where the oxygen tension is below 1 mg O$_2\cdot$L^{-1} and in conditions of deep stratification.

Figure 10.3 shows the nitrogen cycle in lowland aquatic ecosystems.

The nitrogen cycle is also fairly complex because of the existence of a large reserve of nitrogen in the atmosphere (~80%). The transfer processes between the different compartments are extremely important for aquatic productivity. The transfer of atmospheric N$_2$ by microbiological fixation (e.g., cyanobacteria) and its return to the atmosphere via N$_2$O and denitrification are biologically and chemically important features unique to the nitrogen cycle (they do not occur in the phosphorus cycle). Micro-organisms accelerate the reaction and also store available energy from reduced compounds due to a series of chain reactions triggered and catalysed by enzymes. Since the energy sources are inorganic, the organisms are called **chemo-lithotrophic** (Welch, 1980).

The main processes in the nitrogen cycle are nitrification, denitrification, and biological fixation. Nitrification is the process through which NH$_3$ is transformed into NO$_2^-$ and NO$_3^-$. The process occurs under aerobic conditions, as a result of the activity of organisms such as *Nitrosomonas* and *Nitrobacter* bacteria.

$$2NH_3 + O_2 \rightarrow 2HNO_2 + 2H_2O + \text{energy}$$

$$2HNO_2 + O_2 \rightarrow 2HNO_3 + energy$$
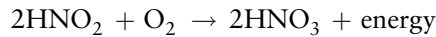
Denitrification occurs mainly in the absence of oxygen or in conditions approaching anaerobiosis. *Thiobacillus denitrificans* is a denitrifying organism.

$$5S + 6NO_3 + 2H_2O \rightarrow 5SO_4 + 3N_2 + 4H + energy$$

Heterotrophic bacteria, such as *Pseudomonas* spp., are **facultative anaerobe** and can be found in sewage and waste-waters.

The **denitrification** process is the reverse of the nitrification process, i.e., bacteria reduce NO_2 and NO_2 to nitrogen gas N_2, which returns to the atmosphere, thus providing a mechanism to reduce nitrogen in waste-water or in excessively eutrophic waters. It is a basic process that commonly occurs in flooded and marshy waters.

Since nitrification needs an aerobic system and denitrification occurs in an anaerobic system, the aerobic/anaerobic shift is an effective process for the transfer of nitrogen to the atmosphere, and is a mechanism for treating waste-water in which an aerobic period precedes an anaerobic period. As a system becomes eutrophized, oxygen levels drop, making **denitrification** possible.

Another important process, the biological fixation of nitrogen, occurs in aquatic systems through bacterial activity (*Azotobacter* and *Clostridium*) and by the cyanophytes *Nostoc, Anabaena, Anabaenopsis, Aphanizomenon* and *Gloeotrichia*. Fixation of atmospheric N_2 can be high, as is the case in Clear Lake (California), in which 43% of the total entrance of nitrogen in the lake occurs through biological fixation (Horne and Goldman, 1994). The cyanophytes occur in cells that fix N_2 (heterocysts or heterocytes), whose number increase with the decrease of NO_3^- Reynolds (1972) showed that in N levels below $300\,\mu g \cdot L^{-1}$, the ratio of heterocysts to vegetative cells increases in an *Anabaena sp*.

Nitrogen-fixing cyanophytes are common in shallow inland waters and oceans, and practically absent from estuaries (McCarthy, 1980). They are important components of the nitrogen cycle in inland waters.

Thus the main processes involved in the nitrogen cycle in water are:

▶ fixation of nitrogen (N) – N_2 (gas) and chemical energy, transformed into ammonium (NH_4^-);
▶ nitrification – reduced forms, such as ammonium, are transformed into nitrite or nitrate$^-$;
▶ denitrification – nitrate, through reduction, is transformed into N_2 (gas);
▶ assimilation – dissolved inorganic nitrogen (ammonium, nitrate or nitrite) is incorporated into organic compounds;
▶ excretion – animals excrete nitrogen in the form of ammonium, urea or uric acid.

10.5 THE SILICA CYCLE

Silica is found in natural waters in the form of silicic acid and colloidal polymers of silicate, originating from soil or organisms such as diatoms, whose frustules do
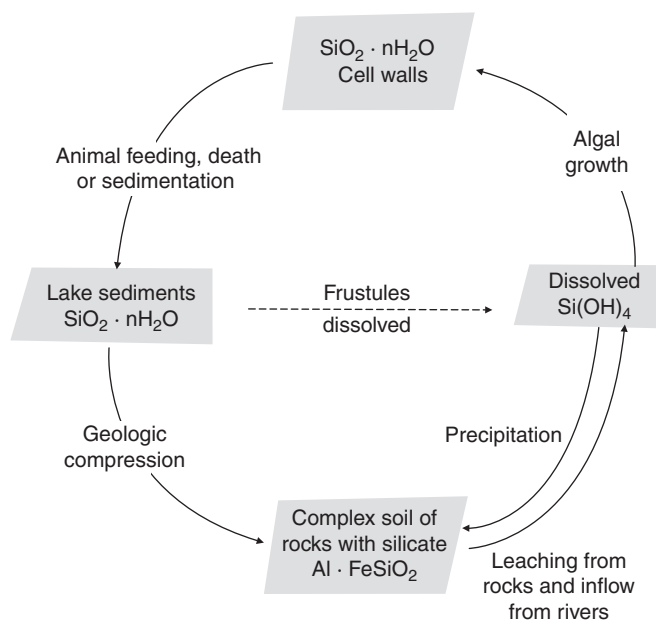
Figure 10.4 Silica cycle.

not present amorphous silica polymers. From this perspective, silica plays a significant ecological role, and its seasonal cycle is related to the growth of diatoms and their subsequent dissolution (Reynolds, 1973a, 1984). Thus, the availability of silica is related to the cycle of growth, decomposition and dissolution of diatomic frustules found in the sediment at the bottom of lakes and reservoirs. Lund (1950, 1964) showed the relationship between the cycle of an *Asterionella* sp. and the silica cycle in the Lake District in England.

Many studies have described this cycle of soluble reactive silicon and the seasonal cycle of diatoms in inland water systems. The de-polymerization of silica forms $SiOH_4$ (silicic acid) that as 'soluble reactive silicon' is measured spectrophotographically by the reaction described by Mullin and Riley (1955).

Levels of soluble reactive silica in natural waters range from a maximum of 200–300 mg $SiO_2 \cdot L^{-1}$ to less than 1.2–10 mg $SiO_2 \cdot L^{-1}$. Silica levels can be important in the development of *Aulacoseira* sp. For example, Kilham and Kilham (1971) showed that *Aulacoseira italica* develops when silica levels are below 5 mg$\cdot L^{-1}$, while *Aulacoseira granulata* also grows at levels greater than 5 mg$\cdot L^{-1}$. Figure 10.4 illustrates the silica cycle.

