



Sao Francisco River,
Photo: Jose G. Tundisi

5 The chemical composition of water

SUMMARY

The chemical composition of natural inland waters is complex because of the large number of **dissolved ions** and organic substances resulting from the natural conditions of drainage basins and human activities. Another contributing source of substances and elements is the atmosphere. The chemistry of natural waters varies greatly due to the **geochemistry** of soil and rocks that constitute the substratum of water basins. Activities of organisms (excretion, respiration, **bioperturbation**) also play a role in the **balance of materials** in aquatic systems.

Dissolved ions and organic substances play diverse biological roles such as regulation of the **physiological processes** in organisms, including activities of membranes and activation of enzyme systems. Of the gases dissolved in water, oxygen and carbon dioxide are key because they are involved in the processes of production of organic matter by primary producers (photosynthesis) and respiration by all organisms. Diurnal variations in the levels of these gases are caused by changes in the processes of photosynthesis, respiration, and circulation of water masses. The vertical distribution of dissolved ions, organic substances, and gases depends on horizontal and vertical circulation processes, stratification mechanisms, and interactions of tributaries with aquatic ecosystems.

5.1 INTRODUCTION

Natural water is chemically complex because it contains a large number of dissolved substances. Dissolved chemicals and elements found in inland aquatic ecosystems originate from the geochemistry of the soil and rocks underlying water basins, through which water drains into rivers and lakes. Another source is the atmosphere, which varies considerably. In many industrial regions with high levels of atmospheric sulphur, rain can become acidic. Especially over deserts, rain water contains dust particles. Rain water varies in concentration from region to region, which affects the chemical composition of water draining through the soil. In coastal regions, the composition of rain water can also be affected by the presence of salt from the sea. Small air bubbles formed by wind action on the sea's surface can carry particles of water and be blown over the continents, thus contributing to the chemistry of inland waters.

Interactions between the main **ions in solution** also affect the chemical composition of inland waters. The **equilibrium theory** can be used to describe the chemistry of these waters, based on the distributions of equilibria between metallic ions and complex ions. Through application of this theory, a prediction can be made whether an ion will be present as a free ion or in complexes of various types.

Air pollution is another component that affects the chemical composition of rain water, contributing various different ions, including HSO_4^- and nitrogen oxides (general formula: NO_x), such as from oil drilling and extraction. The pH of rainwater can drop to 2.1–2.8 (generally below 4.0), as occurs in some industrial regions in England, Scandinavia and the United States. Rainwater with acidic pH affects the chemical composition of the water flowing through drainage basins into rivers and lakes. As water drains through soils of different origins and chemical compositions based on local geology, complex chemical interactions take place that are specific to each water basin and, within each basin, in each sub-basin. Alterations made by human activities also lead to changes in the composition of natural waters. Removal of plant cover, different treatments of soil, and industrial and agricultural effluents are all factors. The chemical composition of natural waters that drain basins on all continents is the result of a complex set of chemical processes and interactions occurring between land and water, and between water and atmospheric systems.

Emissions of **ammonia**, nitrogen and sulphur chemically alter the atmosphere. Oxidation from these chemical substances affects the quality of rainwater and increases N levels in terrestrial and aquatic ecosystems. In northern Europe and northeastern United States, such effects have been recorded for more than 20 years. Recent evidence, however, shows that the same phenomenon is occurring in Southeast Asia (Lara *et al.*, 2001). Martinelli *et al.* (1999) estimated that the total amount of leaves burned by the sugarcane industry in the Piracicaba River drainage basin is 20 tons per hectare annually, which releases approximately 100,000 tons of organic matter and 50 tons of carbon into the atmosphere. This biomass also releases organic acids, **nitrate** and sulphate into the atmosphere, which can substantially alter the chemical composition of rain water and negatively influence surface waters and groundwater.

Lara *et al.* (2001) measured the chemical composition of precipitation in the Piracicaba River basin over one entire year. The study's results are presented in Table 5.1. According to the authors, the three factors determining the composition of

Table 5.1 Average concentrations of ions in rain water at four collection points in the state of São Paulo (values in $\mu\text{eq} \cdot \text{L}^{-1}$; DOC and DIC in $\mu\text{mol} \cdot \text{L}^{-1}$)

	Bragança			Campinas			Piracicaba			Santa Maria		
	Dry	Wet	Annual	Dry	Wet	Annual	Dry	Wet	Annual	Dry	Wet	Annual
pH	4.6	4.4	4.4	4.6	4.5	4.5	4.8	4.5	4.5	4.4	4.3	4.4
H ⁺	22.5	39.2	36.3	26.1	31.1	29.7	17.4	34.0	33.0	35.9	40.6	39.7
Na ⁺	2.2	2.3	2.3	3.1	2.7	2.7	4.2	2.1	2.7	5.6	4.2	4.5
NH ₄ ⁺	23.8	17.2	18.6	19.9	14.3	15.4	26.0	11.6	17.1	21.3	12.7	14.5
K ⁺	2.6	2.5	2.5	2.7	1.6	3.4	4.5	2.1	2.9	3.2	2.5	3.5
Mg ²⁺	1.3	1.2	1.2	1.6	1.2	1.3	3.1	1.9	2.3	2.7	2.3	2.3
Ca ²⁺	3.6	3.4	2.3	3.9	3.6	3.7	7.8	4.3	5.3	10.3	7.0	7.7
Cl ⁻	3.5	5.2	4.9	5.1	6.3	6.0	8.4	6.0	7.0	11.1	8.0	8.8
NO ₃ ⁻	17.0	14.5	15.0	18.6	17.9	18.0	20.6	13.8	16.6	18.3	12.3	13.5
SO ₄ ²⁻	15.1	17.3	17.0	19.6	19.9	19.7	27.4	14.8	18.7	15.3	11.5	12.3
HCO ₃ ⁻	0.4	0.3	0.3	0.3	0.3	0.3	0.9	0.3	0.4	0.9	0.4	1.2
DOC	84.9	57.1	58.8	80.4	47.1	50.8	134.5	78.8	94.4	100.5	43.9	7.66
DIC	55.7	48.4	50.0	23.7	33.5	30.7	34.2	43.5	43.9	81.8	62.4	67.8
Total cations	56.0	65.7	69.3	79.0	63.2	56.1	62.9	56.1	54.5	57.3	64.2	72.3
Total anions	36.6	38.0	37.7	45.3	34.0	45.1	44.7	36.4	60.2	46.6	47.5	38.0
TOTAL	92.5	103.7	101.9	102.6	102.0	102.7	123.1	92.5	107.7	24.1	109.2	113.5
DEF	19.4	27.7	26.6	12.1	7.0	9.5	2.7	19.7	18.3	33.9	35.4	34.3

DEF – Deficit of anions (DEF = E cations – E anions) in $\mu\text{eq} \cdot \text{L}^{-1}$

DOC – Dissolved organic carbon

DIC – Dissolved inorganic carbon

Source: Lara et al. (2001).

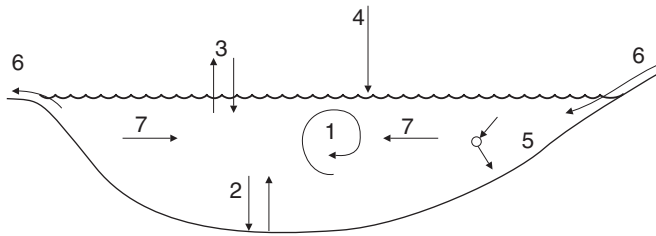
rain water in the Piracicaba River basin are ions coming from the dust of soils (Ca²⁺ and Mg²⁺), the burning of sugarcane, and industrial emissions from the Campinas and Piracicaba regions. These activities caused significant levels of acid rain as well as high rates of nitrogen deposition. Changes in the atmosphere's chemistry and precipitation of chemicals from the rain produce changes in soil and in the chemical composition of waters in the region.

The 'material balance' of a lake, river or reservoir is also the result of activities of organisms that affect the chemical cycles and the chemical composition of the water. Figure 5.1 illustrates these processes (Schwoerbel, 1987).

5.2 DISSOLVED SUBSTANCES IN WATER

As discussed in Chapter 2, water is the universal solvent. Chart 5.1 presents a list of substances commonly dissolved in natural waters.

The most common ions are called 'conservative ions' because their concentrations vary little as a function of activities of organisms. The main nutrient ions are not



- 1 Recycling of biogenic materials
- 2 Sedimentation and processes of exchange at sediment-water interface
- 3 Exchange between water and atmosphere
- 4 Influx from precipitation
- 5 Adsorption and desorption of dissolved substances on the surface of particulates in suspension
- 6 Inflows and outflows
- 7 Lateral transportation

Figure 5.1 Diagram of the principal processes that determine the balance of materials in a lake.

Chart 5.1 Dissolved substances in water and the analytic complexity for their determination.

Increase in analytic complexity	Principal ions	Na ⁺ , K ⁺ , Mg ²⁺ , Ca ²⁺ SO ₄ ²⁻ , Cl ⁻ and HCO ₃ ⁻ Dissolved in mg · L ⁻¹ (parts per million)
	Atmospheric gases	Nitrogen (N ₂) Oxygen (O ₂) Carbon dioxide (CO ₂)
	Principal nutrient ions	PO ₄ ³⁻ , HPO ₄ ²⁻ , H ₂ PO ₄ ⁻ , NO ₃ ⁻ , NH ₄ ⁺ , Si(OH) ₄ , Fe ³⁺ , Mn ³⁺ , CO ₂ and HCO ₃ ⁻ dissolved with concentrations between µg · L ⁻¹ and mg · L ⁻¹
	Trace ions	Cu ²⁺ , V ⁵⁺ , Zn ²⁺ , B ²⁺ , F ⁻ , Br ⁻ , Co ²⁺ , Mo ⁶⁺ and Hg ²⁺ , Cd ²⁺ , Ag ⁺ , As ₁ , Sb ₂ , Sn ⁴⁺ Dissolved in concentrations of mg · L ⁻¹ and µg · L ⁻¹
	Organic refractory substances (difficult to decompose)	Dissolved in various concentrations ng · L ⁻¹ and µg · L ⁻¹
	Labile organic substances (very reactive)	Dissolved in various concentrations from µg · L ⁻¹ to mg · L ⁻¹

¹As³⁺ found in water as H₂AsO₄⁻

²Sb³⁺ found in water as SbO₂

Fe and Mn can be found in water in reduced form (Fe²⁺ or Mn²⁺) or in an oxidized form (Fe³⁺ or Mn³⁺)

Source: Modified from Moss (1988).

conservative, i.e., their concentrations, which are less than those of the most common ions, vary considerably depending on activities of organisms.

N₂, a dissolved gas, is essential in the nitrogen cycle and important for a group of organisms that can fix it from the atmosphere. O₂ is essential in respiratory processes and CO₂ can be a limiting factor for primary producers under certain conditions.

Many organisms require trace ions. The processes of reduction and oxygenation are important for some elements, such as Fe and Mn.

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Chart 5.2 Origins and nature of organic substances dissolved in water.

Origin from living organisms in drainage basins	Dissolved organic derivatives in drainage water
Proteins	Methane, peptides, amino acids, urea, phenols, mercaptans, fatty acids, melanin, 'yellow substances' (Gelbstoff)
Lipids (fats, oils) and hydrocarbons	Methane, aliphatic acids (acetic, glycolic, lactic, citric, palmitic, oleic) carbohydrates, hydrocarbons
Carbohydrates (cellulose, starch, hemicellulose, lignin)	Methane, glucose, fructose, arabinose, ribose, xylose, humic acids, fulvic acids, tannins
Porphyrins and pigments, chlorophylls of plants (carotenoids)	Phytane, pristane, alcohols, cetane acids, porphyrins, isoprenoids

Source: Moss (1988).

Some of these elements are toxic to aquatic organisms when the levels rise due to industrial discharges, human activities, or natural processes such as occur in volcanic areas or in natural waters draining through soils where high levels of these elements occur naturally. Such is the case with mercury and arsenic in certain areas.

Organic substances occurring in natural waters have a complex origin (see Chart 5.2) and countless and varied reactions in the water, depending on photo-reductive and photo-oxidative processes. These **dissolved organic substances** include various stages of decomposition of natural vegetation and they play an essential role in inland aquatic systems.

