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Introduction to the Chemistry of Natural Waters

The topic of *Aquatic Chemistry* (an expression coined by Werner Stumm and Jim Morgan[1] ca 1970 [1]) concerns the processes that control the composition of natural waters—oceans, lakes, rivers, wetlands, groundwaters, and atmospheric water. It focuses on chemical reactions at the earth surface but also necessarily deals with some geological, physical, biological, and ecological processes. In this introductory chapter, we provide an overview of some of the principal reactions and processes that will be examined in detail in the following chapters. But first we focus on the central character in this textbook, the water molecule, and examine its unusual properties and its cycling at the earth surface.

1.1 Water: Its Properties and Global Cycle

The properties of water have profound consequences for life on Earth. Water is very nearly a universal solvent and effectively transports dissolved chemical substances in the environment as well as within the cells and tissues of living organisms. Unlike most substances, water is denser as a liquid than as a solid, making ice float on the surface of lakes and oceans. The extremely high heat of vaporization of water allows the massive transport of latent heat to northern regions, making them habitable. The environmental relevance of the unusual properties of water is summarized in Table 1.1; the molecular basis of these properties is detailed in Section 1.1.1.

1.1.1 Physical and Chemical Properties of Water

A liter of liquid water was used to define the kilogram in the original metric system at the end of the eighteenth century. Definitions have changed, but 1 kg is the mass of 1 L of water at a temperature of 4 °C and a pressure of 1 atm. This liter contains 55.51 mol ($=3.34 \times 10^{25}$ molecules) of H_2O, which has a molecular mass of 18.015 g. The covalent bonds resulting from the sharing of the lone electrons from H atoms and the unpaired electrons from O make the water molecule very stable. It has a tetrahedral shape with the two bonding and the two non-bonding electron pairs from O at each corner and a mean H—O—H angle slightly above 100° (Figure 1.1). As the shared electrons are pulled toward the oxygen nucleus (which has +8 charges compared with +1 in the hydrogen nucleus) this geometry leads to a separation of electrical charge—i.e., the formation of an electrical

1 Werner Stumm (1924–1999). Swiss-American chemist. Professor Harvard University (1952–1969); Director Swiss Federal Institute of Aquatic Science and Technology (EAWAG) (1969–1992). James J. Morgan (1932–2020). Irish-American engineer. First PhD student of Stumm. Professor California Institute of Technology (1965–2000).

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Table 1.1 Physical Properties of Liquid Water.

Property	Comparison with Other Liquids	Environmental Relevance
Density	Maximum at 4 °C, decreases upon freezing	Prevents freezing of deep water and causes seasonal stratification
Melting and Boiling Point	Exceptionally high	Water exists in liquid form at the earth surface
Heat Capacity	Highest heat capacity of all liquids with exception of NH_3	Moderates temperature extremes
Heat of Vaporization	Extremely high	Moderates temperature extremes
Surface Tension	High	Drop formation in clouds and rain
Light Absorption	High in infrared and UV range, moderate in visible range	Clouds can block sunlight from the Sun, and cool the earth but they can also trap heat and warm the earth
Solvent Properties	Because of dipolar properties excellent solvent for salts (ions) and polar molecules	Transport of dissolved substances in hydrological cycle and in biological systems

Source: Modified from [2] and [3].

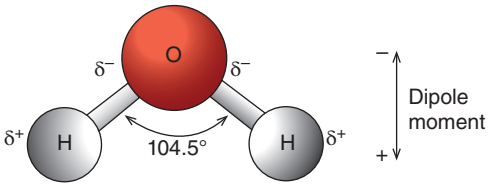

Figure 1.1 Shape of the water molecule with an H-O-H angle of 104.5° and the dipole moment with partial negative charge on O and partial positive charge on H. Source: A-Level. Biology/alevelbiology.co.uk.

dipole with a partial negative charge on the oxygen and a partial positive charge on the hydrogens (Figure 1.1). The attractive dipole–dipole interactions among water molecules, which are known as *hydrogen bonds*, are much weaker than covalent bonds (23.3 kJ mol^{-1} vs. 470 kJ mol^{-1}) but strong enough to organize water molecules in liquid water and even more so in ice (Figure 1.2). The net result is the unusual properties of water listed in Table 1.1, which are critical to geochemical cycles and life on our planet.

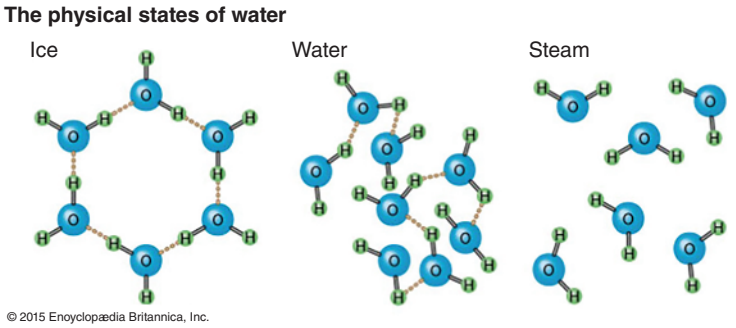

Figure 1.2 Water molecules in ice, water, and vapor. Source: from Encyclopedia Britannica [4] with permission.