10.6 OTHER NUTRIENTS

Various other elements are important for the growth, productivity and physiology of aquatic plants. Among these are calcium, which occupies an important position chemically in the complex system of pH – CO_2 – CO_3^{2-} in inland waters, and cyanobacteria
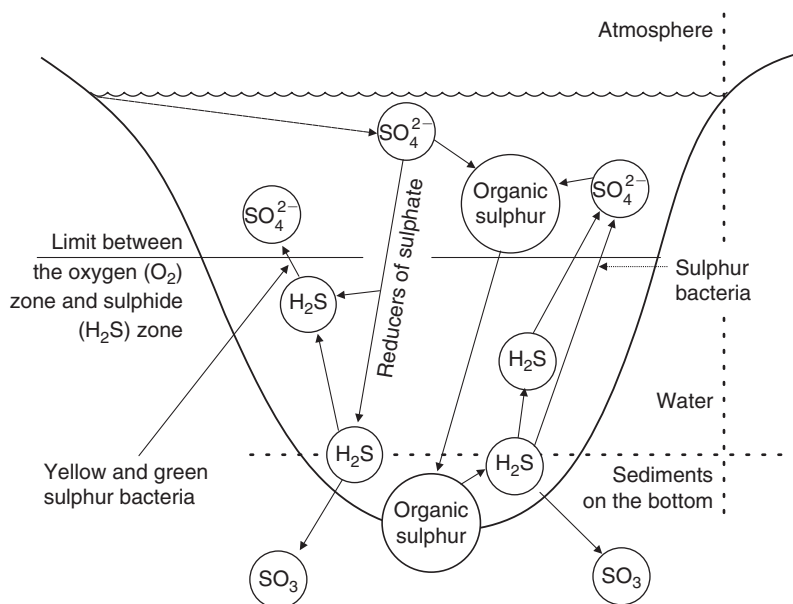
Figure 10.5   Sulphur cycle.
Source: Modified from Schwoerbel (1987).

in inland waters, which appear to have a great affinity with hard (higher alkalinity) water (Reynolds, 1984). Magnesium, found at the core of the chlorophyll molecule, is also important, but there is little evidence that it is a limiting factor in the growth of aquatic plants. Levels of sodium and potassium are higher than those normally needed by aquatic plants. The ratio of monovalent cations to bivalent cations appears to play a role in the phytoplanktonic cycle and succession of species. Major anions (such as chloride and sulphate) rarely are limiting factors due to their high levels in natural waters. The sulphide ion (as S^{2-} and HS^-) is important in an **anoxic hypolimnion** because it can be used by cyanobacteria as an electron donor or as a source of assimilable sulphur (Oréon and Pandan, 1978). Hino *et al*. (1986) found high levels of cyanobacteria in Lake Dom Helvecio (Parque Florestal do Rio Doce – MG) along with an anoxic hypolimnion and high H_2S levels (between 5–$7\,mg\cdot L^{-1}$).

In general, the patches of photosynthetic bacteria found in lakes are associated with the presence of H_2S in the metalimnion. These red bacteria are important in lakes, where they grow in the metalimnion with increasing levels of H_2S and light intensity, which although low, is utilized (between 0.5%–1% of the amount of light on the water's surface). Figure 10.5 illustrates the sulphur cycle.

Other elements that are important for the growth, productivity and physiology of aquatic plants are iron, manganese, molybdenum, copper and zinc, which at high levels can be toxic, and at low levels may be limiting factors in the processes of growth, as already discussed in Chapter 5.

The cycles of most of these metals are related to dissolved organic compounds in the water known as '**chelates**'; two well-known groups are humic and fulvic acids.
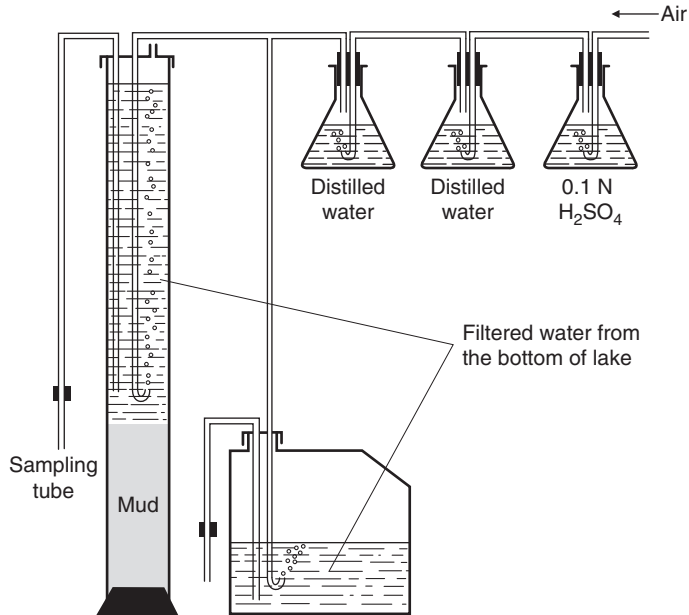
Figure 10.6 Experimental system for measuring the release of phosphorus or nitrogen from the sediment.
Source: Fukuhara *et al.* (1997).

These natural chelates release small quantities of chelated metal, which thus become available, and in the case of excess, function as a plug, removing quantities that could be toxic. Excretion of organic compounds by phytoplankton and aquatic plants also contributes to the reserve of chelates in natural waters.

Iron exists in particulate form and dissolved form and can be reduced (Fe^{2+}) or oxidized (Fe^{3+}). In aquatic systems, the phosphorus and iron cycles directly interact, due to the precipitation of ferrous phosphate during periods of oxygenation in the water column and re-dissolution of ferrous phosphate during periods of reduction. This cycle occurs in stratified lakes during summer, accumulating high levels of Fe^{2+} and PO_4-P in the hypolimnion (soluble), while during periods of intense circulation and re-oxidation, precipitation of $FePO_4$ occurs in sediment (insoluble). The iron and phosphorus cycles and the oxido-reduction (redox) potential in water are thus also interrelated with the circulation process and vertical distribution of oxygen. There is evidence that the dissolution of Fe^{3+} by reduction begins in the metalimnion of stratified lakes.

Experiments showing that the release of inorganic phosphorus or nitrate in anoxic or aerobic conditions can be performed with the equipment shown in Figure 10.6. Figure 10.7 shows the release of nitrate and ammonium (Fukuhara *et al.*, 1985). An experimental anoxia can be induced and inorganic phosphate or ammonium released from the sediment.