In general, **dissolved organic matter** (DOM) in water is classified into two groups:

- ▶ Humic substances: defined as a 'general category of naturally occurring highly heterogeneous biogenic organic substances, characteristically yellow and black in color, with high molecular weight and refractory' (Aiken *et al.*, 1985). The authors defined as 'humic acids' those that are not soluble in water with acidic pH (below 2), but may be soluble at higher pH levels; and
- ▶ Non-humic substances, such as amino acids, carbohydrates, oils and resins.

Fulvic acids are the 'portion of humic substances soluble in all pH conditions,' and humic acids are the 'portion not soluble in water under any pH condition' (Aiken *et al.*, 1985).

Figure 5.2 presents levels of dissolved organic carbon and **particulate organic carbon** in various different natural waters. Figure 5.3 presents the distribution of total organic carbon in Finnish waters, and Figure 5.4 presents total carbon levels in natural waters of Brazil.

Humic substances thus constitute an essential component of dissolved organic matter in natural waters.

Water light brown in color is one of the special characteristics of temperate-region lakes with dissolved humic substances, as described by Naumann (1921, 1931, 1932). Lakes with large concentrations of these waters were called **dystrophic**. Later, Aberg and Rodhe (1942) discovered the predominance of light penetration in the infra-red portion of the spectrum (>800 nanometers). The same observation was made by

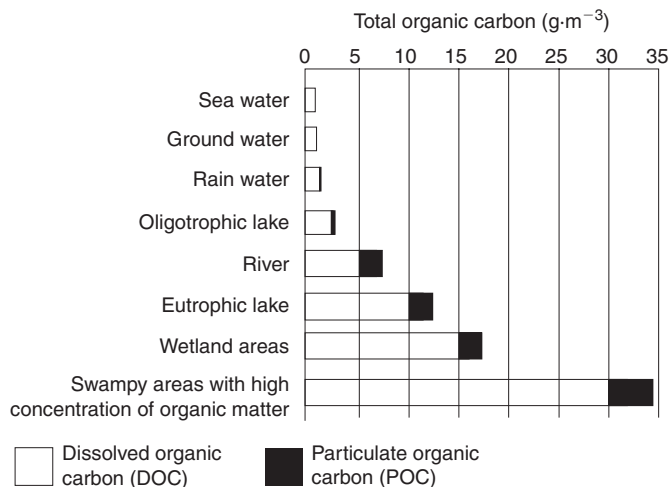


Figure 5.2 Concentration of dissolved organic carbon and particulate organic carbon in several different types of natural waters.
 Source: Thurman (1985).

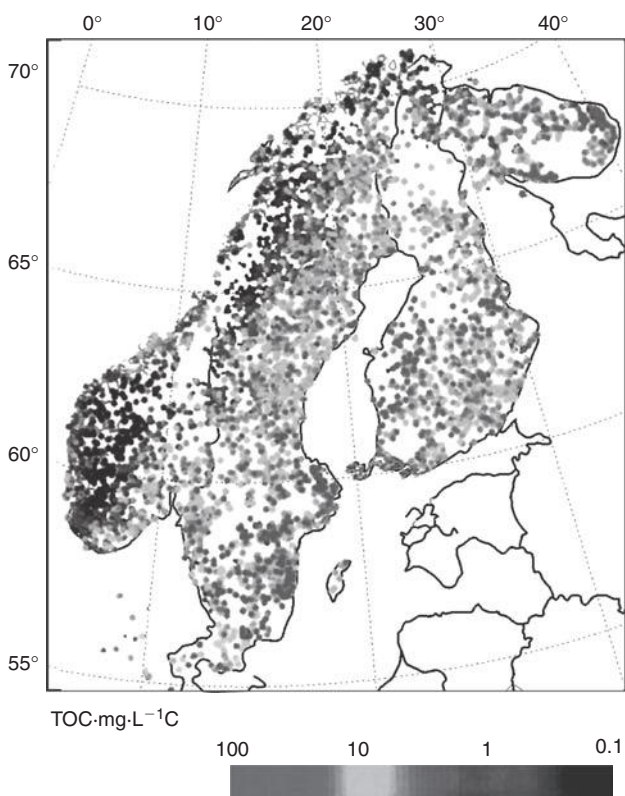


Figure 5.3 Distribution of total organic carbon in waters in Scandinavia (see also color plate section, plate 6).
 Source: Skjelvale *et al.* (2001) in Eloranta (2004).



Figure 5.4 Concentration of total carbon in natural surface water of Brazil (Brazil Water Project) (see color plate section, plate 7).

Tundisi (1970), who measured increased penetration of infra-red light in the dark mangrove waters of the **lagoon area of Cananéia**, in the State of São Paulo. High levels of dissolved organic substances with complex molecules increase oxygen consumption in all layers of the water, from the surface to the bottom, and affect the ‘underwater radiation climate’ of lake systems, reservoirs and rivers.

Humic substances are present in all natural waters as dissolved molecules, **colloidal suspensions** or particulate matter. The dissolved component is always the most significant in terms of impact on the water’s biology and chemistry.

Concentrations of these humic substances can range from 100 to $500 \text{ mg} \cdot \text{m}^{-3}$ in seawater, and between $1\text{--}2 \text{ mg} \cdot \text{m}^{-3}$ up to $15 \text{ mg} \cdot \text{m}^{-3}$ in groundwater. In lakes with large amounts of decomposing macrophytes and peat on the shoreline, concentration levels can reach $60 \text{ mg} \cdot \text{m}^{-3}$.

The concentration of dissolved organic carbon (DOC) in water filtered through $0.45\text{-}\mu\text{m}$ -pore size Millipore filters can be determined by carbon catalysers. In unfiltered waters, the concentration of carbon is called **total organic carbon (TOC)**. The level of carbon calculated is given in $\text{g} \cdot \text{m}^{-3}$.

In many natural bodies of water, humic substances account for about 50% of the dissolved organic carbon.

Important elements in humic substances include oxygen (35–40% by weight), hydrogen (4–5% by weight), and nitrogen (2%). The carbon present in the material retained by fine filters (i.e., 0.45- μm -pore Millipore filters) is the **particulate organic carbon (POC)**.

The terms *total organic material* (TOM), **dissolved organic material** (DOM) and **particulate organic material** (POM) are similar to carbon-based TOC, DOC and POC. However, these terms (TOM, DOM and POM) refer to all material present, including oxygen, hydrogen and nitrogen. In general, the values are twice as high as TOC, DOC and POC alone.

Methods for estimating organic substances in water include biochemical oxygen demand (BOD) and chemical oxygen demand (COD). The latter method uses a powerful chemical oxidant such as permanganate to measure the amount of oxygen consumed, the former measures that consumed by bacteria. The methods do not, however, directly determine carbon concentration in water.

The concentration of humic substances in water can be indirectly determined through the spectrum of water filtered through 0.45- μm Millipore filters and centrifuged. Waters from different sources can be compared to determine which has greater or lesser concentration of humic substances.

The reading of UV absorbance of water samples filtered through 0.45- μm –245-nanometer Millipore filters is a simple and quick way to estimate the levels of organic matter. This method is based on the linear relationship between carbon content and absorption of ultraviolet light.

The variability of dissolved organic carbon in natural waters is large and depends on internal (autochthonous) and external (allochthonous) inputs, periods of drought and precipitation, and internal processes in lakes and reservoirs (decomposition, bacterial action, water temperature, turbulence, and stratification).

Dissolved organic substances, especially humic substances, play an important role in the availability of organic and inorganic nutrients for bacteria, fungi, phytoplankton and aquatic macrophytes.

Dissolved organic matter plays an important role in the complexation, absorption and immobilization of many contaminating organic substances and heavy metals. Such absorption can also make these contaminants available for organisms and increase their bio-availability.

One source of **dissolved salts** in lakes is the steady contribution from drainage through igneous or sedimentary rocks, and because of this, the salt levels vary in inland waters. The composition of waters that drain through these rocks reflects the relative contribution of soluble ions that make up these rocks – in general, $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Na}^+ > \text{K}^+$ – but depending on the region, the sequence may be $\text{Na}^+ > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{K}^+$.

The capacity of water to dissolve these ions increases with temperature, acidity, water flow and levels of dissolved oxygen. Acid hydrolysis, for example, dissolves aluminum below pH 4.5 and silicic acid, $\text{Si}(\text{OH})_4$, is also released. In clay soils of volcanic origin, iron is released. Sedimentary rocks can release sulphate, carbonate and phosphate, or bicarbonate.

Concentrations of dissolved salts vary greatly in inland waters as a result of the particular features of each **region's hydro-geochemistry** and drainage through igneous

Table 5.2 Global distribution of dissolved salts (DS) in lakes.

Type of lake	Area (10^3 km^2)	Volume (10^3 km^3)	DS (kg/m^3)	Tsal (10^{15} g)	
Saline ^a (Vertical)	Caspian	374	78.2	13.0	1,016
	Other endorheic saline lakes	204	4.16	32.0	133
	Coastal saline lakes	40	0.128	5.0 ^c	0.64
	Total	618	82.5	13.9	1,150
Fresh Water ^b (Vertical)	Tectonic	424	54.6	0.29	16.1
	Glacial	1,247	38.4	0.10	3.8
	Fluvial	218	0.58	0.10 ^c	0.058
	Volcanic	3.1	0.58	0.080	0.046
	Miscellaneous	88	0.98	0.30 ^c	0.33
Total	1,980	95.14	0.213	20.3	

Tsal – Total mass of salt

^aTerminal endorheic lakes and coastal lakes

^bExorheic lakes, except coastal lakes and endorheic lakes without terminal outlet

^cEstimated

Source: Meybeck *et al.* (1989).

or sedimentary rocks. Table 5.2 presents the total distribution of dissolved salts (**total dissolved salts** – TDS) in aquatic ecosystems in saline lakes and lakes with different origins.

Climatic and lithological differences explain the different compositions of dissolved salts. For example, in arid or semi-arid regions, high evapotranspiration rates lead to increased salt levels. In other regions, impacts of drainage can occur in areas with high hydrothermal discharge. Volcanic lakes have concentrations similar to rivers that drain through volcanic rocks.

Table 5.3 shows the geographical variability of common dissolved elements (in $\text{mg} \cdot \text{L}^{-1}$) in pristine natural fresh waters draining through the most common types of rocks.

Table 5.4 compares the **chemical composition of fresh waters** (of rivers) with seawater in percentages of total (weight/weight). Table 5.5 shows the average ionic composition in river waters in two temperate regions (North America and Europe) and two tropical regions (South America and Africa). Ionic levels and composition vary significantly. Tropical rivers tend to have much lower concentrations than those in temperate-zone rivers, which have much higher levels of **calcium** and **bicarbonate**. In many tropical regions, there is a predominance of sodium, chlorine, silicate and iron. The calcium carbonate present in the headwaters of the Amazon River is an exception, where 85% of dissolved salts come from recent Andes rocks (Gibbs, 1972).

Figure 5.5a presents the characteristics and effects of the main factors determining the composition of inland surface water, including precipitation and evaporation and their influence in the process. The Figure reaffirms that the principal processes affecting total dissolved salt composition in inland waters are **dissolution**

Table 5.3 Geographic variability of the principal dissolved elements in natural pristine fresh water that drains through the most common types of rocks.

	Conductivity $\mu\text{S}\cdot\text{cm}^{-1}$	pH	$\Sigma\text{Cations}$	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	SO_4^-	HCO_3^-	SiO_2
Granite	35	6.6	3.5 (166)	0.8 (39)	0.4 (31)	2.0 (88)	0.3 (8.8)	0	1.5	7.8	9
Rocks of various origins; schists, quartz, feldspathic	35	6.6	4.1 (207)	1.2 (60)	0.7 (57)	1.8 (80)	0.4 (10)	0	2.7 (56)	8.3 (136)	7.8 (130)
Volcanic rocks	50	7.2	8.0 (435)	3.1 (154)	2.0 (161)	2.4 (105)	0.5 (14)	0	0.5 (10)	25.9 (425)	12.0 (200)
Sandstone	60	6.8	4.6 (223)	1.8 (88)	0.8 (63)	1.2 (51)	0.8 (21)	0	4.6 (95)	7.6 (125)	9.0 (150)
Clayey rocks	ND	ND	14.2 (770)	8.1 (404)	2.9 (240)	2.4 (105)	0.8 (20)	0.7 (20)	6.9 (143)	35.4 (580)	9.0 (150)
Carbonated rocks	400	7.9	60.4 (3,247)	51.3 (2,560)	7.8 (640)	0.8 (34)	0.5 (13)	0	4.1 (85)	194.9 (3,195)	6.0 (100)

The values are in $\text{mg}\cdot\text{L}^{-1}$; the values between parentheses are in $\mu\text{eq}\cdot\text{L}^{-1}$; the values of silica are in $\text{mg}\cdot\text{L}^{-1}$, with $\mu\text{mol}\cdot\text{L}^{-1}$ in parenthesis; ND- Not determined.