Hydrogen bonds are the reason ice floats at the surface of water bodies during the winter at high latitudes, allowing the survival of aquatic life and the spring thaw. The structure of liquid water is controlled by a balance between thermal motion, which makes individual molecules occupy an average volume that increases with temperature and H-bonding that links them to each other. At room temperature, water molecules are moving in all directions, constantly breaking and making new H-bonds (Figure 1.2). As the temperature cools, thermal motion decreases, and the density of water increases like that of other liquids. At 4 °C, water molecules are bound in large dense clusters, and there are on average 33.4 water molecules per nm^3. In ice the thermal motion of water molecules becomes negligible, and the structure is completely and rigidly determined by H-bonding. The ordinary ice crystal on earth (known as I_h ice) is composed of crinkled planes of hexagonal rings of oxygen (Figure 1.2) with each water molecule H-bonded with three other water molecules in the same plane and one in an adjacent plane. The result is a relatively open structure with only 30.7 water molecules per nm^3 and a density of 0.92 g cm^{-3}, nearly 10% lighter than 4 °C water. Between 4 °C and 0 °C the formation of an increasing number of ice-like hexagonal rings of H-bonded water molecules leads to a very small increase in volume and a corresponding decrease in the density of liquid water (Figure 1.3). Both liquid water and ice equilibrate with water vapor (Figure 1.4). At atmospheric pressure and a comfortable ambient temperature of 25 °C liquid water is at equilibrium with a partial pressure of about 3×10^{-2} atm of water vapor (point A on Figure 1.4) while at the less comfortable temperature of −20 °C ice is at equilibrium with only 10^{-3} atm of water vapor (point B on Figure 1.4). Air is usually undersaturated with water and vapor pressure is traditionally reported as relative humidity, the ratio of the ambient vapor pressure to that at equilibrium with liquid water or ice at the ambient temperature.

As a result of their electrical dipole properties, water molecules organize themselves around electrically charged molecules—O toward cations and H toward anions—dramatically decreasing their electrostatic interactions with other charged molecules. This makes water an excellent solvent for ionic solids. For example, in dilute solution, the sum of the electrostatic interactions between water molecules and the ions Na^+ and Cl^- ends up being stronger than that between Na^+ and Cl^- in solid

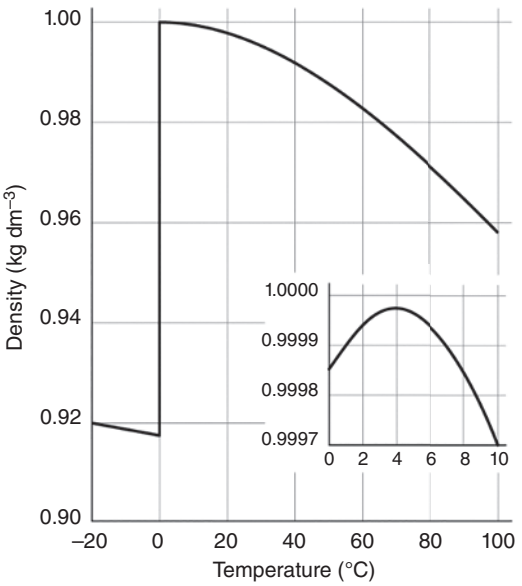

Figure 1.3 Water density (at 1 atm) as a function of temperature. Source: Adapted from [5].

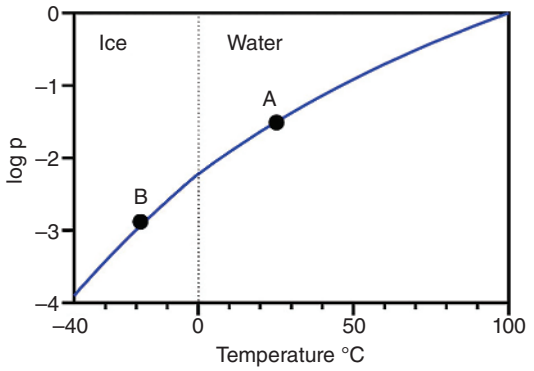

Figure 1.4 Vapor pressure (p, atm) over ice and over water as a function of temperature. Source: Adapted from [6].

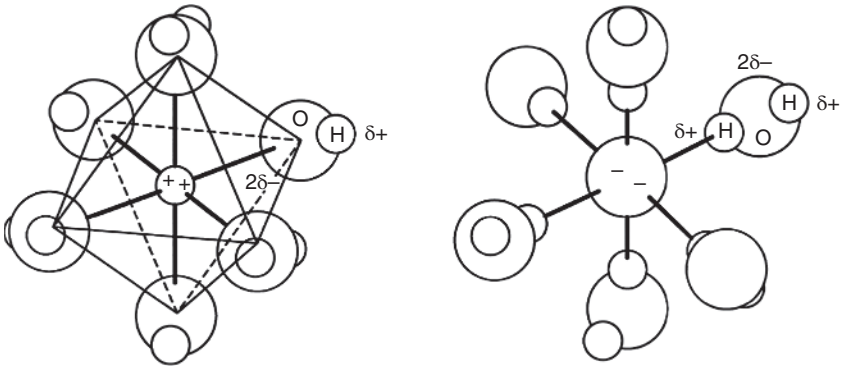

Figure 1.5 Hydrated divalent cation and anion.

NaCl, resulting in the dissolution of the salt. In dilute solutions, many ions have six water molecules in their inner coordination sphere, $Na(H_2O)_6^+$, $Cl(H_2O)_6^-$ (Figure 1.5) or $Ca(H_2O)_6^{2+}$, while some like silver have only four, $Ag(H_2O)_4^+$. The number of water molecules in the inner coordination sphere of complex ions such as sulfate is poorly known, $SO_4(H_2O)_n^{2-}$. The abbreviated notation Na^+, Cl^-, Ca^{2+}, Ag^+, and SO_4^{2-} implicitly comprises the coordinated water molecules. In addition to those that are effectively bonded to the central ion, up to dozens of more distant water molecules are organized around it as a result of electrostatic interactions. For the same reason, water is also a good solvent for organic compounds that contain electrically charged moieties such as amino acids and nucleic acids and their polymers, even when they have no net charge. *Polar molecules*, which have an uneven distribution of electrons between covalently bonded atoms, are also soluble in water.