Chart 10.1 shows the interrelations between levels of dissolved O_2, redox potential and concentrations of iron, phosphate and sulphide gas.
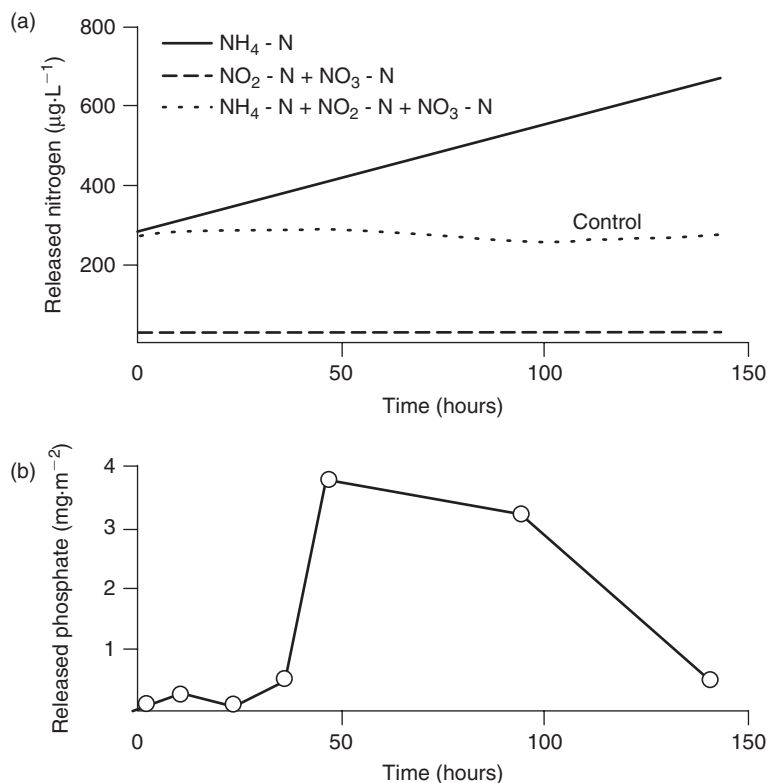
(a)

(b)

Figure 10.7 Release of inorganic nitrogen (NO_3), ammonia (NH_4), and phosphate in experiments conducted with the equipment shown in Figure 10.6.

Chart 10.1 Interrelations of O_2 levels, redox potential E_H and levels of iron, phosphate and hydrogen sulphide gas in stratified oligotrophic, mesotrophic and eutrophic lakes.

Trophic status	O_2 level	E_H	Fe^{2+} level	H_2S	PO_4-P
Oligotrophic	High	400–500 mV	Absent	Absent	Low
Eutrophic	Reduced	250 mV	High	Absent	High
Hypereutrophic	Reduced or absent	100 mV	Decreasing	High	Very high

Source: Modified from Wetzel (1975).

10.7 THE SEDIMENT-WATER INTERFACE AND INTERSTITIAL WATER

Sediment and the water-sediment interface play an important role in biogeochemical cycles. Depending on the oxido-reduction conditions of the water-sediment interface, precipitation and re-dissolution occur. For example, the oxido-reduction potential in the sediment-water interface determines the exchange rate of phosphate between the hypolimnion and the sediment. The influence of the oxidized or reduced layer is

extremely important. Generally, a layer of ferric phosphate (oxidized layer) can form, which acts as a barrier to interactions between the sediment and subjacent water. The transport of phosphate through this layer depends on the degree of perturbation in the sediment, which is also developed by the activity of organisms (**bioturbation**). This **bioturbation** in part determines the characteristics of flux through the interface. Whitaker (1988) showed that rapid shifts occur in the degree of **oxidation** or **reduction** of iron, depending on the condition of anoxia or re-oxygenation in the system.
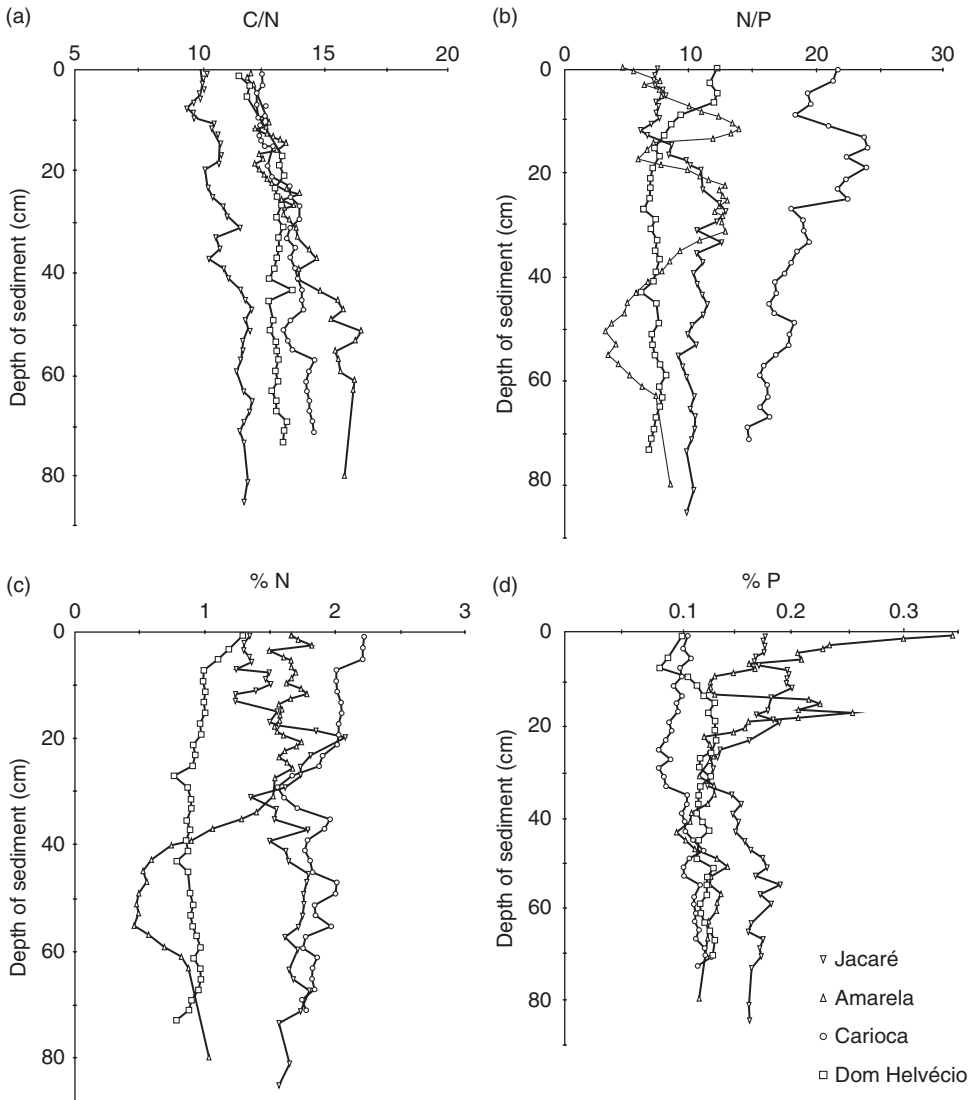

Figure 10.8 Vertical distribution of (a) the carbon/nitrogen ratio, (b) nitrogen/phosphorus ratio, (c) nitrogen, and (d) phosphorus in bottom sediments of four lakes of the Parque Florestal do Rio Doce (MG).
Source: Saijo *et al*. (1997) in Tundisi and Saijo (1997).

These shifts can occur in a few hours, and also partially depend on the diurnal stratification and destratification cycle and associated oxygenation.

Börstrom *et al.* (1982) described the following aspects of phosphorus transport mechanisms in the sediment-water interface:

▶ At the molecular level, the mobilization of phosphorus can be related to physical-chemical processes such as **dissolution**, and to biochemical processes resulting from the enzymatic decomposition of organic substances;

▶ At the compartment level, the transfer of phosphorus from the sediment to the hypolimnion is characterized by hydrodynamic mechanisms, mainly diffusion, ebullition, bioturbation and wind-induced turbulence.