Source: Meybeck et al. (1989).

Table 5.4 Comparison between the chemical composition of river waters and sea water in total % (weight/weight).

	Ocean water	River water
CO_3^{2-}	0.41 (HCO_3^-)	35.15
SO_4^-	7.68	12.14
Cl^-	55.04	5.68
NO_3^-	–	0.90
Ca^{2+}	1.15	20.39
Mg^{2+}	3.69	3.41
Na^+	30.62	5.79
K^+	1.10	2.12
$(\text{Fe}, \text{Al})_2 \text{O}_3$	–	2.75
SiO_2	–	11.67
$\text{Sr}^{2+}, \text{H}_3\text{BO}_3, \text{Br}^-$	0.31	–

Source: Schwoerbel (1987).

and draining of salts from rocks, atmospheric precipitation (rainfall) and processes of evaporation (crystallization). Precipitation, a primary influencing factor in the tropics, is not only a direct source of ions, but it also provides a means to dissolve rocks and soils (Payne, 1986).

Table 5.5 Average ionic composition of river water in different continents (in $\text{mg} \cdot \text{L}^{-1}$).

	HCO_3^-	SO_4^-	Cl^-	SiO_2^-	NO_3^-	Ca^{2+}	Mg^{2+}	Na^+	K^+
North America	67.7	40.3	8.1	4.2	0.23	42.0	10.2	9.0	1.6
South America	31.1	9.6	4.9	5.6	0.16	14.4	3.6	3.9	0.0
Europe	95.2	48.0	6.7	3.5	0.84	62.4	11.4	5.3	1.6
Africa	68.9	9.3	20.2	22.2	0.17	7.9	7.8	21.5	–

Source: Payne (1986).

Figure 5.5b shows the relationship (in weight) of $\text{Na}/\text{Na} + \text{Ca}$ with total dissolved salts in surface waters, and Figure 5.5c shows the ratio (in weight) of HCO_3^- ($\text{HCO}_3^- + \text{CO}_3^{2-}$) with total dissolved salts in waters on all continents.

Table 5.6 presents the ionic composition of lakes and rain water in tropical Africa. The table also presents electrical conductivity (K_{20} , in $\mu\text{S cm}^{-1}$), approximate salinity, and pH level.

Table 5.7 presents the ionic composition of Lake Carioca, in Parque Florestal do Rio Doce in East Minas Gerais. In the vertical profile there are increased levels of Ca, Fe, Mn, Na and SO_4 , probably also due to the increase in dissolved salts resulting from the stratification period, water-sediment interactions, the organisms, and the chemistry of the water.

Table 5.8 shows the ionic composition of **Lagoon 33** in the same park. This is a wetland area where aquatic macrophytes predominate, especially *Typha dominguensis*.

The **ionic composition of reservoir waters** varies depending on the characteristics of the terrain, flooded areas and the presence of vegetation, retention time and land use over time, which affect the characteristics of the drainage water. Table 5.9 shows the ionic composition of the Barra Bonita reservoir and Promissao reservoir, both on the **Tietê River**, in February/March 1979.

Poorly mineralized waters, with low dissolved ionic composition, occur in many regions of Brazil.

Ionic levels in Amazonian waters illustrate well the regional differences as well as the chemical characteristics of natural waters, including rivers and lakes that are hydrologically and chemically dependent.

Table 5.10 (Sioli, 1984) presents the average levels of different ions in the waters of the Solimões, Negro and Tarumã-Mirim Rivers; Lakes Jacaretinga, Calado and Castanho; from rivers in the forest and rain water. According to Furch (1984), comparing the natural waters of the Amazonian aquatic systems with the world average for surface waters, Amazonian waters may be considered '**chemically poor.**' However, there are major differences in the way the various different chemical components express this shortage. For example, alkaline-ferrous metals ($\text{Ca} + \text{Mg} + \text{Sr} + \text{Ca}$) are less than 0.5% of the world average. Amazonian waters are 50 times richer in trace elements than the world average.

Furch (1984) classified the waters in the western region of the Amazon – including the **Solimões River** and associated floodplain lakes – as carbonate-rich waters. They

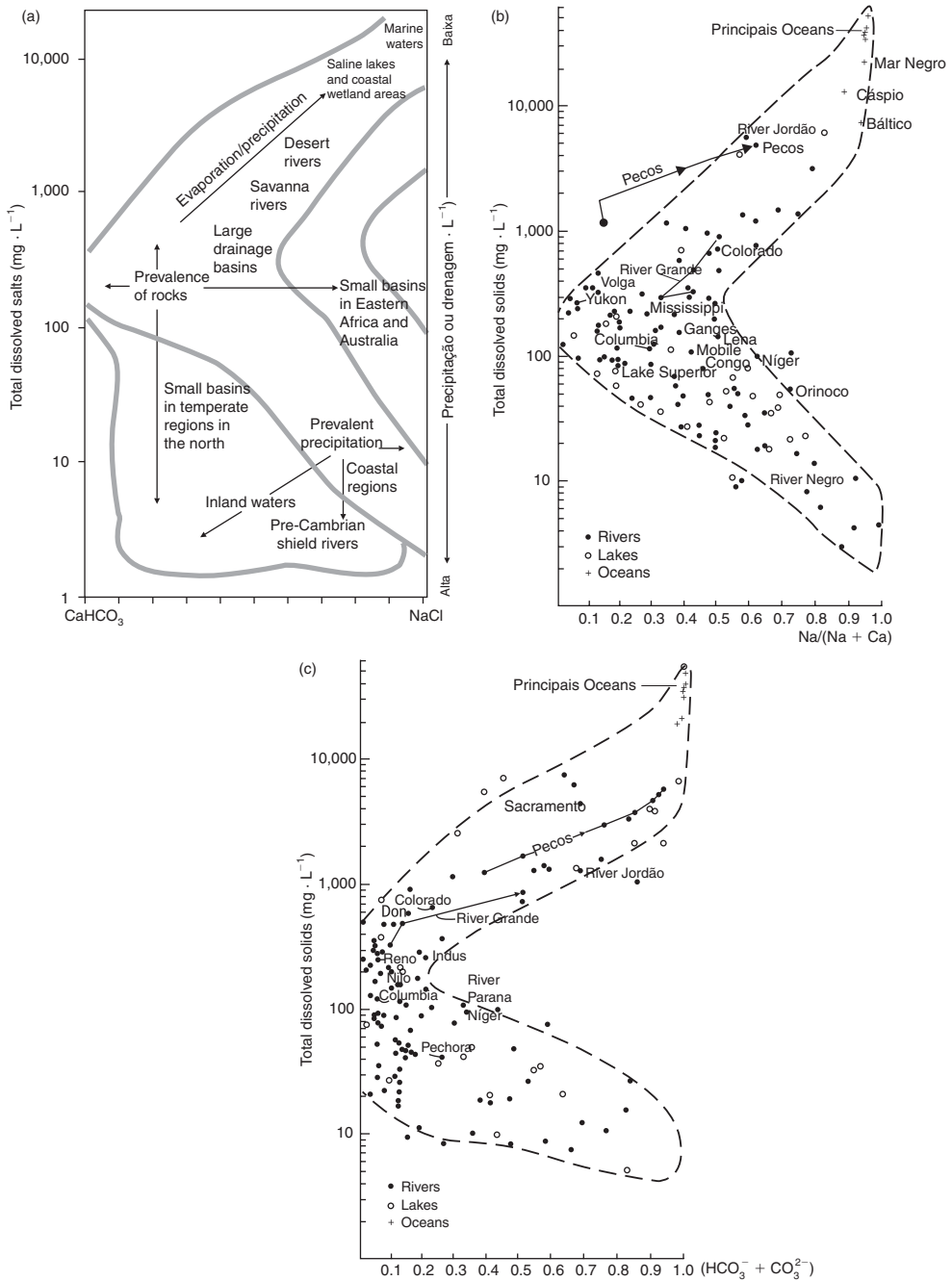


Figure 5.5 a) Schematic representation of mechanisms that control the chemistry of surface water; b) Ratio (by weight) of $\text{Na}/(\text{Na} + \text{Ca})$ with total dissolved salt in surface waters of rivers, lakes and oceans; c) Ratio (by weight) of $(\text{HCO}_3^- + \text{CO}_3^{2-})$ with the total dissolved salt in inland waters.

Source: Modified by Gibbs (1970).

Table 5.6 Ionic composition (units meq · L⁻¹) of some lakes in tropical Africa and rain waters.

Lakes	Data sampling	K ₂₀ Conductivity ($\mu\text{mho} \cdot \text{cm}^{-1}$)	Approx. salinity % (g/L)	pH interval	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	CO ₃ ⁻ + HCO ₃	Cl ⁻	SO ₄ ²⁻	Cations	Anions	Reference
Lungwe	1953	15–17	0.010	6.5–6.7			0.07	0.030						Dubois (1955)
Tumba	1955	24–32	0.016	4.5–5.0			0.03	0.020	0					Dubois (1959)
Nabugabo	June 1967	25	0.015	7.0–8.2	0.090	0.028	0.060	0.020	0.140	0.04	0.019	0.198	0.199	Beadle and Heron, in Talling and Talling (1965)
Bangweulu	1960	35	0.023	7.0–8.3	0.114	0.033	0.075	0.066	0.260	0.009	0.021	0.288	0.290	Harding and Heron, in Talling and Talling (1965)
Victoria	May 1961	96	0.093	7.1–8.5	0.430	0.095	0.280	0.211	0.900	0.112	0.037	1.02	1.05	Talling and Talling (1965)
George	June 1961	200	0.139	8.5–9.8	0.59	0.90	1.00	0.67	1.91	0.25	0.23	2.35	2.39	Talling and Talling (1965)
Chad (Baga Sola)	July 1967	180	0.165	8.0–8.5	0.5	0.2	0.8	0.3	1.8	0	0.1	1.8	1.9	Maglione (1969)
Malawi	Sept. 1961	210	0.192	8.2–8.9	0.91	0.16	0.99	0.39	2.36	0.12	0.11	2.46	2.56	Talling and Talling (1965)
Tanganyika	Jan. 1961	610	0.530	8.0–9.0	2.47	0.90	0.49	3.60	6.71	0.76	0.15	7.46	7.62	Talling and Talling (1965)
Albert	Feb. 1961	735	0.597	8.9–9.5	3.96	1.67	0.49	2.69	7.33	0.94	0.76	8.81	9.03	Talling and Talling (1965)
Edward	June 1961	925	0.789	8.8–9.1	4.78	2.23	0.57	3.98	9.85	1.03	0.89	11.65	11.77	Talling and Talling (1965)
Kivu	Feb. 1954	1,240	1.115	9.1–9.5	5.7	2.17	1.06	7.00	16.40	0.89	0.33	15.93	17.62	Van der Ben (1959)
Turkana	Jan. 1961	3,300	2.482	9.5–9.7	35.30	0.54	0.28	0.25	24.50	13.50	1.40	36.37	39.40	Talling and Talling (1965)
Rain waters														
Kampala (Uganda)	1960			7.7–8.1	0.28	0.10	0.005			0.05	0.05			Visser (1961)
Gambia	1963 (9 km from coast)				0.026	0.01	0–1.10							Thornton (1965)

Table 5.7 Ionic composition of water in Lake Carioca (Parque Florestal do Rio Doce – MG) in 7 September 1978 (in mg·L⁻¹).

Depth (m)	SO ₄ ⁻	Ca ²⁺	Fe ²⁺	Ions K ⁺	Mg ²⁺	Mn ²⁺	Na ⁺	Si
0.0	<1.00	2.06	0.12	0.90	0.80	<0.01	2.16	1.99
1.0	<1.00	2.12	<0.10	0.95	0.80	<0.01	1.80	2.00
2.0	<1.00	2.09	<0.10	0.95	0.80	<0.01	2.09	2.00
3.0	<1.00	2.11	0.10	0.95	0.82	0.05	2.28	2.01
4.0	<1.00	2.42	0.41	0.95	0.86	0.22	2.56	2.07
5.0	1.62	2.41	2.41	0.95	0.84	0.18	1.82	2.03
6.0	1.62	2.50	1.61	1.00	0.86	0.86	2.52	2.06
7.0	3.60	2.45	3.74	1.00	0.86	0.86	2.36	2.10
9.0	4.59	2.43	3.94	0.95	0.86	0.86	2.35	2.12

Table 5.8 Ionic composition of surface water in Lagoon 33 (Parque Florestal do Rio Doce – MG) in different seasons of the year (in mg·L⁻¹).