In liquid water, H_2O molecules are very stable as a result of hydrogen bonding. Nonetheless, at any point in time a very small number of them (about two in a billion in pure water) become *hydroxide ions*, OH^-, by losing the nucleus of one of their hydrogen atoms which is captured by another water molecule to become a *hydronium ion*, H_3O^+:

$$H_2O + H_2O \rightleftarrows H_3O^+ + OH^- \tag{1.1}$$

As will be seen this dissociation of water (also called self-ionization of water) is a fundamental aspect of all aqueous solutions including natural waters. For simplicity in this text we omit the

water in the formula of the hydronium ion and usually refer to H^+ as a proton or a hydrogen ion. The reaction of the dissociation of water is then written as:

$$H_2O \rightleftarrows H^+ + OH^- \tag{1.2}$$

Natural waters have properties that are not identical to those of pure water as a result of their dissolved constituents and suspended particles. Freshwaters in which the total concentration of dissolved material remains relatively low have physical properties that differ only slightly from those of pure water. For example, the freezing point decreases by less than 0.04 °C at a concentration of NaCl = 0.01 M. The situation is different for waters with high solute concentrations. In particular, seawater, which accounts for the bulk of water at the earth surface and contains a mean salt concentration of about 36 g L^{-1}, has properties that are significantly different from those of pure water. For example, seawater density is about 1.024 g cm^{-3} at the surface at 25 °C (for a typical salt content of 3.5% by mass) and keeps increasing with decreasing temperature until it freezes at −1.9 °C. Despite the very high pressure encountered near the ocean bottom, the density increases only slightly, e.g., by 1.5% at 4,000 m, the average depth of the Pacific Ocean. Because salt is released from seawater when it freezes, sea ice is not fundamentally different from freshwater ice and floats on high-latitude oceans.

1.1.1.1 The Global Water Cycle

The hydrologic cycle is driven by solar radiation, the primary energy input to the earth surface. Only about half of the incoming solar radiation, which is in the visible and near UV range, is absorbed by the earth surface (ca 160 Wm^{-2}); the rest is either absorbed in the atmosphere or reflected by clouds and the surface of the earth. But the efficient absorption and re-emission of the infrared emission of the earth surface by the blanket of greenhouse gases, chiefly water and CO_2, greatly increases the energy absorbed (and re-emitted) at the surface, for total of about 500 Wm^{-2}. Seventeen percent of that energy is used to evaporate water. As seen in Figure 1.6, the yearly amount of water that is evaporated and precipitated is about 40 times the amount in the atmosphere but only 0.1% of what is at the surface of the earth. About a tenth of the water evaporating from the sea surface ends up in rain and snow at the surface of continents, of which two-third is re-evaporated or transpired by

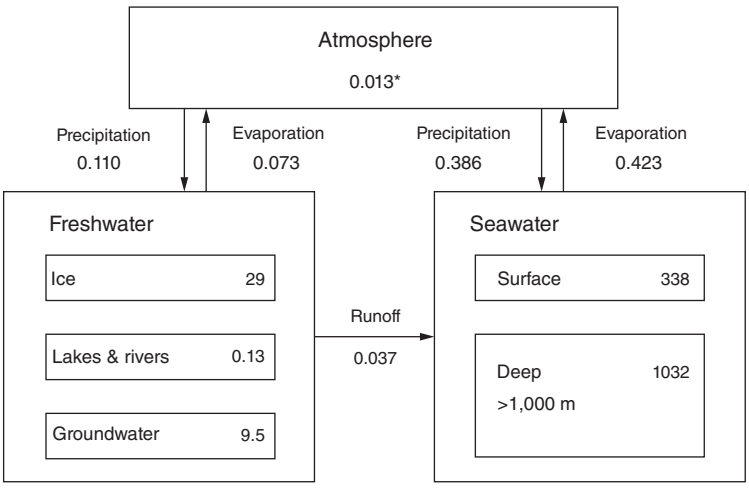

Figure 1.6 The hydrologic cycle: distribution of water among atmospheric, freshwater, and seawater reservoirs and fluxes between reservoirs. Units: fluxes in 10^6 km^3 yr^{-1}; inventories in 10^6 km^3. The atmospheric inventory (starred value) is reported as the liquid equivalent of water vapor.

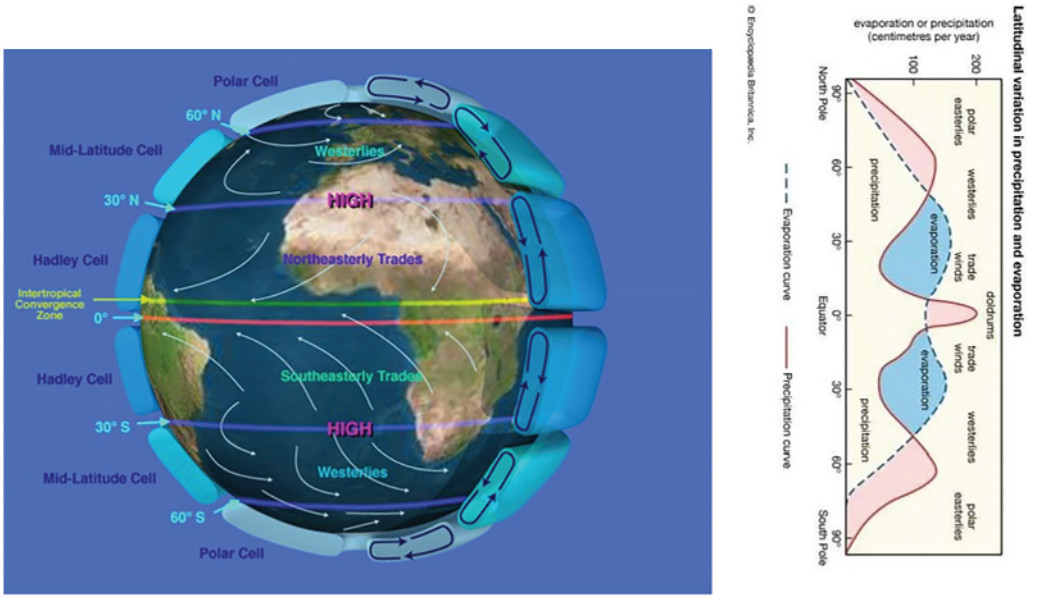

Figure 1.7 A simplified view of wind patterns (NASA depiction of earth global atmospheric circulation.jpg - Wikimedia Commons) and of precipitation as a function of latitude. Source: [4]/Encyclopedia Britannica.