Interstitial water can be an important reserve of nutrients. This interstitial water, which can be separated from the sediment by centrifugation, presents high levels of ammonium, phosphate and nitrate. Figure 10.8 shows the vertical distribution of nutrients in the interstitial water in the sediment at the bottom of Carioca lagoon (Parque Florestal do Rio Doce – MG).

Sediment and hypolimnion are interrelated with the oxidation-reduction system at the interface layer, the formation of a ferric phosphate barrier and the perturbation of this barrier by various processes, including biological processes.

The sediment thus provides a place for nutrients to concentrate; in particular, the phosphorus cycle is closely related to **sediment-water interactions,** circulation processes, stratification and destratification, and changes in the redox potential. Phosphorus can be released from decomposing particles in sedimentation. According to Golterman (1972), 80% of phosphorus can be regenerated during the sedimentation process. The availability of phosphorus in the **trophogenic zone** also depends on the regeneration and vertical distribution of oxygen. In the study of nutrient cycles in aquatic systems, it is important to determine a mass-balance that characterizes the concentration of each element in the various compartments, including inputs, outputs (losses), sedimentation and regeneration, based on the operating physical and chemical processes.

10.8   VERTICAL DISTRIBUTION OF NUTRIENTS

In aquatic systems, there is a process of **sedimentation of organic matter**, starting from the surface, causing consumption of oxygen mainly within the metalimnetic and hypolimnetic levels in stratified lakes. The vertical distribution of carbon, nitrogen and phosphorus is thus related to the processes of vertical stratification and circulation. In stratified lakes, nutrients accumulate in the hypolimnion, as shown in Figures 10.9 and 10.10.

The availability of nutrients for aquatic plants is fundamentally related to this spectrum of nutritional resources (along the vertical and horizontal axes of the system) and to the regenerative processes determined by chemical conditions, principally the **oxido-reduction** (redox) potential. This availability is also related to the absorption mechanisms of aquatic plants, at both the physiological and morphological levels. Undoubtedly, in the interfaces of discontinuity in the distribution of nutrients, the metalimnion is fundamentally important in the processes of regeneration and/or concentration of nutrients. The anoxic hypolimnion is a great reservoir of resources, which become available for plants in the epilimnion through processes of excretion and decomposition of organisms or through external sources (tributaries and rainwater).
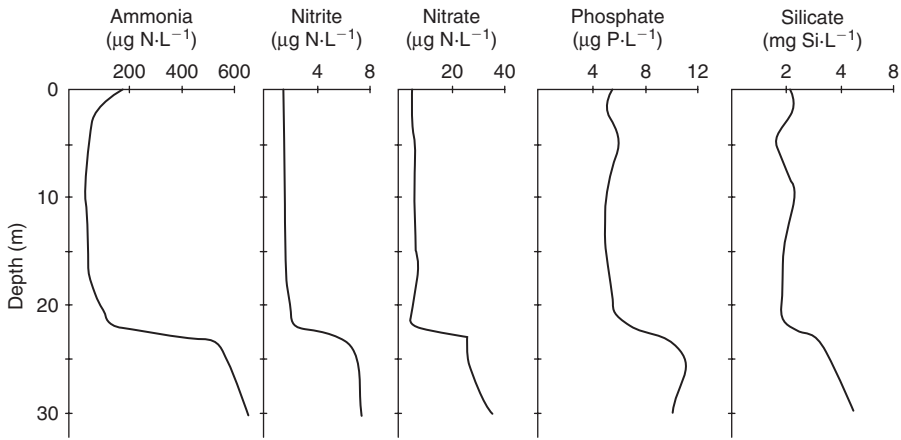
Figure 10.9 Vertical distribution of nutrients in the hypolimnion of Lake Dom Helvécio (Parque Forestal do Rio Doce – MG) during the period of stratification.
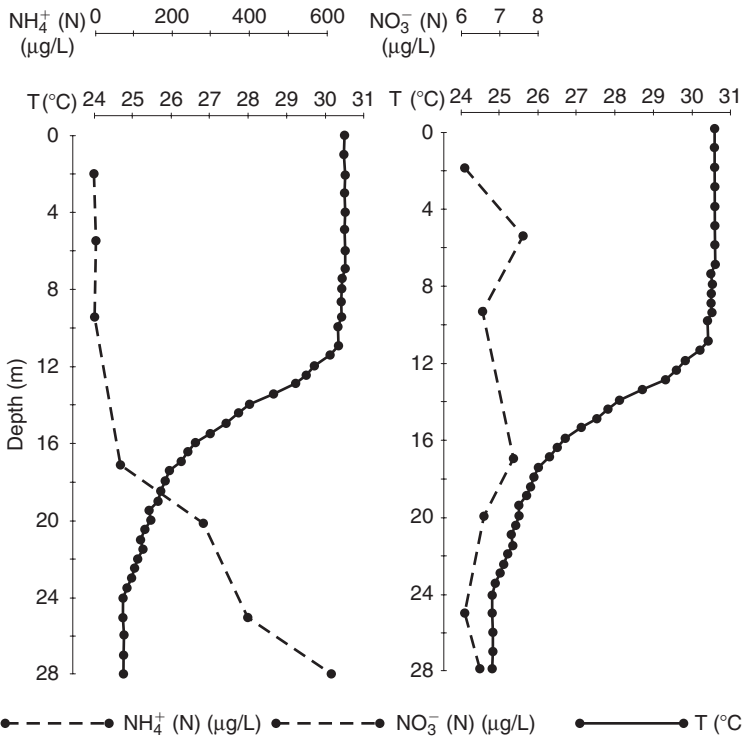*Source:* Tundisi and Saijo (1997).

Figure 10.10 Vertical distribution of ammonia and nitrate in Lake Dom Helvécio (Parque Florestal do Rio Doce – MG) during the period of thermal stratification.

10.9 TRANSPORT OF SEDIMENTS FROM TERRESTRIAL SYSTEMS AND BIOGEOCHEMICAL CYCLES

The rapid transport rate of sediment from a terrestrial system to an aquatic system during periods of intense precipitation can be affected by deforestation or agricultural practices in the areas around reservoirs, lakes and rivers. Such transport produces a continuous influx of sedimentation with absorption of phosphate in the particles and immobilization of nutrients in the bottom sediment. This pulse of sediment also causes multiple changes in the aquatic system, affecting several ecological processes.

Desorption of phosphate from the sedimentation process can also occur during the movement of sediments through the water mass or during their settling.

In wetland areas or flooded fields, this transport of sediment by rivers plays an important role in the ecological cycle and metabolism of permanent or temporary lakes.

10.10 ORGANISMS AND BIOCHEMICAL CYCLES

Aquatic organisms are important in biogeochemical cycles for the following reasons:

▸ They excrete nitrogen, phosphate and organic compounds;
▸ They decompose after death and contribute nitrogen and phosphorus;
▸ They contribute to the active transport of nutrients along the vertical and horizontal axes of the system;
▸ Aquatic plants biologically fix elements.