Depth(m)	Data	SO ₄ ²⁻	Ca ²⁺	Fe ²⁺	Ions K ⁺	Mg ²⁺	Mn ²⁺	Na ⁺	Si
0.00	19/3	2.61	2.43	0.26	0.58	0.92	0.05	2.93	0.36
0.00	19/5	2.61	1.70	0.88	0.32	0.68	0.05	2.07	0.03
0.00	21/7	3.93	2.35	2.20	0.58	0.91	0.05	2.29	<1.00
0.00	23/9	4.59	2.31	1.94	0.43	0.92	0.03	2.19	<1.00
0.00	21/11	4.92	2.16	1.81	0.43	0.87	0.04	2.29	<1.00

Table 5.9 Ionic composition of water in Barra Bonita reservoir and Promissao reservoir (Tiete River – SP), in February/March 1979 (in mg·L⁻¹).

Sta	Dep (m)	pH	Conductiv μS·cm ⁻¹	SiO ₃ ²⁻	SO ₄ ²⁻	Ca ²⁺	Mg ²⁺	Fe ²⁺	Na ⁺	K ⁺	Cl ⁻	Total CO ₂	Temp °C
Barra bonita reservoir	0.0	8.70	112	2.44	0.00	4.10	2.15	1.07	7.35	2.45	6.39	24.3	29.7
	0.2	8.50	112	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	24.3	
	0.5	8.40	111	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	24.7	29.7
	0.7	8.50	114	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	25.1	
	1.3	8.60	111	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	24.6	29.1
	5.0	7.80	112	3.87	0.00	4.37	2.14	1.07	7.40	6.39	6.39	24.7	28.0
	10.0	7.60	113	3.94	0.00	4.37	2.14	1.14	7.19	6.39	6.39	25.5	26.0
	15.0	7.60	113	3.90	0.00	4.37	2.14	1.17	7.50	6.39	6.39	25.8	25.7
Promissao reservoir	0.0	8.10	90	2.81	0.00	4.19	1.94	0.10	6.09	1.77	4.20	0.0	28.6
	5.0	7.80	89	3.06	0.00	4.19	1.94	0.10	6.24	1.64	4.20	0.0	27.8
	10.0	7.60	90	2.74	0.00	4.19	1.94	0.10	6.14	1.64	4.20	0.0	27.6
	15.0	7.50	100	3.02	0.00	4.19	1.94	0.10	6.14	1.64	4.20	0.0	27.2
	20.0	7.50	98	3.16	0.00	4.19	1.97	0.10	5.94	1.64	4.20	0.0	27.1

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Table 5.10 Average concentration (x) for different chemical variables in waters of Amazonia.

	Solimões River			Lake Jacaretinga			Lake Calado (1)			Lake Castanho			Lake Calado (2)			Negro River			Taruma-mirim			Forest Rivers			Rain Water		
	n	x	s	n	x	s	n	x	s	n	x	s	n	x	s	n	x	s	n	x	s	n	x	s	n	x	s
Na (mg·L ⁻¹)	29	2.3	0.8	25	2.5	0.7	23	1.6	0.6	30	1.6	0.4	27	1.3	0.5	24	380	124	23	335	88	20	216	58	25	119	97
K (mg·L ⁻¹)	29	0.9	0.2	25	1.4	0.4	23	0.9	0.7	30	0.9	0.2	27	0.6	0.3	24	327	107	23	312	98	20	150	108	25	100	104
Mg (mg·L ⁻¹)	29	1.1	0.2	25	1.4	0.4	23	0.9	0.5	30	0.9	0.2	27	0.7	0.4	24	114	35	23	99	44	20	37	15	25	21	17
Ca (mg·L ⁻¹)	29	7.2	1.6	25	8.5	1.8	23	6.2	3.1	30	5.0	1.2	27	4.3	2.5	24	212	66	23	186	83	20	38	34	25	72	78
Na+K+Mg +Ca (mg·L ⁻¹)	29	11.5	2.6	25	13.8	3.1	23	9.6	4.6	30	8.4	1.7	27	6.9	3.6	24	1020	312	23	926	285	20	441	182	25	312	275
Conductivity (μS·cm ⁻¹)	27	57	2.6	23	60	18	23	47	19	27	42	9	24	38	12	22	9	2	21	9	2	20	10	3	N.D.		
pH	27	6.9	0.4	23	6.9	0.3	23	6.6	0.4	27	6.7	0.3	24	6.5	0.4	22	5.1	0.6	21	5.0	0.5	20	4.5	0.2	N.D.		
total P (μg·L ⁻¹)	28	105	58	25	57	26	21	62	38	25	40	14	26	50	33	24	25	17	23	22	21	20	10	7	N.D.		
total C (mg·L ⁻¹)	28	13.5	3.1	25	16.2	5.8	22	12.8	4.2	28	12.4	1.8	26	10.8	2.7	24	10.5	1.3	23	9.9	1.6	20	8.7	3.8	N.D.		
HCO ₃ -C (mg·L ⁻¹)	26	6.7	0.8	24	8.5	1.7	22	5.6	2.2	28	5.0	1.1	26	4.3	1.9	24	1.7	0.5	23	1.6	0.3	20	1.1	0.4	N.D.		
Cl (mg·L ⁻¹)	26	3.1	2.1	24	2.9	1.7	22	2.5	1.2	28	2.0	1.0	26	2.1	1.0	24	1.7	0.7	23	1.8	0.7	20	2.2	0.4	N.D.		
Si (mg·L ⁻¹)	28	4.0	0.9	25	4.3	1.1	22	3.6	1.1	28	3.8	1.3	26	3.0	0.9	24	2.0	0.5	23	1.7	0.4	20	2.1	0.5	N.D.		
Sr (μg·L ⁻¹)	29	37.8	8.8	25	39.7	11.0	23	27.5	11.2	30	24.4	8.0	27	23.0	13.3	24	3.6	1.0	23	2.8	1.1	20	1.4	0.6	23	0.7	0.5
Ba (μg·L ⁻¹)	29	22.7	5.9	25	21.7	6.6	23	16.1	6.2	30	16.9	6.1	27	15.0	7.0	24	8.1	2.7	23	7.1	3.2	20	6.9	2.9	23	4.4	3.0
Al (μg·L ⁻¹)	29	44	37	25	20	14	23	26	18	30	23	16	27	21	14	24	112	29	23	119	40	20	90	36	23	10	8
Fe (μg·L ⁻¹)	29	109	76	25	123	79	23	111	68	30	83	38	27	85	49	24	178	58	23	136	59	20	98	47	23	26	31
Mn (μg·L ⁻¹)	29	5.9	5.1	25	3.0	2.3	23	4.4	3.2	30	2.8	2.5	27	3.5	2.7	24	9.0	2.4	23	7.9	2.9	20	3.2	1.2	23	1.4	0.7
Cu (μg·L ⁻¹)	29	2.4	0.6	25	1.6	0.9	23	2.1	0.9	29	2.2	1.1	27	1.7	0.6	24	1.8	0.5	23	1.6	0.6	20	1.5	0.8	23	3.3	2.1
Zn (μg·L ⁻¹)	29	3.2	1.5	25	2.2	1.1	23	3.4	1.7	30	2.9	1.6	27	3.0	1.6	24	4.1	1.8	23	4.0	1.6	20	4.0	3.3	23	4.6	3.5

n – number of samples; s – standard deviation; N.D. – not determined

Source: Furch (1984).

have the highest ionic concentration of HCO_3^- , Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Ba^{2+} , and Sr^{2+} , approximating the global averages for natural waters.

In the waters of the Negro River and adjacent lakes, there is a shortage of carbonates and a high level of trace elements such as Fe and Al (ten times more than in the Solimões River). These waters are acidic (pH circa 5.1) and also have high levels of humic substances and dissolved organic matter.

The most unusual chemical characteristics are in small streams in the forests of the central Amazon, where carbonate levels are absent or much lower than in the Negro River and its tributaries, the pH is acidic (4.5), and there is a high percentage of trace elements and predominance of **alkaline metals**, with low Ca^{2+} and Mg^{2+} levels.

Amazonian rain water, also analyzed by Furch (1984), contains trace metals, and proportions of alkaline-ferrous metals and alkaline metals similar to the waters of the Negro River.

Table 5.11 shows the conductivity values for different aquatic ecosystems. Table 5.12 shows statistical correlations between water conductivity and the levels of several different elements and ions.

Salinity of natural waters

The salinity of natural waters, in milligrams per liter ($\text{mg} \cdot \text{L}^{-1}$) or milli-equivalents per litre ($\text{meq} \cdot \text{L}^{-1}$), is the sum of the dissolved salts in the water.

The electrical conductivity or specific conductance, is an indicator of the salinity resulting from concentration of salts, acids and bases in the natural waters. It is measured by the electrolyte content of water, through the flow of current between two platinum electrodes: the higher the measurement the greater the concentration. Conductivity also increases with temperature.

The units that express conductivity (at 25°C) are: micro-Siemens ($\mu\text{S} \cdot \text{cm}^{-1}$), milli-Siemens ($\text{mS} \cdot \text{cm}^{-1}$) ($1 \text{ mS} \cdot \text{m}^{-1} = 1000 \mu\text{S} \cdot \text{cm}^{-1}$), or micromho (cm^{-1}) ($1 \text{ micromho} \text{ cm}^{-1} = 1 \mu\text{S} \cdot \text{cm}^{-1}$).

The conductivity of different waters reflect a large number of complex phenomena: depending on the ionic concentration, there is a correlation between conductivity and nutrients of phytoplankton and macrophytes. In certain lakes and reservoirs, conductivity also depends on the alkalinity or acidity (pH) of the water.

The total dissolved solids (TDS) include all salts present in the water and non-ionic components. Dissolved organic compounds contribute to total dissolved solids and can be measured by the total content of dissolved carbon (TDC), as already explained.

The content of TDS is obtained by filtering a sample of water, evaporating the filtrate and measuring the dry weight from the principal solutes remaining. Total content of TDS is used by geomorphologists interested in determining the effects of chemical erosion in different regions.

Golterman (1988) verified that the salinity (S) of fresh water can be estimated as: $S = \sim 0.75C$ (where $C = \mu\text{S} \cdot \text{cm}^{-1}$) and $S = \text{mg} \cdot \text{L}^{-1}$, or $S = \sim 0.01C$ (where $C = \mu\text{S} \cdot \text{cm}^{-1}$ and $S = \text{meq} \cdot \text{L}^{-1}$).

Williams (1986) examined the inter-relationships between salinity and conductivity. In a gradient of conductivity (C) from 5,500–100,000 $\mu\text{S} \cdot \text{cm}^{-1}$, the salinity in $\text{mg} \cdot \text{L}^{-1}$ is $\sim 0.6\text{--}0.7C$.

Table 5.11 Values of conductivity for different aquatic ecosystems.

Carlos Botelho (Lobo/Broa) reservoir	10–20 $\mu\text{S} \cdot \text{cm}^{-1}$
Natural waters in the Negro River	9–10 $\mu\text{S} \cdot \text{cm}^{-1}$
Barra Bonita (SP) reservoir	100 $\mu\text{S} \cdot \text{cm}^{-1}$ (1974)
Barra Bonita (SP) reservoir	370 $\mu\text{S} \cdot \text{cm}^{-1}$ (2002)
Saline lakes of Africa (Turkana Lake)	2.482 $\mu\text{S} \cdot \text{cm}^{-1}$
Rain water in regions not impacted by human activity	10–15 $\mu\text{S} \cdot \text{cm}^{-1}$
Solimões River	57 $\mu\text{S} \cdot \text{cm}^{-1}$
Jacaretinga River (Amazonia)	60 $\mu\text{S} \cdot \text{cm}^{-1}$
Salto de Avanhandava reservoir (Tiete River, SP)	74 $\mu\text{S} \cdot \text{cm}^{-1}$
Capivara reservoir (River Paranapanema)	54 $\mu\text{S} \cdot \text{cm}^{-1}$
Atlantic Ocean	43.000 $\mu\text{S} \cdot \text{cm}^{-1}$

Table 5.12 Statistical correlations (example-set) between the conductivity of water and the concentration of different elements and ions.