plants and one-third is returned to the oceans by rivers (Figure 1.6). Almost all water on earth is salt water in the oceans, and nearly 80% of freshwater is in polar ice. As land-bound organisms, we are greatly dependent on the tiny fraction that falls as rain or snow and is stored on continents at relatively low latitudes.

The distribution of precipitation on earth is controlled by evaporation and the movement of air masses, both of which depend on temperature and wind. The maximum evaporation occurs near the tropics, decreasing to near zero at the poles (Figure 1.7). Between the tropics, atmospheric water is transported toward the equator (and westward) by trade winds, while outside the tropics it is transported toward the poles (and eastward) by westerlies (Figure 1.7). The net result is very high precipitation near the equator, a prevalence of deserts around latitudes of 30° north and south, and abundant rainfall in mid-latitudes.

1.2 Chemical Processes in Natural Waters

In this text we examine what chemical elements and compounds are present in natural waters and the processes that determine their concentrations and their chemical forms. The chemical composition of a body of water—i.e., the concentrations of the *chemical species* that are present in it—is controlled by chemical reactions in the water, by interactions with the atmosphere and the solid earth, and, directly and indirectly, by the biota and human activities.

1.2.1 Water and CO_2: Acid–Base Reactions

Our atmosphere is made up mostly of N_2 (78%), O_2 (21%), and Ar (0.93%) plus a variable amount of water vapor. But it is CO_2 that will receive much of our attention in this text, although it accounts

for only 0.04% of our air. This is because $CO_2(g)$ dissolves readily in water to produce $CO_2(aq)$, which reacts with water to form bicarbonate, HCO_3^-, carbonate, CO_3^{2-}, and hydrogen, H^+ ions.

$$CO_2(g) \rightleftarrows CO_2(aq) \tag{1.3}$$

$$CO_2(aq) + H_2O \rightleftarrows HCO_3^- + H^+ \tag{1.4}$$

$$HCO_3^- \rightleftarrows CO_3^{2-} + H^+ \tag{1.5}$$

1.2.2 The Global Carbon Cycle

Taking a synoptic view of the exchange of carbon among different compartments at the earth surface averaged over time and the interconversion among the different chemical forms of carbon allows us to understand the relative importance of various natural processes and human activities (Figure 1.8, global carbon cycle). The great bulk of carbon at the earth surface (99.94%) is contained in rocks and sediments and only 0.001% in the atmosphere. The yearly uptake of carbon from the atmosphere by photosynthesis and its release into the atmosphere by respiration are roughly equal over the sea and land surfaces even though the carbon in living matter in the sea is a small fraction of that on land. This reflects the very fast turnover of planktonic biomass. On land, about half of CO_2 taken up by plants is respired back by them into the atmosphere; the other half is stored in soil, peat, and litter before being respired by microorganisms and returned to the atmosphere. In the oceans, most of the CO_2 fixed into biomass is recycled in the surface ocean; only 10% is exported to the deep ocean as detritus and only about 0.1% is buried in the sediments.

Carbon inventories in the hydrosphere are divided into inorganic and organic carbon with inorganic carbon (i.e., CO_2 (aq), HCO_3^-, and CO_3^{2-}) being vastly more abundant. Importantly, the largest carbon fluxes involve transfer to and from one of the smallest reservoirs, the atmosphere.

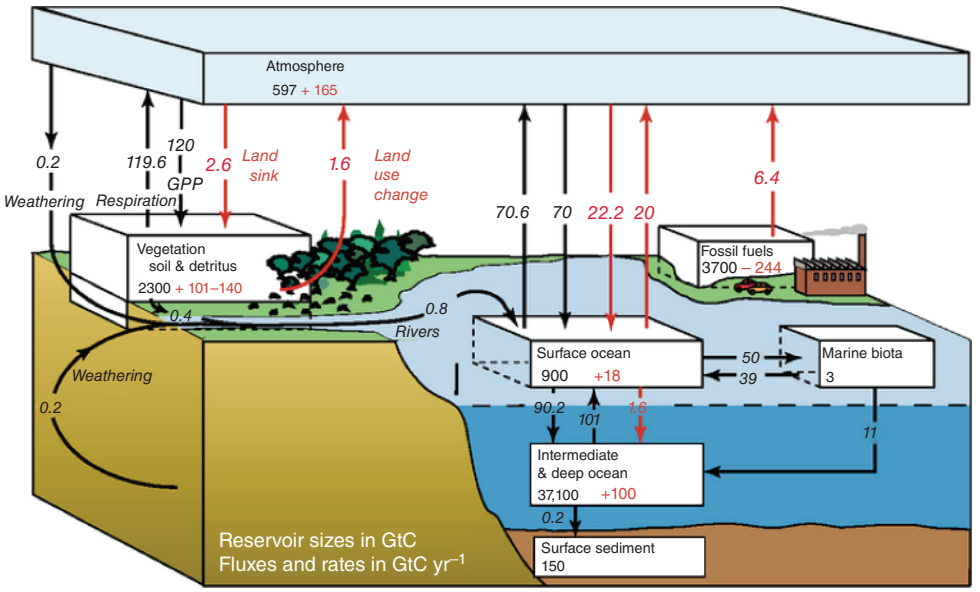

Figure 1.8 Global carbon cycle. Mean annual fluxes in GtC/year and reservoirs in GtC. The fluxes in black are the natural preindustrial fluxes, the fluxes in red are caused by human activities. A large contribution to the C reservoir in the atmosphere is the flux from fossil fuels, leading to the large increase of CO_2 in the atmosphere. Source: [7]/Intergovernmental Panel on Climate Change (IPCC)/Public domain.