Aquatic organisms can play a key role in recycling and transporting nutrients. Tundisi (1983), for example, considered that the contribution of **zooplanktonic excretion** in the epilimnion of tropical lakes is extremely important. In general the epilimnion has low levels of inorganic phosphorus and nitrogen (10–$20\,\mu g \cdot L^{-1}$ P-PO_4^{3-} and 20–$50\,\mu g \cdot L^{-1} N$-NO_3^-). One possibility for maintaining a biomass of phytoplankton in the epilimnion of stratified lakes, even if extremely low, is precisely the excretion of zooplankton, which, through the process of diurnal vertical migration, successively fertilizes several levels of water (see Figure 10.11).

In addition to the planktonic organisms, fish and benthos can also recycle considerable quantities of inorganic nutrients through excretion and active transport. Large vertebrates that live in the interface between terrestrial and aquatic systems, such as the hippopotamus in Africa and the capybara in South America, can supply aquatic systems with nitrogen and phosphate. For example, Viner (1975) estimated that close to 2–3% of the nitrogen and phosphate lost in the outflow of Lake George is recycled through hippopotamus faeces. A typical statistic shows, for example, that 1.6–2.2 kg C/animal/day is excreted, which represents 2,930–4,000 tons/year/total population. A large part of the contribution is dissolved or suspended (30%), which is more readily available.

In the case of lakes with many birds present, in wetland areas or permanent lakes, rapid recycling also occurs. For example, Tundisi (unpublished results) reported that in a hyper-eutrophic lake in the Mato-grosso swamp, a large portion of the phosphorus and nitrogen came from the excretion of birds nesting in vegetation on the lake.
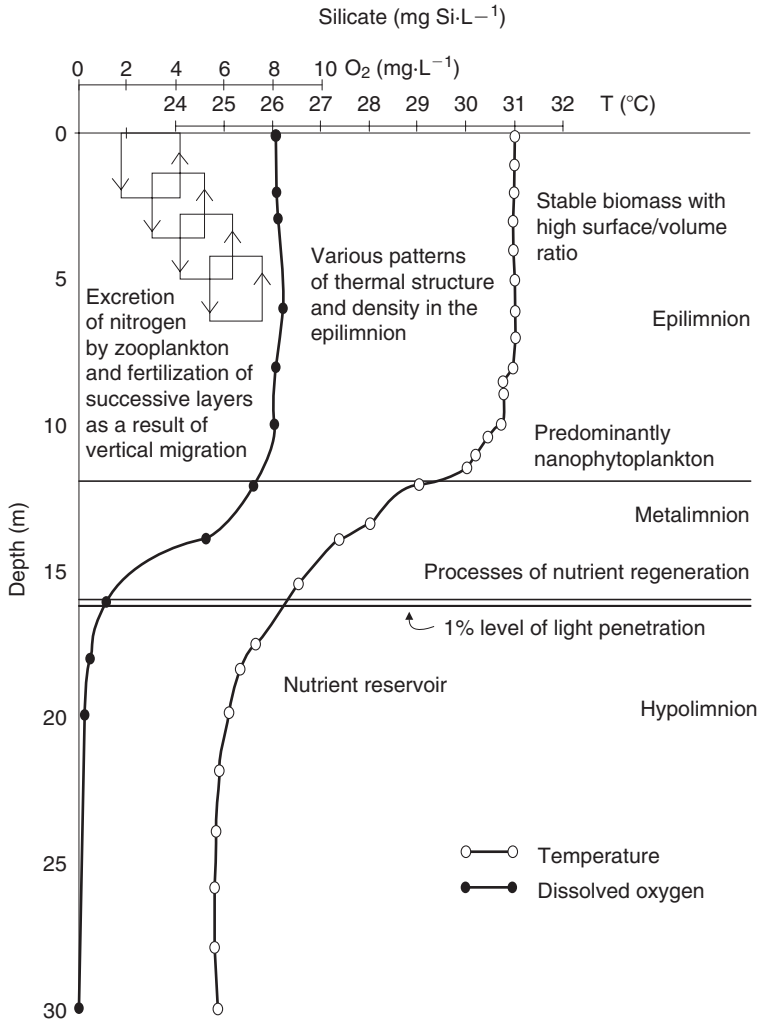
Figure 10.11 Possible mechanism of fertilization and nutrient recycling by zooplankton in the epilimnion of a tropical stratified lake (Lake Dom Helvécio – Parque Florestal do Rio Doce – MG).
Source: Tundisi (1983).

10.11 THE CONCEPT OF LIMITING NUTRIENTS

The supply of nutrients to aquatic plants can be below or above the levels required. Measuring a nutrient level, however, is not sufficient to identify whether or not it is a limiting factor. It is first desirable to determine the growth rate of the plants, the size of the reserve of nutrients, and the **recycling rate** among the various compartments. The total nitrogen and phosphorus dissolved in water control the organic-inorganic cycle. The compartmentalization of nitrogen and phosphorus at various levels of the food chain regulates the recycling rates. For example, nitrogen and phosphorus are

retained longer in fish than in phytoplankton, because of the different **recycling rates** of these organisms (Allen and Starr, 1984). Phosphorus represents 12% of the dry weight of fish skeletons, which shows that this element can be retained outside the cycle.

Dugdale (1967) demonstrated that a hyperbolic relationship exists between the rate of fixation of a limiting nutrient by phytoplankton and the nutrient's levels in water. In general, the Monod equation can be applied to parallel the Michaelis-Menten enzymatic kinetics:

$$V_s = V_{s\ max}(V_s / V_s + V_{s'})$$

where:
Vs is the 'fixation' rate;
Vs_{max} is the maximum fixation rate;
S is the nutrient level;
Ks (coefficient of saturation) represents the nutrient level at which the 'fixation' rate, Vs, is half of the maximum rate ($Vs_{max}/2$).

Consider that Ks is specific for each type of nutrient. When nutrient levels are low, species with low Ks probably have a competitive advantage over those with high Ks. The concept of limiting nutrient is related to Liebig's Law of the Minimum, i.e., the growth of new biomass of aquatic plants is limited by one critical nutrient. The question related to the possible limiting nutrients in aquatic systems has been much discussed. In some studies, nitrogen is considered to be the main limiting factor, in others, phosphorus. One important conclusion is that it is difficult to generalize; nitrogen and phosphorus or nitrogen or phosphorus may constitute the limiting factor (or another nutrient), depending, of course, on the lake system under consideration and on its interrelationships. The individualism of lakes, in this aspect, is also very characteristic.

Chart 10.2 outlines several studies on limiting nutrients, and Chart 10.3 shows the set of experiments on enrichment conducted on many tropical lakes to identify the limiting nutrients for primary productivity and the growth of phytoplankton.

Figure 10.12 shows experimental systems for determining the response to enrichments. Figure 10.13 presents the results of an experiment conducted on artificial enrichments on the surface of the UHE Carlos Botelho reservoir (Lobo/Broa), obtained in response to consumption of dissolved oxygen in water.

Redfield (1934) and Fleming (1940) examined the content of organic matter in ocean water to determine the cellular content of carbon, nitrogen and phosphorus in phytoplankton and zooplankton. The average atomic ratio in the plankton samples was 106 to 16 to 1, that is, 106C:16N:1P. This ratio is generally seen as a reference standard to evaluate limiting factors in any mass of freshwater or ocean water.