Component	Correlation with Conductivity
Ca	0.973
HCO ₃	0.961
Cl	0.928
Na	0.090
Sr	0.898
Mg	0.862
SO ₄	0.730

Source: Margalef (1993).

5.3 IONIC COMPOSITION IN SALINE LAKES AND INLAND WETLANDS

The ionic composition of inland saline lakes varies considerably and differs greatly from the ionic composition of rivers with low conductivity. Ionic composition depends on the evaporation rate, which produces precipitation of ions as a function of **solubility**. As evaporation occurs and the volume of water **decreases**, there is **differential precipitation** of Na⁺, Mg²⁺, Cl⁻ and SO₄²⁻ ions. In waters with high levels of Ca²⁺ and Mg²⁺, MgCO₃ precipitates as crystals of dolomite [CaMg(CO₃)₂]. Salts deposited in dry river-beds may be transported by wind, causing **impacts on human health** and on the agriculture in surrounding regions (see **Aral Sea**, Chapter 18).

The relationship of **water temperature to evaporation and precipitation** is critical for the precipitation of ions and solubility in lakes in arid and semi-arid regions.

5.4 THE ROLES OF CATIONS AND ANIONS IN BIOLOGICAL SYSTEMS

The roles of cations and anions in biological systems are many and varied. Important functions include:

- ▶ activation of enzyme systems;
- ▶ stabilization of proteins in solution;
- ▶ the development of electrical excitability;
- ▶ regulation of membrane permeability;

- ▶ maintenance of a state of dynamic isotonic equilibrium between cells and extracellular fluids.

High levels of salt in solutions absorb much free water in solution and therefore tend to precipitate proteins. An ion that activates enzymes can be an integral part of an enzyme, function as a bond between the enzyme and the substrate, alter the balance of an enzymatic reaction, or inactivate the enzyme system (Lokwood, 1963).

Sodium – is the main cation in extracellular fluids in many animals. High concentrations can inhibit **enzyme** systems.

Potassium – is the principal cation in cells. It plays a role in establishing membrane potential, and is also a component in the activation of certain enzymes.

Calcium – decreases the permeability of cell membranes and ions. Some enzyme systems are also inhibited by high calcium levels. As a divalent ion, calcium is important in stabilising colloids.

Magnesium – forms the nucleus of the chlorophyll molecule. It is an ion that activates many enzymes involved in energy transfer. Large quantities of magnesium and calcium can decrease membrane permeability, and reduce the oxygen consumption by cells.

pH – chemical properties of proteins shift with pH. Changes in pH can play an important role in enzymatic activity, the osmotic pressure of colloids, and shifts in the acidity or basicity of extracellular fluids.

Anions – phosphate and bicarbonate have buffering effects on cells and extracellular fluids. High phosphate levels tend to inhibit activities that depend on calcium. Bicarbonate correlates with the retention of potassium in muscles.

Osmotic regulation in freshwater organisms (plants, vertebrates and invertebrates) is an essential physiological feature. As the levels of cations and anions in inland waters vary, these organisms also regulate their cation and anion levels to enable the functioning of enzymes. Such osmotic regulation is performed by the active absorption of water, elimination of the water in urine and the subsequent absorption of cations and anions through surfaces and gills. Freshwater organisms tend to maintain higher internal concentrations of salt than is found in the medium.

Ionic levels in aquatic ecosystems constitute a key factor in the distribution of aquatic organisms and the **colonisation of environments** (with different conductivities), which trigger regulatory processes and tolerance that vary for different groups of aquatic animals and plants. For example, changes in the **diversity** of calanoid species in zooplankton in reservoirs in the Medio Tietê can be related to successive increases in the electrical conductivity of the water and its shifts in ionic levels (Matsumura Tundisi and Tundisi, 2003).

Colonisation by **invasive species** largely depends on tolerance to ionic levels, availability of cations and anions, and their total amounts in water.

Of course, the anions PO_4^{3-} , NO_3^- , NO_2^- and the cation NH_4^+ are fundamentally important as nutrients for **photosynthetic phytoplankton**, aquatic macrophytes, and photosynthetic bacteria.

5.5 DISSOLVED GAS: AIR-WATER INTERACTIONS AND THE SOLUBILITY OF GASES IN WATER

The air-water interface is important in aquatic ecosystems because of the **exchange of energy** and gases that takes place there. Of the gases dissolved in water, oxygen and

Table 5.13 Principal gases in the atmosphere.

Gas	%
Nitrogen (N ₂)	78.084
Oxygen (O ₂)	20.946
Argon (Ar)	0.934
Carbon dioxide (CO ₂)	0.038

carbon dioxide are chemically and biologically important. Table 5.13 shows the main gases found the atmosphere.

The solubility of gases in water depends on the physical and chemical characteristics of the water mass, as well as on pressure, temperature and salinity. According to Henry's law, 'the quantity of gas absorbed by a determined volume of liquid is proportional to the atmospheric pressure exercised by the gas.' According to this law (Cole, 1983):

$$C = K \times p$$

where C is the concentration of gas, p is the partial pressure exercised by the gas, and K is a solubility factor that differs for each gas.

Levels of dissolved gases in water can be expressed in mg/liter ($\text{mg} \cdot \text{L}^{-1}$) or millimoles/liter ($\text{mmol} \cdot \text{L}^{-1}$). Most gases follow Henry's law. The solubility of gases in water depends, then, on altitude, water temperature (the solubility of gas decreases with increased temperature) and salinity. The solubility of dissolved oxygen drops, for example, in waters with high saline levels, as in the case of inland saline lakes. Copeland (1967) observed that in the **Tamaulipas Lagoon** (Mexico), levels of dissolved oxygen decreased from $6.6 \text{ mg} \cdot \text{L}^{-1}$ (for 25°C ocean water) to $3 \text{ mg} \cdot \text{L}^{-1}$ (for water with salinity of 22%).

5.5.1 Dissolved oxygen

The level of dissolved oxygen in water is one of the most important variables in limnology. Oxygen is extremely important biologically, and in water it participates in many chemical reactions. It quickly dissolves in water, depending on air/water interactions, i.e., on the water temperature and atmospheric pressure.

Dissolved oxygen levels can be measured by $\text{mg} \cdot \text{L}^{-1}$, $\text{mL} \cdot \text{L}^{-1}$ or millimoles $\cdot \text{L}^{-1}$, and also by the percentage of **saturation** of dissolved oxygen in the water. Thus, 100% saturation theoretically means the maximum dissolved oxygen possible for a given temperature and pressure. This percentage, in a sea-level water mass, can represent higher saturation values than at 1000 meters of altitude, for example. Figure 5.6 shows a nomogram in which the percentage of **saturation of dissolved oxygen** in water can be determined as a function of temperature, levels measured in $\text{mg} \cdot \text{L}^{-1}$ or $\text{mL} \cdot \text{L}^{-1}$ and atmospheric pressure. Corrections in altitude, atmospheric pressure and solubility factors for gases in general can be obtained by using tables (Wetzel, 1975).

It is worth noting that solubility is always considered to be a relationship between the levels of O₂ in solution and the levels above the solution – in the air – hence, saturation is presented in relative terms.

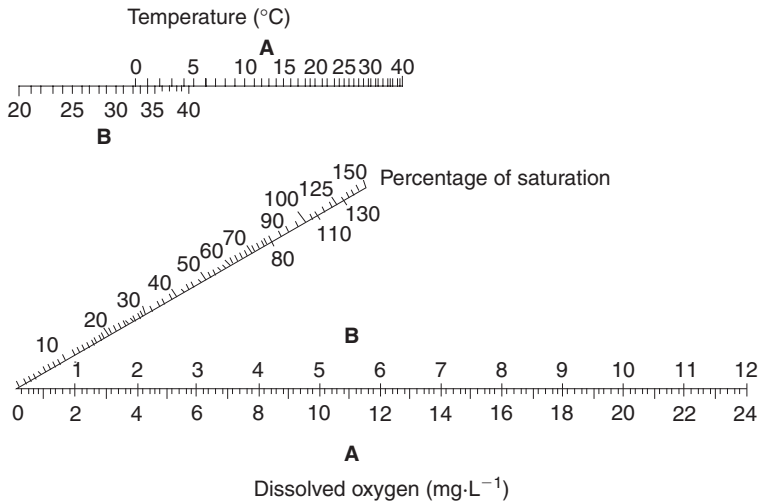


Figure 5.6 Nomogram for determining the percentage of saturation of dissolved oxygen in water.
Source: Hutchinson (1957).

Table 5.14 presents the solubility of oxygen in pure water in equilibrium with the air saturated with water vapour at 1 atmosphere.

Dissolution of oxygen through the air-water interface generally occurs under conditions of intense vertical movement or in a process of slow diffusion and transport by convection. **Dissolution of oxygen** by molecular diffusion through a calm surface is extremely slow and insignificant (Hutchinson, 1957).

The levels of dissolved oxygen in water depend on the coefficients of oxygen exchange between the atmosphere and the water surface. Movement of oxygen through the air-water interface is given by the Bohr equation (Hutchinson, 1957):

$$\frac{dO}{dt} = a \cdot \alpha(P - p_t)$$

where:

a = area of interface;

P = partial atmospheric pressure of the gas;

p_t = pressure at which the level of gas in the water at a determined time is in equilibrium.

α = coefficient of entry

An exit coefficient (B) is also considered.

Another important dissolution mechanism results from thermal cooling, which occurs during evaporation and results in increased salinity with subsequent vertical movement by convection currents. The process results in exchanges of gases.

Major sources of dissolved oxygen in water

The atmospheric source of dissolved oxygen and its dissolution in water depends, as described, on the specific conditions of the liquid mass. **Processes of vertical transport**

Table 5.14 Solubility of dissolved oxygen in pure water and in equilibrium with the air saturated at 1 atmosphere.

Temperature (0°C)	Concentration mg · L ⁻¹	Temperature (0°C)	Concentration mg · L ⁻¹
0	14.62	21	8.91
1	14.22	22	8.74
2	13.83	23	8.58
3	13.46	24	8.42
4	13.11	25	8.26
5	12.77	26	8.11
6	12.45	27	7.97
7	12.14	28	7.83
8	11.84	29	7.69
9	11.56	30	7.56
10	11.29	31	7.43
11	11.03	32	7.30
12	10.78	33	7.18
13	10.54	34	7.06
14	10.31	35	6.95
15	10.08	36	6.84
16	9.87	37	6.73
17	9.66	38	6.62
18	9.47	39	6.51
19	9.28	40	6.41
20	9.09		

To convert to ml · L⁻¹, multiply by 0.70.

Source: Cole (1983).

of oxygen resulting from the effects of wind-caused turbulence play a decisive role in this dissolution. The turbulent flow promotes oxygenation in the upper layers. In some cases, dissolution from turbulence can lead to supersaturation. This is the case, for example, in outflows of water from dams, usually in volume-regulating floodgates. Cases of up to 150% saturation have been reported. This mechanism of increasing dissolved oxygen levels has generally been explored in reservoirs. In turbulent rivers, the saturation levels of dissolved oxygen increase. As a result, rivers can provide an effective aeration system and replenishment of dissolved oxygen in water, resulting in **auto-purification**.

Photosynthetic activity is an important source of dissolved oxygen in water. Such production of oxygen is restricted to the euphotic zone and occurs during the day. Therefore, the vertical distribution of dissolved oxygen is strongly related to the vertical distribution of phytoplankton in the euphotic zone. In lakes with high levels of chlorophyll due to phytoplankton in the epilimnion in eutrophic conditions, **supersaturation of dissolved oxygen** can occur with values up to 130–150% during the day. Tundisi (unpublished results) measured levels of 120% saturation on the surface in Barra Bonita reservoir, São Paulo, with chlorophyll levels of approximately 200 µg/liter.

Supersaturation can also occur in transparent shallow waters, with high biomass levels in the form of immersed macrophytes, phytobenthos and **periphyton**. Tundisi

et al. (1984) showed that, in general, the relatively high diurnal levels of dissolved oxygen in Lake Jacaretinga (Central Amazon) were the result of photosynthesis by **submerged macrophytes** near the surface and by **periphyton**.

The presence of high biomass levels from primary producers leads to intense diel fluctuations in the levels of dissolved oxygen, which will be described below.