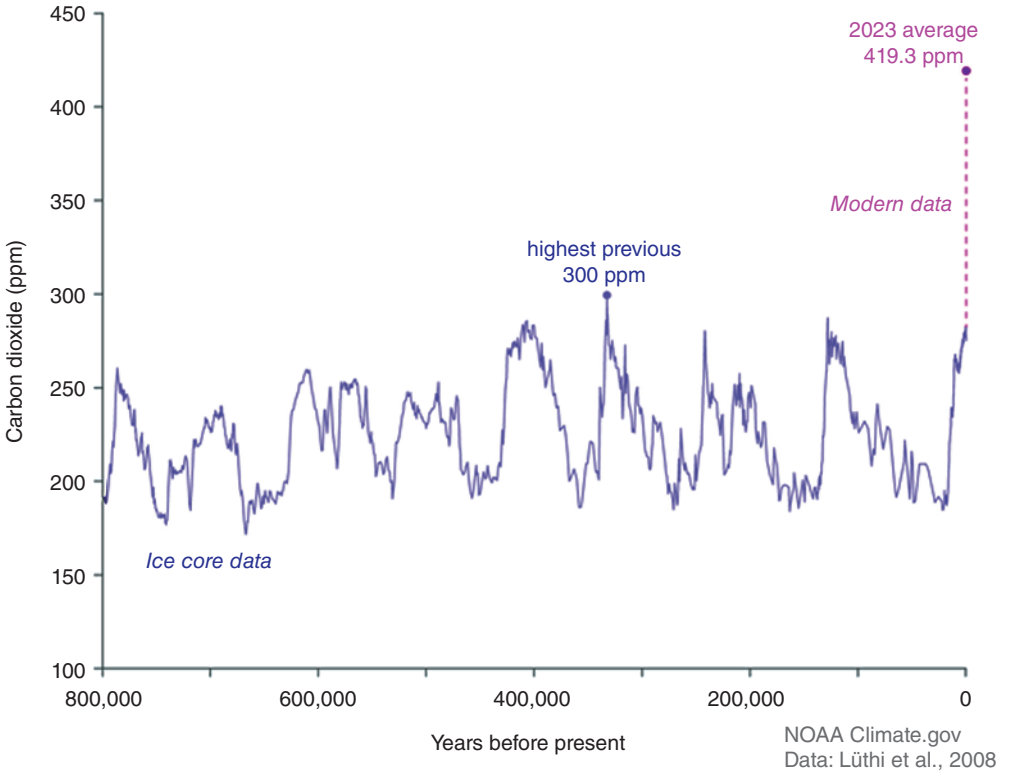

Figure 1.9 Carbon dioxide in the atmosphere over 800,000 years before present (from ice cores) and the modern data. Source: NOAA, Global climate dashboard [8], Lüthi et al. [9].

The residence time of carbon in the atmosphere, defined as its inventory divided by the flux, is on the order of only a few years. Human activities such as fossil fuel combustion and deforestation have resulted in large net emissions of CO_2 to the atmosphere. About half of this CO_2 remains in the air, resulting in a steady increase in concentration which began in the mid-1800s and accelerated rapidly in the twentieth century (Figure 1.9). The other half of our CO_2 emissions are in about equal proportions taken up by vegetation and soils and dissolved into the surface ocean, making it more acidic as will be discussed in later chapters.

1.2.3 Weathering Processes: Water, CO_2, and Minerals

Rainwater on land percolates through the soil and reacts with minerals in the rocks near the surface. These *weathering reactions* provide the solutes to natural waters. A few minerals like the relatively rare halite (NaCl) dissolve readily (up to >1 M), and others like gypsum ($CaSO_4 \cdot 2H_2O$) and the very abundant silica (SiO_2) more sparingly (up to 0.01 M):

$$NaCl \rightleftarrows Na^+ + Cl^- \tag{1.6}$$

$$CaSO_4 \cdot 2H_2O \rightleftarrows Ca^{2+} + SO_4^{2-} + 2H_2O \tag{1.7}$$

$$SiO_2 + H_2O \rightleftarrows H_2SiO_3 \tag{1.8}$$

The dissolution of many minerals requires a source of hydrogen ions, often CO_2 (reactions 1.4 and 1.5) or organic acids. This is the case for some abundant minerals such as calcium carbonate, $CaCO_3(s)$:

$$CaCO_3(s) + H^+ \rightleftarrows Ca^{2+} + HCO_3^- \tag{1.9}$$

and iron hydroxide $Fe(OH)_3(s)$, which is only sparingly soluble:

$$Fe(OH)_3(s) + H^+ \rightleftarrows Fe(OH)_2^+ + H_2O \tag{1.10}$$

The dissolution of halite, gypsum, or calcium carbonate releases the free cation (i.e., Na^+ or Ca^{2+}) into solution, but this is not the case for iron hydroxide. As will be discussed in Chapter 5 the hydrolysis of Fe^{3+} (e.g., to form $Fe(OH)_2^+$, as shown in Eq. (1.10), and other hydroxide complexes), influences the extent of solid dissolution.