Carbon can tend to be a limiting factor for phytoplanktonic growth when growth is saturated with nitrogen and phosphorus or when there is intense sunlight and high temperatures (even when the transport of CO_2 from the atmosphere to water is very slow). This limitation can also occur at low pH values with little dissolved bicarbonate in the water. Carbon as a limiting factor can also occur in super-fertilized tanks and wastewater in stabilization ponds (Schindler; 1977; Rast & Lee, 1978).

Chart 10.2 Several techniques to study limiting nutrients.

	Types of bioassay	C^{14} Technique to measure limiting nutrients	'Batch' bioassay	Continuous bioassay of culture	Enrichment in large tubes	Enrichment of the environments
Parameters	Locale of possible incubation	in situ, in vitro	in situ, in vitro	in vitro	in situ	in situ
	Biological inoculation used	Natural populations or test organism	Natural populations or test organism	Natural populations or test organism	Natural populations	Natural populations
	Number of possible treatments	Numerous	Numerous	One	Few (equal to the number of tubes installed in the locale)	One per lake
	Time of incubation	2 hours (2 to 5, could be more but never more than 24 hours)	Variable (from hours to days)	Variable (from hours to annual cycle)	Long (weeks up to a year)	Long (indefinite)

Source: Henry et al. (1983).

Chart 10.3 Addition of nutrients and responses of phytoplankton in tropical aquatic ecosystems.

Lake or reservoir	Locale	Limiting factors Primary	Secondary	Responses	References
Victoria	0–2°S 32–34°E	P	N	Cell count	Evans (1961)
Chilwa		N + P + S		Cell count	Moss (1969)
Mala		N + P + S		Cell count	Moss (1969)
Malombe		N + P		Cell count	Moss (1969)
Domabi		N		Chlorophyll	Moss (1969)
Makoka	15–17°S 34–35°E	N + P + S		Chlorophyll	Moss (1969)
Mpyupya		N		Chlorophyll	Moss (1969)
Mlungusi		N + P + S		Chlorophyll	Moss (1969)
Coronation		N + P + S		Chlorophyll	Moss (1969)
Shire		N + P + S		Chlorophyll	Moss (1969)
Malawi		N + P + S		Chlorophyll	Moss (1969)
Malombe		N + P + S		Chlorophyll	Moss (1969)
Domasi	15–17°S 34–35°E	N + P		Chlorophyll	Moss (1969)
Makoka		N		Chlorophyll	Moss (1969)
Mpympym		N		Cell count	Moss (1969)
Coronation		N + P + S		Cell count	Moss (1969)
George	0° 30–20°E	N + P		Cell count	Viner (1983)
Rietvlei	25°52.5′S 28°15.75′E	N – P		Potential for algal growth	Steyn et al. (1975a)
		N – P		Potential for algal growth	Steyn et al. (1975a)
		Microelement-n		Potential for algal growth	Steyn et al. (1975a)

Chart 10.3 Addition of nutrients and responses of phytoplankton in tropical aquatic ecosystems (continued).

Lake or reservoir	Locale	Limiting factors Primary	Secondary	Responses	References
Hartbeespoort	25°43′S 27°51′E	N – Fe N – P N – P N – P N – P		Potential for algal growth Potential for algal growth Potential of algal growth Potential of algal growth Potential of algal growth	Steyn *et al.* (1975a) Steyn *et al.* (1975a) Steyn *et al.* (1975b) Steyn *et al.* (1975b) Steyn *et al.* (1975b)
Roodeplast	25°37′S 28°23′E	P – N P – N N – P P – N		Potential of algal growth Potential for algal growth Potential for algal growth Potential for algal growth	Steyn *et al.* (1975b) Steyn *et al.* (1975a) Steyn *et al.* (1975a) Steyn *et al.* (1975a)
Vall	26°53′S 28°07′E	N – P P – N N – P		Potential for algal growth Potential for algal growth Potential for algal growth	Steyn *et al.* (1975b) Steyn *et al.* (1975b) Steyn *et al.* (1975b)
Ubatuba	23°45′S 45°01′W	P – N		Potential for algal growth	Teixeira and Tundisi (1981)
Kariba		N		C^{14} and chlorophyll	Robarts and Southhall (1977)
Henry Gallam		P – N		Potential for algal growth	Robarts and Southhall (1977)
Prince Edward		P – N		Potential for algal growth	Robarts and Southhall (1977)
Mazoe	27–32°S 16–22°E	P – N		Potential for algal growth	Robarts and Southhall (1977)
Little		P – Fe		Potential for algal growth	Robarts and Southhall (1977)
Connemara		N		Potential for algal growth	Robarts and Southhall (1977)
Umgasa		N		Potential for algal growth	Robarts and Southhall (1977)
UHE Carlos Botelho (Lobo/ Broa) dam	22°15′S 47°45′W	N + micronutrients		Respiration of phytoplankton community	Tundisi (1977)
Ebrié	0°10′N 4°E	N P C		Chlorophyll-*a*	Dufour *et al.* (1981)
Jacaretinga	3°15′S 59°48′W	N-P		Chlorophyll-*a*	Zaret *et al.* (1981)
Sonachi	0°47′S 36°16′E	P		Chlorophyll-*a*	Melack *et al.* (1982)
UHE Carlos Botelho (Lobo/Broa) reservoir	22°15′S 37°49′W	N-P N + P N + Mo N		Cell counts and chlorophyll-*a* Cell counts and chlorophyll-*a* Cell counts and chlorophyll-*a* Cell counts and chlorophyll-*a*	Henry and Tundisi (1982a) Henry and Tundisi (1983) Henry and Tundisi (1982b) Henry *et al.* (1984)
Dom Helvécio	19°10′S 42°01′W 19°10′S 42°01′W	N + P N + P		Cell counts and chlorophyll-*a* Cell counts and chlorophyll-*a*	Henry and Tundisi (1986) Henry and Tundisi (1983)
Barra Bonita	19°10′S 48°34′W	P		Cell counts and chlorophyll-*a*	Henry *et al.* (1985)
Jacaretinga	3°15′S 59°48′W	N		Cell counts and production of O$_2$	Henry *et al.* (1985)

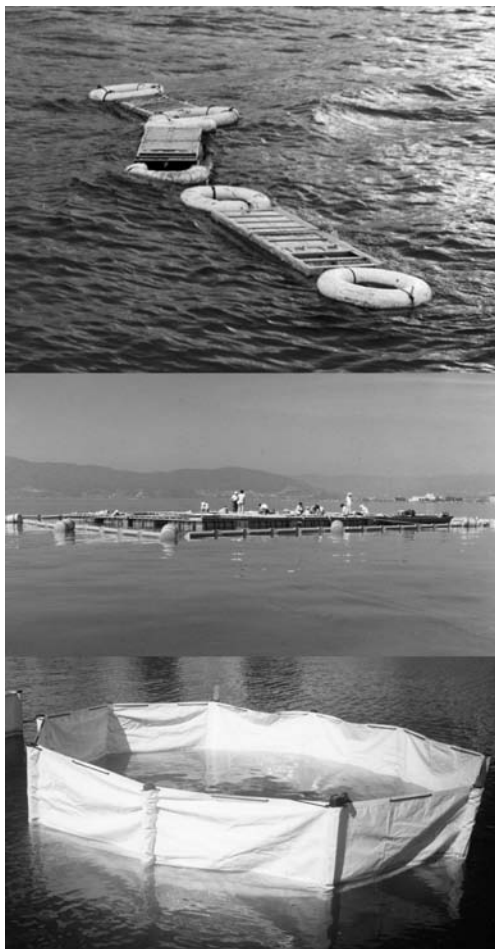*Source:* Henry *et al.* (1985a, b).