Losses of dissolved oxygen

Respiration by aquatic plants and animals and decomposition through bacterial activity are important sources of loss of dissolved oxygen. At the **sediment-water interface**, substantial loss of oxygen can occur in the water because of bacterial activity and **chemical oxidation**. The effects of oxidation on oxygen consumption can be measured by various techniques. One method is to place sediment in closed flasks with water and periodically determine the dissolved oxygen in the **supernatant** water.

Wind agitation in shallow lakes also leads to decreased oxygen levels in the water, due to the resuspension of sediments and organic materials. Oxygen loss in water can also result from high levels of mortality of aquatic organisms. In the eutrophication process, with extensive cyanobacterial blooms, a mass kill occurs after a **period of senescence**, producing increased oxygen consumption. Such episodic processes of decreased dissolved oxygen may also result from periods of intense stratification followed by circulation, in which the anoxic hypolimnion undergoes a mechanical action from the effects of wind and the layer of epilimnetic water comes into contact with the anoxic water. On these occasions, fish kills and mass deaths of other organisms can occur.

The levels of dissolved oxygen drop drastically when the levels of suspended matter markedly increases after heavy precipitation and drainage into lakes, ponds or rivers. Tundisi (1995, unpublished results) recorded a drastic drop in dissolved oxygen in the Barra Bonita reservoir, São Paulo, with levels ranging from $0.00 \text{ mg} \cdot \text{L}^{-1}$ to a maximum of $5.00 \text{ mg} \cdot \text{L}^{-1}$ at the surface and anoxic environment at depths below 12 m (to a maximum depth of 25 m) with high levels of NH_4^+ . This process caused a fish kill. The low levels of dissolved O_2 were the result of high levels of suspended material draining into the reservoir after heavy precipitation.

Vertical distribution of dissolved oxygen

Varying oxygen levels at different depths in lakes result from the processes of stratification, de-stratification, vertical circulation and its efficiency, and the vertical distribution and activity of organisms.

Surface waters generally present oxygen levels close to saturation. Supersaturation on the surface or subsurface can occur in cases of high levels of phytoplankton. Higher temperatures in the epilimnion cause loss of oxygen through the air-water interface. When complete circulation occurs in an unproductive lake, dissolved oxygen is distributed uniformly all the way to the bottom. This type of vertical distribution is called **orthograde**. The slight increase in dissolved oxygen that occurs with depth is due to higher solubility at lower temperatures.

In productive lakes, summer stratification is characterized by a vertical distribution with an anoxic hypolimnion and oxygen levels close to saturation or supersaturation

in the epilimnion. This curve, **clinograde**, is typical of a stratified, eutrophic lake in summer. Decaying material accumulates in the hypolimnion and consumption of oxygen there is high.

There is an increase in dissolved oxygen in some stratified lakes due to the accumulation of phytoplankton in the upper metalimnion. Accumulation of cyanobacteria in the metalimnion was described for several lakes in temperate and tropical regions. For example, dense layers of *Oscillatoria agardhii* were observed in many temperate lakes, and the presence of *Lyngbya limnetica* was described for Carioca Lake (Parque Florestal do Rio Doce – MG) by Reynolds *et al.* (1983).

This type of curve is called positive **heterograde**, with saturations of up to 300%. Circulation and horizontal transport resulting from the production of oxygen in photosynthesis by macrophytes, in the shallowest parts of the lakes, can also cause an increase in oxygen, producing this **positive heterograde curve**.

On the other hand, high consumption of oxygen, resulting from the levels of organisms or decomposing organic material, can occur in the lower portion of the metalimnion, resulting in a **negative heterograde curve**. This minimum in the metalimnion, associated with density gradients and increased respiration, is common in monomictic and meromictic lakes.

Another less-common type of vertical distribution occurs when there is a maximum in the hypolimnion. This results from transport mechanisms and horizontal circulation caused by the inflow of denser and cooler waters. Rivers commonly cause horizontal stratification in temperature and dissolved oxygen.

Figure 5.7 shows the various types of curves and vertical profiles of dissolved oxygen in lakes.

In polymictic lakes, dissolved oxygen is generally distributed homogeneously in the vertical profile. In reservoirs, the processes of circulation and vertical distribution of dissolved oxygen can be more complex. For example, in flooded areas of reservoirs with no deforestation after filling, there is almost permanent anoxia resulting from decomposing plant material. The process of re-oxygenation on the surface is difficult, since the presence of vegetation prevents horizontal and vertical circulation (see Chapter 12).

In meromictic lakes, there is permanent anoxia in the hypolimnion.

The vertical distribution of oxygen in lakes is also important in relation to the chemical processes of precipitation, re-dissolution, and biogeochemical cycles of elements (see Chapter 9).

Dissolved oxygen deficit

A lake's oxygen deficit is defined as 'the difference between the saturation level of dissolved oxygen and water temperature, the lake's surface pressure and the observed value' (Hutchinson, 1957). The real oxygen deficit is the difference between the amount of O_2 measured at a certain depth and the amount presented if the water were saturated in the same conditions of pressure and temperature (Cole, 1975).

An assessment of the real deficit of oxygen (RDO) in a lake at a certain time of the year can be calculated by the formula:

$$RDO = \sum_{i=1}^n G_i \cdot V_i$$

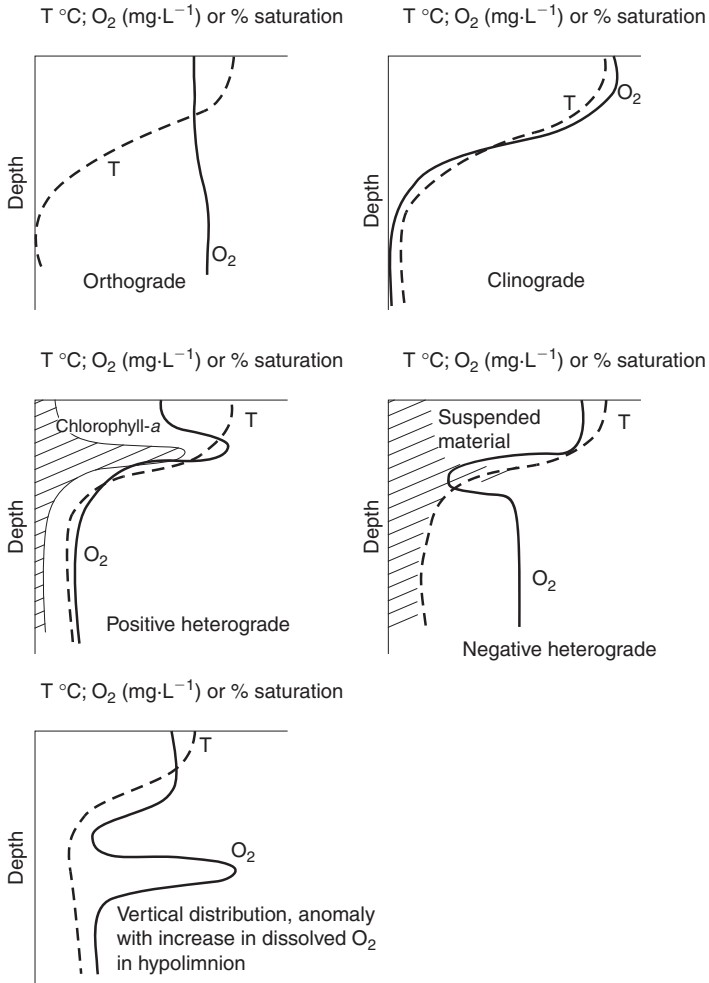


Figure 5.7 Vertical curves and profiles of dissolved oxygen in lakes.
 Source: Modified from Cole (1983).

where:

- G_1 – measures the real oxygen deficit ($\text{mg} \cdot \text{cm}^{-3}$) found in the upper and lower limits of each of the lake's strata (or that which can be considered as a layer in cm);
- V_1 – volume (cm^3) of each stratum in the lake, which can be calculated by the formula:

$$V_1 = \frac{h}{3} (S_1 + S_2 + \sqrt{S_1 \cdot S_2})$$

where:

- h = height between the upper and lower planes of each strata;
- S_1 and S_2 = areas (in cm^2) in each layer between two strata.

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The **relative deficit** of dissolved oxygen is the difference between two calculations: one made during the period of maximum stratification and the other during the period of maximum circulation. The relative deficit makes it possible to calculate the depletion of oxygen during a given period by unit area in the hypolimnion. Indications of biological productivity in lakes can also be estimated through this calculation.

The relative oxygen deficit is calculated for the entire hypolimnion and expressed in unit of area (Deficit of Hypolimnion Oxygen by Area – DOHA, $\text{mg O}_2 \cdot \text{cm}^{-2} \cdot \text{day}^{-1}$) applying the formula:

$$DOHA = \frac{M_1 - M_2}{\Delta t}$$

where:

M_1 = content of oxygen in the period of maximum circulation in a volume equal to the volume of the hypolimnion at M_2 ;

M_2 = content of oxygen observed in the hypolimnion at a specific time of year;
 (Δt) = time interval (days) between M_1 and M_2 .

$$(M_1 - M_2) = \sum^i G_i - V_i/H$$

where:

G_1 = average concentration of oxygen in the upper and lower limits of each stratum of the hypolimnion ($\text{mg} \cdot \text{cm}^{-3}$)

V_1 = volume (cm^3) between the metalimnion and the hypolimnion

H = border plane (cm^2) between the metalimnion and hypolimnion, calculated using the lake's thermal profile corresponding to the inflection point of the curve.

In long series of sequential data, it is important to determine the oxygen deficit in the hypolimnion, as an indication of progression of eutrophication. Eberly (1975) described a method for determining the level of eutrophication in a dimictic lake in the **temperate region** from the deficit of dissolved oxygen in the hypolimnion. This methodology uses the volume of various different strata in the hypolimnion and saturation values at the hypolimnetic temperature. Table 5.15 presents these values for **Lake Mendota** (Wisconsin, United States) over a period of 50 years.

Table 5.15 Deficits of dissolved oxygen and temperatures of the hypolimnion in Lake Mendota (USA).

Date	Temperature of hypolimnion ($^{\circ}\text{C}$)	Deficit of oxygen (%)	Deficit by area (g/m^2)
18 Aug. 1912	8.3	74.9	54.78
13 July 1927	9.4	82.8	56.55
16 July 1931	8.3	96.3	70.01
21 July 1953	8.3	99.1	72.87
12 Sept. 1962	7.3	99.9	75.97

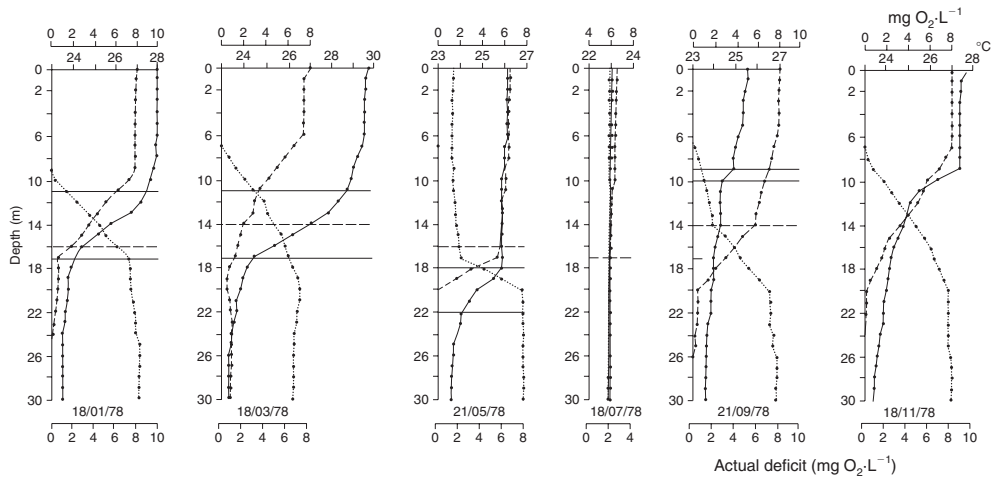


Figure 5.8 Results of oxygen deficit for Lake Dom Helvécio (Parque Florestal do Rio Doce – MG).
Source: Henry *et al.* (1989).

In this case, the eutrophication process resulting from the increase in the deficit per area was caused by allochthonous material, mainly domestic sewage. Hutchinson (1957) suggests that an oxygen deficit of $0.05 \text{ mg} \cdot \text{cm}^{-2} \cdot \text{day}^{-1}$ already indicates eutrophication.