The weathering of aluminosilicates, which are, along with silica, the most abundant minerals in the earth crust, often occurs through an *incongruent* reaction, leading to the formation of a new mineral. For example, the weathering of sodium feldspar (albite) $Na_2O{\cdot}Al_2O_3{\cdot}6SiO_2$ (s) often leads to the formation of kaolinite $Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$ (s)

$$Na_2O{\cdot}Al_2O_3{\cdot}6SiO_2(s) + 2H^+ + 5H_2O \rightleftarrows 2Na^+ + Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O(s) + 4H_2SiO_3 \tag{1.11}$$

These reactions and similar ones contribute the bulk of solutes to aquatic systems. **To a first approximation, the composition of natural waters can thus be viewed as resulting from the combined action of H_2O and acidic CO_2 that dissolves minerals in the earth crust.** We will see in the following chapters how the concentrations of major cations, Ca^{2+}, Mg^{2+}, Na^+, and K^+, and anions, HCO_3^-, Cl^-, and SO_4^{2-}, can be quantified on the basis of such reactions. As illustrated in Figure 1.10 the positive charge from the cations must necessarily be balanced by the negative charge from the anions:

$$\begin{aligned} &2[Ca^{2+}] + 2[Mg^{2+}] + [Na^+] + [K^+] + \text{minor cations} \\ &\quad = \left[HCO_3^-\right] + [Cl^-] + 2\left[SO_4^{2-}\right] + \text{minor anions} \end{aligned} \tag{1.12}$$

where the brackets indicate the molar concentrations (M or mol L^{-1}) of the various ions.

The major ion composition illustrated in Figure 1.10 is typical of a surface water in contact with carbonate rocks. The major ion composition of some of the large rivers of the world and of seawater is given in Table 1.2. The concentrations of the major cations and anions reflect the varying geology

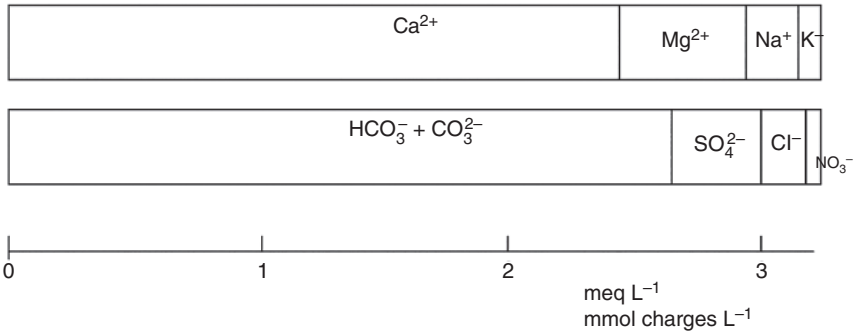

Figure 1.10 Charge balance of cations and anions in a surface freshwater.

Table 1.2 Chemical composition of large rivers and seawater.

River	Mississippi	Amazon	Congo	Yangtze	Rhine	Lena	World	Seawater
Site	Belle chasse	Obidos	Brazzaville	Datong	Bimmen	Kusur	average	
pH	7.90	6.75	6.4	8.00	8.20	7.61		8.10
Ca^{2+} m*M*	1.04	0.17	0.05	0.88	2.03	0.34	0.30	10
Mg^{2+} m*M*	0.53	0.05	0.06	0.31	0.49	0.14	0.12	55
Na^{+} m*M*	1.20	0.10	0.05	0.47	2.74	0.27	0.24	500
K^{+} m*M*	0.09	0.03	0.04	0.07	0.13	0.01	0.04	10
HCO_3^- m*M*	2.49	0.41	0.18	1.95	3.99[a)]	0.80	0.80	2.4
Cl^- m*M*	0.84	0.06	0.03	0.36	2.50	0.24	0.17	565
SO_4^{2-} m*M*	0.45	0.03	0.01	0.32	0.64	0.09	0.09	29
Si m*M*	0.13	0.13		0.13	0.08	0.06	0.15	0.04–0.16
References	[14]	[15]	[16]	[17]	[18]	[19]	[20]	[21]

a) Calculated from the ion balance.

of the catchments. For example, the Mississippi, Yangtze, and Rhine rivers are representative of rivers with calcium carbonate rocks in their catchment. In contrast, the large rivers in tropical regions Amazon and Congo have low Ca and carbonate concentrations. The northern Lena river drains a large basin with a variety of rocks that include carbonates, evaporites (NaCl, $CaSO_4$), and aluminosilicates. In many rivers the concentrations of ions such as Na^+ and Cl^- are influenced by anthropogenic inputs. The concentration of silicate, which is provided by weathering of silicate minerals and limited by the solubility of silica (SiO_2(s)), is quite similar in many rivers. The world average in the table corresponds to the weighted mean of river discharges into the oceans. As can be seen, seawater is not simply concentrated river water; for example, the concentration of Cl^- in seawater is 3,000 times greater than the mean river concentration, while the corresponding ratio for Ca^{2+} is only a factor of 30.

1.2.4 Interactions Between Organisms and Water: Photosynthesis and Respiration

As mentioned above, the chemical compositions of natural waters and the atmosphere are not simply determined by (abiotic) chemical reactions but also by the direct and indirect action of the organisms on the earth surface. The most consequential role of life can be described by the opposing processes of photosynthesis (P), which results in the formation of organic matter and oxygen, and respiration (R), which consumes them. Biomass is formed from CO_2 and H_2O mainly by photosynthetic organisms, including plants and phytoplankton using sunlight as a source of energy. Conversely "burning" of the biomass by the respiration of heterotrophic organisms including bacteria and animals as well as plants and phytoplankton oxidizes the organic matter back to CO_2 and H_2O. While photosynthesis and respiration are accomplished by biochemical pathways involving many biochemical reactions and intermediates, the overall processes can be symbolized by the reaction:

$$CO_2 + H_2O \underset{R}{\overset{P}{\rightleftharpoons}} \{CH_2O\} + O_2 \tag{1.13}$$