Figure 10.12   Experimental systems for study and response of limiting nutrients (see also color plate section, plate 18).

The concept of a limiting nutrient generally applies, therefore, to phosphorus and nitrogen levels in water and conditions of equilibrium (Odum, 1971). In this case, the limiting nutrient for phytoplanktonic growth is near the 'critical minimum' (according to Odum, 1971). Frequently, in the case of intermittent pulses of phosphorus and nitrogen, the concept of limiting nutrient is less useful.

Different phytoplanktonic species have different nutritional requirements, since they assimilate nutrients at different rates. Nutrient assimilation rates and fixation rates differ from species to species, conferring varying competitive advantages (Hutchinson's 'competition for resources' theory, 1961).

In conditions of nutrient deficiencies, small algal cells can be more efficient in assimilating nutrients than larger cells. The competitive ability of small cells ($<20\,\mu$m) to assimilate nutrients was examined theoretically more than 50 years ago by Munk and Riley (1952).
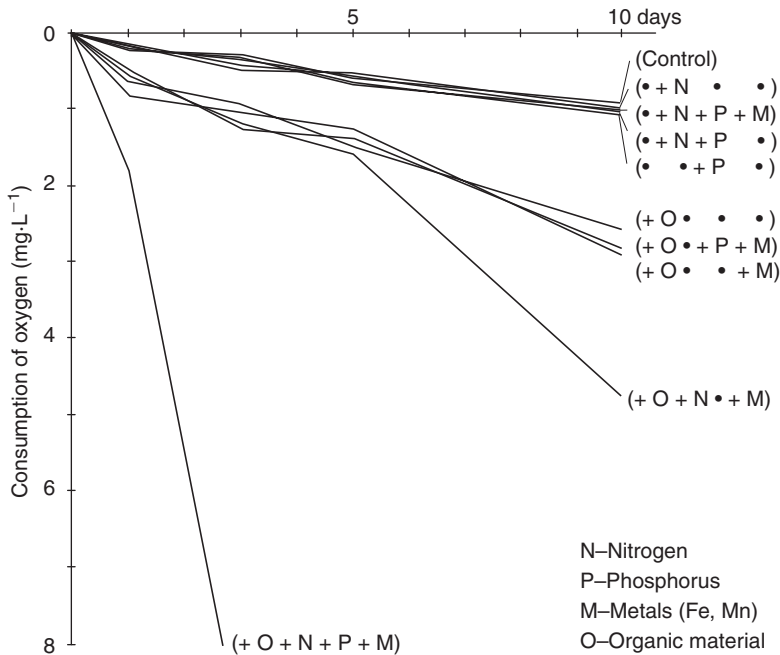
Figure 10.13 Experiment system to measure the response and enrichment in UHE Carlos Botelho reservoir (Lobo/Broa).
Source: Tundisi *et al.* (1977).

The relative proportions of nitrogen and phosphorus levels in lakes and reservoirs vary seasonally or annually, and therefore the limiting nutrients can vary through time and space (Nakamoto *et al.*, 1976). A single nutrient required by algae could be the limiting factor, according to Droop (1973) and Rhee (1978), who showed experimentally that algal growth is stimulated by a single nutrient present at a lower level relative to the alga's requirements.

Growth of phytoplankton in a specific aquatic ecosystem (reservoir, lake or river) thus can be proportional to nutrient levels and these levels are dependent on the internal and external loads, that is, the nutrients in the sediment. Phytoplankton can assimilate nutrients in the water column in the mean atomic ratio of 106C:16N:1P. By identifying the C:N:P levels and ratios in a water column and comparing them with the concept of the Redfield Index (of 16N:1P), it is possible to deduce which nutrient is in excess and which is a limiting factor. Nutrient levels much in excess of the 16N:1P ratio (necessary for phytoplankton growth) should not be the limiting factor for the growth of algal biomass. Therefore, it is important to determine not only total nitrogen and phosphorus levels (dissolved and particulate) in the water and tributaries, but also the forms of biologically available nitrogen and phosphorus, in addition to total nitrogen and phosphorus.

For example, it is desirable to determine the level of reactive soluble phosphorus and the levels of ammonium, nitrate and nitrite (if present). Practical experience (Ryding and Rast, 1990) suggests that levels of biologically available phosphorus

$<5\,\mu g$ P may indicate that phosphorus is the limiting factor. Levels of biologically available nitrogen $<10\,\mu g\,N\cdot L^{-1}$ indicate that nitrogen is the limiting factor. If both present lower levels than the above, the two nutrients are limiting. If the nitrogen and phosphorus levels are above these levels, then neither is limiting.

If the absolute levels of biologically available phosphorus and nitrogen do not markedly drop, the rates identified in the aquatic ecosystem can indicate which nutrient will be limiting. Using the 16N:IP ratio as a comparative figure, any strong deviation from this ratio indicates which nutrient is potentially the limiting factor in the water mass (Stumm, 1985).

10.12 'NEW' AND 'REGENERATED' PRODUCTION

The concepts of 'new production' and 'regenerated production' refer to production of organic matter that depends on nutrients recycled in the aquatic system, based on organisms and sediments (regenerated production), or that production which depends on nutrients from external sources (new production). The 'new production'/'regenerated production' relationship in inland aquatic systems depends on the **internal load** accumulated in these systems, on the excretion from organisms, on the metabolic rates of the organisms and their decomposition, on the contribution of external nutrient loads from water basins, and on the use and condition of conservation or deterioration of the water basin.

The internal characteristics of circulation and redox potential also influence the recycling of nutrients for 'regenerated production'. Polymictic lakes, for example, tend to have patterns of homogenous vertical distribution of oxygen and phosphorus, both dissolved and precipitated in the sediment. Stratified lakes have a high internal load due to the release from sediment accumulated in the hypolimnion. The **internal load** of lakes and reservoirs can be determined through experiments on the varying oxido-reductive conditions, in addition to the estimates of nitrogen, phosphorus and other elements in the sediment. The relationship of 'new production' to 'regenerated

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Phosphorus-chlorophyll ratio in lakes and reservoirs