Henry *et al.* (1989) calculated the oxygen deficit in Lake Dom Helvécio (Parque Florestal do Rio Doce – MG) from vertical profiles of water temperature and dissolved oxygen levels. The results are presented in Figure 5.8. In July (winter period with no stratification), the real deficit in the water column was $2.0 \text{ mg} \cdot \text{L}^{-1}$. The deficit rises gradually, reaching $8.0 \text{ mg} \cdot \text{L}^{-1}$ of oxygen during thermal stratification of the hypolimnion. The relative deficits of dissolved oxygen in the water column do not exceed $6.5 \text{ mg} \cdot \text{L}^{-1}$. The real total oxygen deficit, expressed per unit of the lake's surface area, ranges from 119.07 tons of O₂ and $1.73 \text{ mg O}_2 \cdot \text{cm}^{-2}$ (September, period of stratification) to 163.28 of O₂ and $2.37 \text{ mg O}_2 \cdot \text{cm}^{-2}$ (May, period of limited circulation). The hypolimnetic oxygen deficit, expressed per unit area, varies from 0.56 to $1.30 \text{ mg O}_2 \cdot \text{cm}^{-2}$.

Henry *et al.* (1989) attribute the lake's oxygen deficit to several factors, such as decomposition of organic matter in the water column and oxygen consumption in the sediment produced by accumulation of non-decomposed organic matter in the water column. Such consumption can vary in different lake regions (Lasemby, 1975).

5.6 THE CO₂ SYSTEM

Carbon dioxide is another biologically important gas. It dissolves in water to form soluble carbon dioxide, which reacts with water to produce non-dissociated

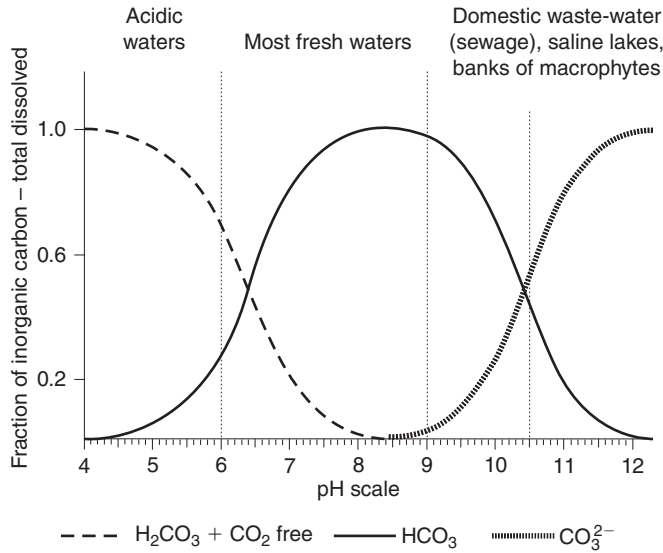


Figure 5.9 Interrelations of pH, free dissolved CO_2 , bicarbonate ion (HCO_3^-) and carbonate ion (CO_3^{2-}).

carbonic acid. The following equation describes the main phases of the CO_2 system in water:

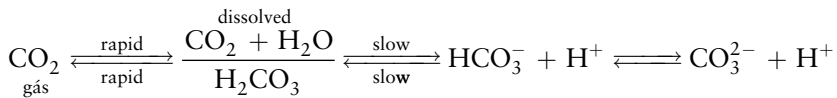


Figure 5.9 lists the various different forms of carbon occurring in water at different pH levels. The levels in each phase depend on the water's temperature and ionic level. The level of free CO_2 to maintain HCO_3^- in solution is called the equilibrium CO_2 .

Aquatic plants can use CO_2 , HCO_3^- , and more rarely, CO_3^{2-} as sources of carbon. Some aquatic macrophytes use HCO_3^- , after converting it to CO_2 by the action of carbonic anhydrase enzyme. The majority of lakes have sufficient HCO_3^- levels for photosynthesis, in a pH range that varies from approximately 6.0 to 8.5. CO_2 is the dominant form at low pH and CO_3^{2-} is the dominant form for pH >10.5.

5.6.1 CO_2 levels and pH

The term pH is defined as the negative logarithm of the concentration of hydrogen ions. On a scale from acidity to alkalinity, 0–7 pH indicates acidity and 7–14 indicates alkaline status. Most lakes have a pH value between 6.0 and 9.0; lakes with high concentrations of acids have a pH of between 1.0–2.0; extremely eutrophic lakes with extreme CO_2 depletion or high levels of carbonate (soda lakes) can have pH values >10.

In the photosynthetic process, CO_2 and HCO_3^- are removed by primary producers. As a result, the water's pH increases because the carbon fixation capacity is greater than the dissolution of atmospheric CO_2 in the air-water interface. Therefore, by reducing the carbon available in water, the photosynthetic process leads to increased pH and, consequently, a shift in the reaction of the carbonate system. As shown in the equation, the transfer of H_2CO_3 and HCO_3^- into CO_2 is extremely fast, but continuous reduction in the level of free CO_2 in water can limit photosynthesis. Under normal conditions, the pH of water is regulated by the CO_2 , HCO_3^- – CO_3^{2-} system. The formula:

$$\log \frac{[\text{HCO}_3^-]}{[\text{CO}_2 \text{ total}]} = \text{pH} - \text{pK}_1$$

applies between 15–20°C and below pH 7:

$$[\text{HCO}_3^-] = 4 [\text{CO}_2 \text{ total}]$$

The CO_2 system is the principle source of inorganic dissolved carbon for aquatic plants, and the three forms tend to equilibrium with each other and the atmosphere. CO_2 is more abundant in water than in air and nearly 200 times more soluble than oxygen. The photosynthetic process plays an important role in the reduction of CO_2 in water. Diel fluctuations in the CO_2 and O_2 in water, produced by photosynthetic cycles and respiration, will be discussed below.

The terms alkalinity, alkaline carbonate, and alkaline reserves are used to designate the total quantity of base that can be measured with a strong acid titration. In general, alkalinity can be expressed in $\text{mg} \cdot \text{L}^{-1}$ or $\text{meq} \cdot \text{L}^{-1}$.

Alkalinity can be expressed as:

- ▶ alkalinity in $\text{mg} \cdot \text{L}^{-1}$ of HCO_3^- ;
- ▶ alkalinity in $\text{mg} \cdot \text{L}^{-1}$ of CO_3^{2-} ;
- ▶ alkalinity in $\text{mg} \cdot \text{L}^{-1}$ of HCO_3^- and CO_3^{2-} ;

According to Hutchinson (1957), alkalinity of bicarbonates is the most useful, since the pH of many natural waters is in the range associated with HCO_3^- .

By titrating a water sample with strong acid and calculating the water's alkalinity, we can start to estimate the total amount of CO_2 present ($\text{CO}_2 + \text{HCO}_3^- + \text{CO}_3^{2-}$). With a complete titration curve and potentiometric determination of pH, total CO_2 can be calculated. CO_2 can also be measured by means of gas chromatography or infra-red detectors.

Calculation of the total **inorganic carbon** present in a body of water is also important because of the relationship of CO_2 to the processes of photosynthesis and respiration in the epilimnion and hypolimnion. In the case of slightly buffered water, the release of CO_2 in the hypolimnion significantly reduces pH. In general, the pH of water is related to its chemical properties, the **geochemistry of the water basin**, in addition to the effects of **biological processes** such as photosynthesis, respiration

and the decomposition of organisms. Hutchinson (1957) presented examples of **heterograde pH distribution** in lakes with slightly buffered water, in which ferrous and manganese ions balanced by bicarbonates accumulated in the hypolimnion within increase of bicarbonate alkalinity. Also, vertical distribution of **heterograde pH** can occur with an increase of pH in the metalimnion, as a result of an increased photosynthesis and removal of CO_2 in the layer.

Total alkalinity corresponds to the excess of cations compared with **strong anions**.

$$\text{Total alkalinity} = \text{HCO}_3^- + \text{CO}_3^{2-} + \text{OH}^- - \text{H}^+$$

Alkalinity resulting from boric acid, important in seawater, may be insignificant in fresh water. The interrelationship between total inorganic carbonate and alkalinity depends on the water's pH. Alkalinity – and thus total inorganic carbon – can be determined by the titration and displacement of weak acids (for example: HCO_3^- ; H_2BO_3^- ; H_3SiO_4^-) by strong acid (sulphuric or hydrochloric) up to a pH in which all inorganic carbon present has definitely been dislocated (usually in the pH range 2–3). Inorganic carbon levels can be determined, therefore, from the water's alkalinity. Table 5.16 presents a factor that can be used (multiplied by alkalinity, in $\text{meq}\cdot\text{L}^{-1}$) to determine the level of inorganic carbon (Margalef, 1983).

The term **hardness** or **degree of hardness** expresses the amount of carbonates, bicarbonates or sulphates present in water. Scales can be used to calculate hardness. For example, in the French scale, hardness is given in parts of CaCO_3 per 100,000 parts of water. Table 5.17 presents ratios (in percentage) between the main chemical forms of calcium and inorganic carbon.

5.6.2 Vertical distribution of CO_2

In lakes with a vertical temperature gradient and a clinograde curve of dissolved oxygen, CO_2 accumulates in the hypolimnion, which can result from metabolic activity. In part, bicarbonate increases due to the presence of $(\text{NH}_4)\text{HCO}_3$. Transport of bicarbonate by solution, from the sediment in the bottom, occurs more easily in **anaerobic sediment** than in aerobic sediments.

Vertical distribution of CO_2 in general accompanies the distribution of dissolved oxygen and the oxygen deficit. Ohle (1952) concluded that accumulation of CO_2 in the hypolimnion is a more accurate measurement of a lake's metabolism than the oxygen deficit.

Sedimentation of CaCO_3 , which occurs in some lakes with high rates of photosynthesis and elevated calcium levels, increases the CO_3^{2-} precipitating to the bottom of lakes, thus increasing the carbon available for photosynthesis. Introduction of calcium ions and bicarbonate in the lake (there is excess bicarbonate) produces the following reaction:

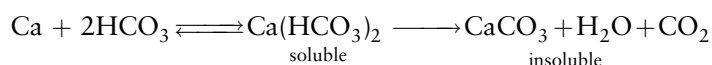


Table 5.16 Factor by which the alkalinity (in meq·L⁻¹) multiplies to obtain the total concentration of inorganic carbon (in mg·L⁻¹). Temperature 15°C. For lower temperatures, increasing 1% per degree, for higher temperatures, decrease at the same proportion.

<i>pH</i>	<i>Factor</i>	<i>pH</i>	<i>Factor</i>
6.0	44.16	8.0	12.60
6.5	22.08	8.2	12.12
7.0	17.16	8.5	12.00
7.5	14.04	9.0	11.64
7.8	12.96		

Source: Margalef (1983).

Table 5.17 Relationship (in %) between the principal species of calcium and inorganic carbon in sea water and in fresh water.

	<i>Sea water</i>	<i>Fresh water</i>
Free HCO ₃ ⁻	63–81	99.23
NaHCO ₃ ⁰	8–20	0.04
MgHCO ₃ ⁺	6–19	0.21
CaCO ₃ ⁺	1–4	0.52
CaO ₃ ²⁻	8–10	31.03
NaCO ₃ ⁻	3–19	0.03
MgCO ₃ ⁰	44–67	6.50
CaCO ₃	21–38	62.44
Free Ca ²⁺	85–92	96.89
CaSO ₄ ⁰	8–13	1.45
CaHCO ₃ ⁺	0.1–1	1.32
CaCO ₃	0.1–0.9	0.33

Sources: Atkinson *et al.* (1973); Hanor (1969); Pytkowicz and Hawley (1974); Garrels and Thompson (1962); Millero (1975a, b); Dyrssen and Wedborg (1974); Kester and Pytkowicz (1969).

Increased photosynthetic activity always produces increased insoluble CO₃²⁻, which precipitates to the bottom or remains in suspension.

When the dissolved oxygen curve is orthograde, so is the CO₂ curve. When vertical distribution of dissolved oxygen occurs with a clinograde curve, an inverse CO₂ clinograde curve also occurs. When a heterograde dissolved oxygen curve occurs, there is also an inverse vertical heterograde distribution of CO₂.