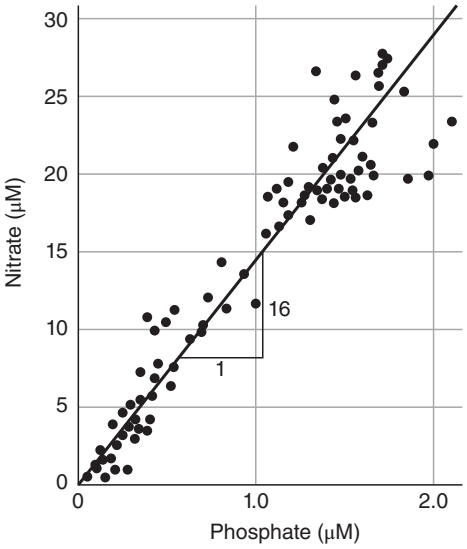

Figure 1.11 Stoichiometric ratio of the nitrate and phosphate concentrations in the Atlantic Ocean (molar N : P = 16). Source: Adapted from [10].

where $\{CH_2O\}$ represents organic matter with the rough 1 : 2 : 1 stoichiometric ratio of carbon, hydrogen, and oxygen (as in the simple sugar glucose $C_6H_{12}O_6$). But life requires more than these three elements and more complete reactions can be written by including the major nutrients nitrogen and phosphorus, here in the form of nitrate, NO_3^-, and phosphate HPO_4^{2-}:

$$106CO_2 + 16NO_3^- + HPO_4^{2-} + 18H^+ + 122H_2O \underset{R}{\overset{P}{\rightleftharpoons}} \{C_{106}H_{263}O_{110}N_{16}P\} + 138O_2 \qquad (1.14)$$

Organic matter also incorporates major ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, and SO_4^{2-}) as well as a number of essential trace elements such as Fe and Zn.

The stoichiometry of algal biomass—i.e., the 106 : 16 : 1 mol ratio of C, N, and P—in this reaction is known as the Redfield ratio, in honor of Alfred Redfield[2] who first observed that the utilization of C, N, and P by marine phytoplankton followed fairly constant proportions and resulted in the simultaneous disappearance of N and P from surface seawater (Figure 1.11). While significant variations in the composition of algal biomass have been documented, the stoichiometry of reaction (1.14) provides an extremely convenient way to quantify the effects of the growth of aquatic organisms on the chemistry of the ambient water. The C, N, P compositions of freshwater phytoplankton are not fundamentally different from those of marine phytoplankton. But the ratio of N to P in the water column of lakes is influenced by additional processes, such as the release of P from sediments and the conversion of nitrate to N_2 by denitrification, making it more difficult to relate changes in the composition of the ambient water to algal growth.

1.2.5 The Global Nitrogen Cycle

The nitrogen cycle (Figure 1.12) illustrates that quantifying the reservoirs and fluxes of the total mass of an element is insufficient to comprehend the processes governing its cycles.

2 Alfred C. Redfield (1890–1983). Professor Harvard University (1921–1956) and Senior Scientist Woods Hole Oceanographic Institution (1930–1956).

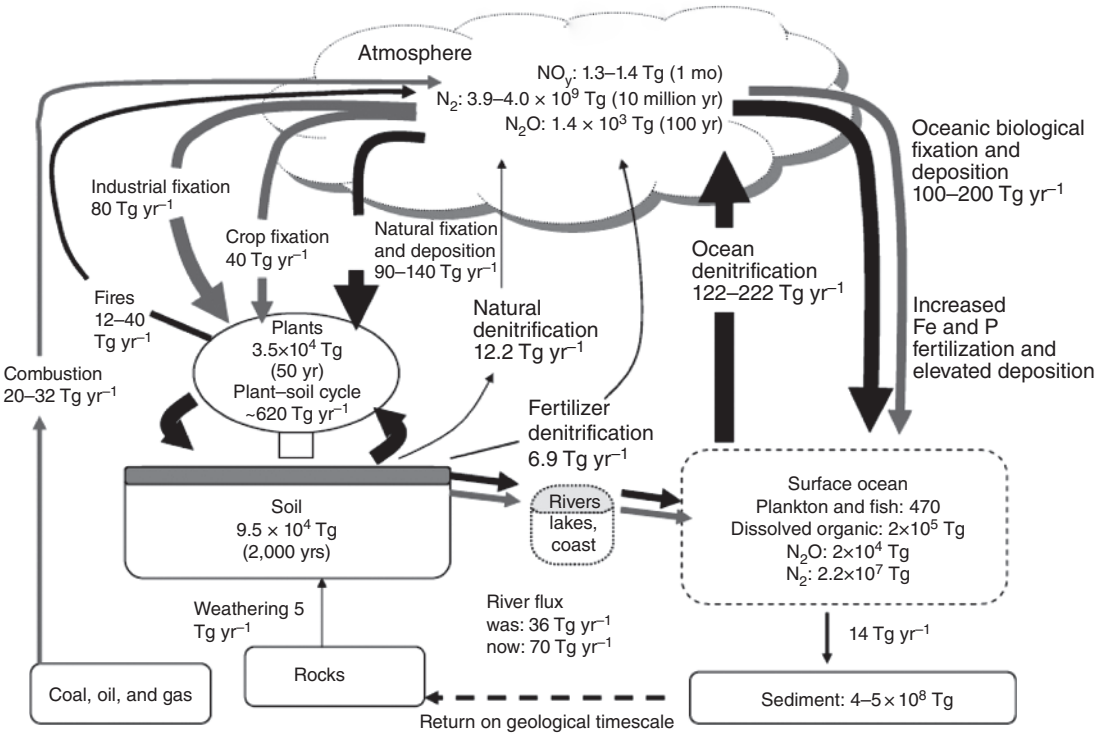

Figure 1.12 Global nitrogen cycle as modified by human activities. Pools are in Tg N (10^{12} g N) and fluxes in Tg N/year. The turnover times in the pools are also given. Black arrows indicate the natural fluxes, such as natural N_2 fixation by microorganisms in plants and in plankton in the oceans. Gray arrows represent the fluxes influenced by human activities, in particular the industrial N_2 fixation and the input of NO_x to the atmosphere by combustion processes. N_2 is returned to the atmosphere by denitrification processes in soils and in the oceans. Source: [11]/Millenium ecosystem assessment.