In many lakes and reservoirs, there is a direct relationship between the concentration of phosphorus in water and the concentration of chlorophyll-*a*. In many lakes in temperate regions, this correlation can reach coefficients of regression of 0.9 (R^2). This means that the majority of total phosphorus in lakes is in the particulate state, and phytoplankton constitutes the greatest portion of this particulate phosphorus. When the ratio of total phosphorus/chlorophyll-*a* is extremely low, it means that other factors may control the abundance of phytoplankton. This correlation has been used to estimate the levels of phytoplankton based on the total phosphorus. Data for lakes and reservoirs in temperate regions function very well, as shown in Figure 10.14. However, for tropical lakes there is still some uncertainty for two reasons. First, there is still a lack of data compared with temperate regions. And second, the recycling of phosphorus is more rapid in tropical regions and these rates still need to be determined (see Chapter 7).
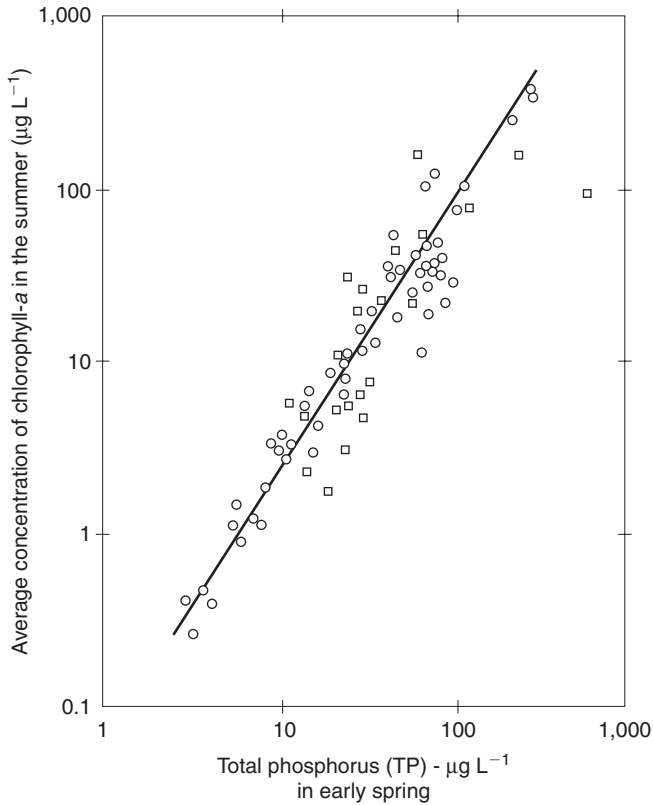
Figure 10.14   Ratio between total phosphorus (TP) and chlorophyll-*a* in some lakes of the temperate region.
Source: Horne and Goldman (1994).

production' can vary seasonally in the same lake, reservoir or other aquatic system. For example, in the UHE Carlos Botelho reservoir (Lobo/Broa), Tundisi *et al.* (1977) showed that in summer, the external load is higher due to precipitation, and 'new production' is thus efficient during this period. On the other hand, the production of organic matter in winter depends more on the internal load and processes of excretion and decomposition in the water column. Picocyanobacteria (<2 μm) play an important role, using both 'new production' and 'regenerative production' efficiently and in recycling organic matter.

10.13   GREENHOUSE GAS AND BIOGEOCHEMICAL CYCLES

Many gases – such ammonium, hydrogen, methane and **volatile gases** in the sulphur cycle – are found in anoxic oxygen-deficient environments. Some of these gases are the final products of microbial decomposition of organic matter. Evidence of a link between the accumulation of gases and climate changes and the chemistry of the atmosphere has increased (Adams, 1996). Gases are involved in oxidation/reduction

and are produced in inland aquatic ecosystems, in anoxic conditions in water and sediments. Greenhouse gases and their emission into the atmosphere that have been studied in lakes, reservoirs, wetlands and sediment of surrounding areas are: hydrogen (H_2), ammonia (NH_3), volatile sulphide (H_2S, organic sulphur) and methane (CH_4). Decomposition of organic matter by micro-organisms provides the energy source for growth through fermentation and anaerobic respiration, promoting reactions of oxidation and reduction in cycles of carbon, nitrogen and sulphur. There are numerous groups of bacteria that use hydrogen (H_2) as a source of energy, and also a group of organisms that produces H_2 during the metabolism of carbohydrates, fatty acids and amino acids. Important sources of ammonia (NH_3) are wetlands. Anaerobic environments emit H_2S, carbon disulphide (CS_2) and **methyl mercaptan** (MSH, CH_3SH). H_2S gas is the most important emitted by anaerobic systems. Most of the carbon that is recycled in aquatic ecosystems and land is mineralized under anaerobic conditions, with products such as methane (CH_4). The decomposition of organic matter yielding methane in anaerobic sediments is the result of fermentation reactions involving organic compound > fatty acids > amino acids > carbohydrates > humic substances.

Emissions of greenhouse gases from the hydrosphere have been the object of numerous recent works in wetlands and anoxic sediments lakes and dams. Interactions between these cycles of gases and the effects of human activities, as well as other microbial processes, climatological and physical-chemical effects, have been intensively studied (Adams, 1996).

These gas emissions are fundamental in the biogeochemical cycles of carbon, nitrogen and sulphur and are extremely important for the chemistry of the atmosphere and its relationship with the hydrosphere.

Redox potential

Redox potential, or oxidation-reduction potential – Eh – represents alterations in the state of oxidation of many ions or nutrients. In pH 7.0 at 25°C, water saturated with oxygen presents a redox potential of +500 mV. Redox potential is measured in millivolts as an electrical voltage between two electrodes, one of hydrogen and another of the material whose status is being measured (iron, manganese or another metal). Gradients of redox potential are often found in nature; for example, in interfaces of anoxia and oxygenation, in systems of inland or marine waters, in sediment-water interfaces, or in soils. The transport of iron and manganese in sediment or in water receives much attention in limnology and oceanography, given the important role that these elements play in the biogeochemical cycles of other elements. In states of oxidation at high redox potential (400 or 500 mV), iron and manganese are insoluble (Fe^{3+} and Mn^{3+}). In reduced states (Fe^{2+} and Mn^{2+}), they are soluble and free of complexation. Thus, vertical profiles of iron and manganese related to the redox potential indicate their state of complexation or solubility. Vertical profiles in the sediment and interstitial waters of sediment illustrate these states of complexation and insolubility or solubility, and the transport processes at these interfaces occur through molecular diffusion. In sediment-water interfaces, the processes are rapid and depend on the turbulence or stratification and the grade of oxygenation or anoxia of the water.

Trace elements and their effects on the primary productivity and growth of phytoplankton

The effect of trace elements on the primary productivity and growth of phytoplankton can be illustrated by the study conducted by Henry and Tundisi (1982) at the UHE Carlos Botelho reservoir (Lobo/Broa). In this system, the surface water of the reservoir was enriched with different concentrations of potassium phosphate (KH_2PO_4), potassium nitrate (KNO_3) and sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$). Various concentrations were utilized for each sample suspended at the surface of water for a period of 14 days in 2-liter Erlenmeyer flasks. After this period, the primary productivity of phytoplankton and the concentration of chlorophyll-*a* were determined. Molybdenum is present in the enzyme nitrate reductase and plays a key role in the assimilation of NO_2^- by phytoplankton, because NO_3^- is reduced to NO_2^- by the action of the enzyme nitrate reductase at the level of the cell wall. With the simultaneous addition of nitrate and molybdenum, a significant increase occurs in the growth and response of the phytoplanktonic community. These experiments show that, even with adequate concentrations of nitrogen for the stimulation or growth of phytoplankton, the presence of molybdenum is essential to promote the utilization of NO_3^- for the phytoplanktonic community.

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