5.6.3 Respiratory quotient in lakes

The total **respiratory quotient** of lakes can be estimated by calculating the balance between dissolved oxygen produced by photosynthesis, the consumption of oxygen

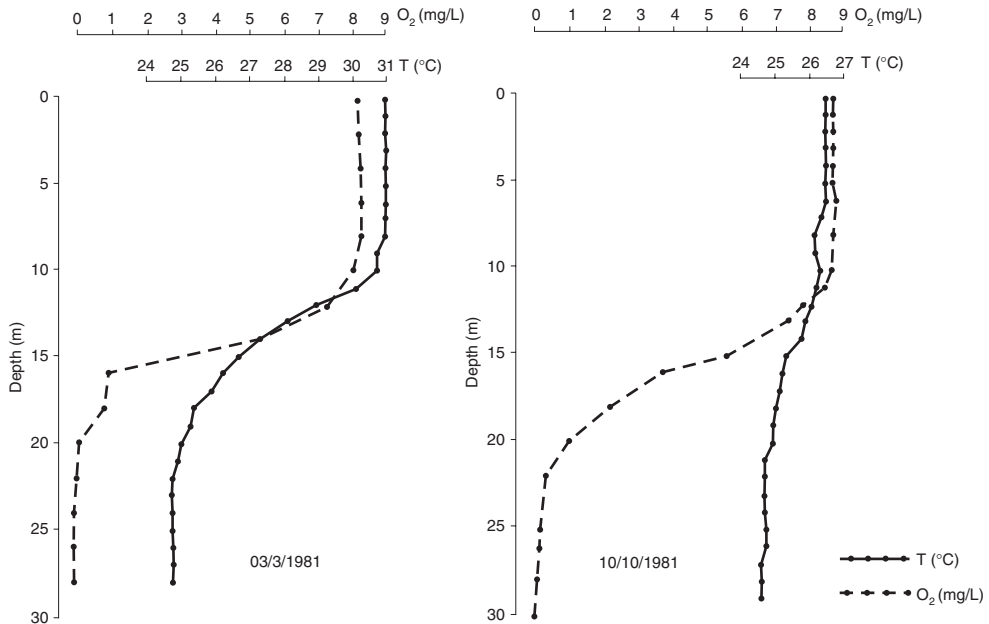


Figure 5.10 Vertical profile of dissolved oxygen in periods of thermal stratification in Lake Dom Hevécio (Parque Florestal do Rio Doce – MG).

for total respiration, and the amount of CO_2 produced by respiration. According to Hutchinson (1957), the metabolic $\text{CO}_2:\text{O}_2$ quotient is 0.85.

Calculating these relationships in a lake's metabolism is essential for studying the balance of gases, the interrelationship between photosynthesis and respiration, and interactions in the air-water interface.

Figure 5.10 presents the typical distribution of dissolved oxygen and water temperature in a stratified lake (warm monomictic lake) in summer.

5.7 SEASONAL AND DIURNAL VARIATIONS IN O_2 AND CO_2

Patterns of diurnal variation of dissolved O_2 and CO_2 gases, and their interrelationship with the processes of thermal stratification, nocturnal cooling and vertical circulation were described for several lakes, particularly focusing on the studies in tropical lakes by Talling (1957, 1969) Barbosa (1981), Ganf (1974), Ganf and Horne (1975), Hare and Carter (1984), and Melack and Fisher (1983).

Variations occurring in the epilimnion of lakes during the diurnal and nocturnal periods are related to the distribution of CO_2 through photosynthetic activity, increased pH and, in some cases, high levels of chlorophyll, an increase in dissolved O_2 that can reach high saturation values. Measurements of the processes of daily variations related to dissolved gases and modifications in thermal structure show that in some cases these changes are more significant than those occurring in the seasonal cycle.

In many shallow tropical lakes, increases in pH and supersaturation of O_2 , as well as depletion of O_2 and low pH during the nocturnal period, depends on the vertical

distribution of phytoplankton, periphyton and aquatic macrophytes. Wide variations also occur in regions with high levels of solar energy.

Studies by Ganf and Horne (1975) in Lake George (Uganda), a shallow equatorial lake with high levels of cyanophytes, illustrate these variations. Thermal stratification was present by day, with values of 10°C difference from a lake's surface temperature to its bottom temperature (maximum depth 2.50 m), along with the stratification of chlorophyll *a*, which, in the afternoon period (16 h), could be 100 mg · m⁻³ at the surface and 400 mg · m⁻³ on the bottom. During the nocturnal period, vertical distribution of chlorophyll remains homogeneous. In periods of intense thermal stratification (35°C), photosynthesis drops on the surface, along with increased respiration.

The **inhibition of photosynthetic activity** in conditions of intense solar radiation and high temperatures is a fairly common phenomenon in tropical lakes with reduced diurnal circulation.

Levels of dissolved O₂ and pH also fluctuated widely in Lake George. During the day, values of up to 250% saturation were found, with a pH up to 9.7, the result of intense photosynthesis. This shift in pH was accompanied by a reduction in total CO₂ from 70 to 49.5 mg · L⁻¹.

The study also identified fluctuations in the vertical distribution of photosynthesis and the point of optimum photosynthesis in the vertical profile. Diurnal fluctuations in photosynthetic activity and vertical distribution of high photosynthesis were also observed by Tundisi (1977) in the Lobo reservoir. Such fluctuations reflect alterations in the vertical distribution of CO₂ and O₂.

In a study on diurnal variations in water temperature, dissolved gases, chlorophyll and photosynthesis in the Carioca lakes (Parque Florestal do Rio Doce -MG), Barbosa (1981) found that during the months of greatest thermal stability (summer), chlorophyll is sharply stratified, with high levels in the hypolimnion, following thermal stratification. Small oscillations of dissolved oxygen in the epilimnion resulted from photosynthetic and respiratory activity. Diel variations in 24-hour cycles of oxygen and CO₂ were also described by Tundisi *et al.* (1984) for Lake Jacaretinga (Amazons) and Tundisi *et al.* (results unpublished) for Lake Dom Helvécio (Parque Florestal do Rio Doce - MG).

The diurnal O₂ and CO₂ cycles enable the calculation, based on variations in dissolved gases, of the community's photosynthetic production and respiration. Hourly measurements of dissolved gases coupled with thermal measurements allow calculations that provide approximate and valuable information on the cycles of O₂/CO₂, respiration/photosynthesis and metabolism in lakes (see Figure 5.11).

The diurnal balance between production of dissolved O₂ and consumption and production of CO₂ (i.e., photosynthesis and respiration) is also important for maintaining ecological stability in shallow lakes (Ganf and Viner, 1973). As Ganf and Horne pointed out in the case of Lake George, the seasonal variations occurring in temperate-zone lakes appear to have been compressed into a 24-hour cycle.

Seasonal variations in levels of dissolved oxygen and CO₂ depend on biomass levels, stratification and thermal de-stratification cycles, the seasonal inflow of precipitation, and the processes of advection. In warm monomictic lakes, a hypolimnion develops during the period of stratification, and a more uniform distribution of oxygen occurs during the circulation period. CO₂ accumulates in the hypolimnion during periods of intense stratification. High levels of other gases such as methane can also

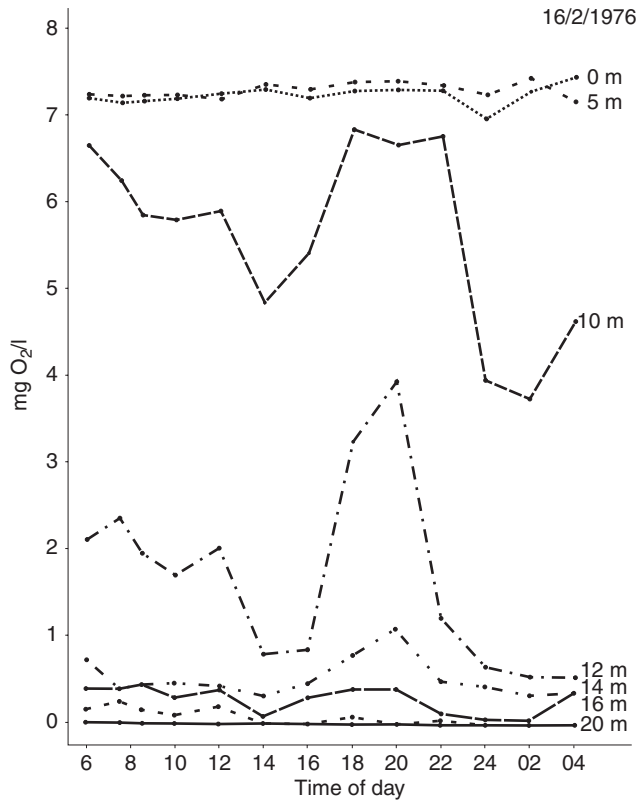


Figure 5.11 Diel variations in levels of dissolved oxygen in summer at various depths in Lake Dom Helvécio (Parque Florestal do Rio Doce – MG).

occur. Meromictic lakes have an anoxic hypolimnion, as well as high levels of methane and H_2S .

Polymictic lakes have high levels of dissolved oxygen during most of the seasonal cycle, with short periods of anoxia or reduced levels.

Seasonal variations of CO_2 and O_2 are thus related to the seasonal cycle of stratification, de-stratification and circulation, the vertical activity and distribution of organisms in different periods, and the lake's interactions with climatic factors such as precipitation and wind activity.

In a study of 80 diurnal cycles of dissolved oxygen in an **Amazon floodplain lake** (Lake Calado), Melack and Fisher (1983) concluded that the diurnal variation of dissolved oxygen in the lake showed the prevalence of respiration of organisms over phytoplankton photosynthesis. **Aerobic and anaerobic respiration** are important, producing oxygen depletion and significant quantities of reduced substances. After vertical mixing, the reduced substances cause oxygen levels to drop in the epilimnion. The main implication of this cycle is that the planktonic organisms of Lake Calado consume more oxygen than they produce by photosynthesis.

Floodplain lakes in the Amazon produce abundant amounts of organic matter. The predominance of respiration over production of oxygen by photosynthetic

activity explains why waters in these lakes are generally subsaturated with dissolved oxygen and supersaturated with carbon dioxide. According to Melack and Fisher (1983), plankton organisms in these lakes most likely use **allochthonous** organic matter as a source of energy. Inflow of atmospheric oxygen is the main source of dissolved oxygen in Lake Calado.

Scientific studies have shown evidence for sub-saturation of dissolved oxygen and anoxic hypolimnion in **lakes of the Amazon floodplain** (Schmidt, 1973; Santos, 1973; Marlier, 1967) and in the Negro River (Rai and Hill, 1981; Reiss, 1977), **Purus River** (Marlier, 1967) Tapajós River (Braun, 1952) and Trombetas River (Braun, 1952). Gessner (1961) also identified sub-saturation in the Negro River. In areas with high levels of organic matter, in floating aquatic forests, sub-saturation of oxygen is common (Junk, 1973).

5.8 OTHER GASES DISSOLVED IN WATER

Despite high atmospheric levels of N_2 , N_2 in water is almost chemically inert, and its gaseous cycle is much less significant compared with that of O_2 and CO_2 . In water, nitrogen is present in high amounts as a gas but is virtually inert. It is used only by organisms that can fix nitrogen, such as some cyanobacteria and bacteria. In some lakes and reservoirs, **biological fixation** of nitrogen is an important source of nutrient (in this case, nitrogen).

Methane (CH_4) gas is extremely common in the hypolimnion of permanently stratified lakes or lakes or with reduced circulation (see Chapter 10).

Levels of dissolved oxygen in reservoirs with submerged forests are extremely low (see Chapter 12).

Principles for measuring dissolved oxygen and CO_2 in the water

Calculations of the levels of O_2 and CO_2 in water are important ecologically and chemically and also from the experimental viewpoint as well, since the two gases are involved with the process of photosynthesis. These calculations can thus be used to quantify photosynthesis, primary production and respiration of aquatic plants and organisms in general.

Dissolved oxygen in water is generally estimated using the traditional Winkler method (which has undergone many technical modifications). Manganese sulphate and potassium iodide are added to the water in an alkaline medium. The oxygen in the water oxidizes the Mn^{2+} , which becomes Mn^{3+} , forming a complex. The amount of Mn^{3+} is proportional to the concentration of O_2 present. The manganese oxide complex is formed and settles to the bottom of the 250–300-ml amber bottle and is dissolved by the action of H_2SO_4 . The iodine released is equivalent to the concentration of dissolved O_2 and titration is done with thiosulphate sodium $Na_2S_2O_3$, using starch as indicator.

Total CO_2 and inorganic carbon can be calculated from the level of alkalinity of the water, which consists of adding a strong acid (usually H_2SO_4 or HCl) to the water sample and titrating until the pH reaches ~4–5.