Several forms of inorganic nitrogen, such as dinitrogen (N_2), nitrate (NO_3^-)and ammonia (NH_3), must be considered separately because of their very different biological availabilities, chemical reactivities, and volatilities. Note that the cycling (or interconversions) of these different chemical species within a given global reservoir is not included. In this case, a great deal of information would be lost if only the conservation of elemental nitrogen were considered.

The largest reservoir is that of dinitrogen gas, N_2, in the atmosphere, which is about a million times larger than the next reservoir, that of organic matter in soils. N_2 in the atmosphere is not available to most organisms and its fixation into bioavailable N (e.g., nitrate and ammonium) is effected in about equal proportions by specialized nitrogen-fixing microorganisms and the industrial production of fertilizers.

1.2.6 The Global Phosphorus Cycle

The global cycle of P is different from that of C and N because P is not produced during fossil fuel combustion, and most phosphorus species are not volatile (Figure 1.13). This does not mean that the phosphorus cycle is unperturbed by human activity. On the contrary, the mining of phosphate rock, the application of phosphate fertilizer in agriculture, and the runoff of the excess fertilizer into rivers and oceans are a very important part of the modern P cycle.

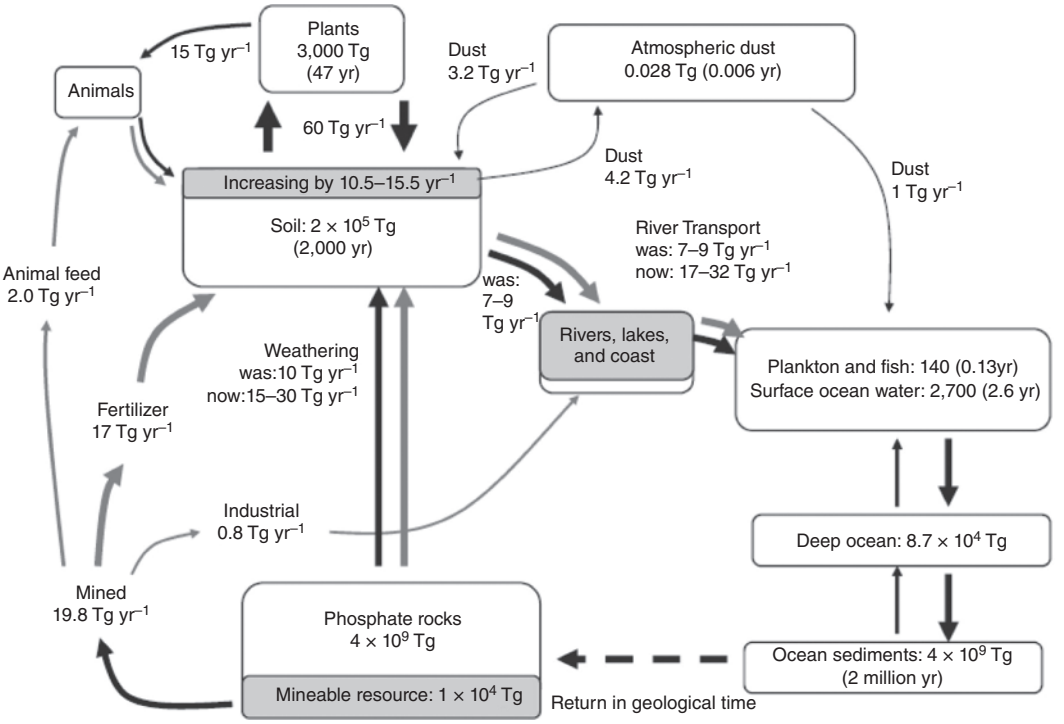

Figure 1.13 Global phosphorus cycle. Pools are in Tg P, fluxes in Tg P/year. The major fluxes are weathering and mining of phosphate rocks and the use of P as a fertilizer for plants, which leads to increase of P in soils and in rivers and lakes. Source: [11]/Millenium ecosystem assessment.

1.3 Conservation, Thermodynamics, and Kinetics

Our purpose in this text is not just to describe the processes that control the chemistry of natural waters but to provide a quantitative explanation for the concentrations of chemical species in a particular water body and predict how they will change in response to natural and human induced perturbations. For this purpose, we shall make use of three types of equations that relate or constrain the concentrations of chemical species in any system: *mole balance equations*, *mass law equations*, and *kinetic rate laws*.

The conservation of chemical elements is one constraint on their global cycling as illustrated in Figures 1.8, 1.12, and 1.13. The inputs of any element in any reservoir such as the atmosphere or the ocean must be balanced by its outputs if the system is at steady state. An imbalance between inputs and outputs leads to the accumulation (or depletion) of an element in a reservoir as is the case for C in the atmosphere due to fossil fuel emissions and deforestation. Conservation also applies to chemical reactions which we need to *balance* for each element involved and also for electrical charge. When chemical species react with each other in a closed system without inputs or losses, the conservation principle applies to *chemical components* and is expressed in *mole balance equations*. For example, in the absence of sources or sinks, such as photosynthesis and respiration or exchange with the atmosphere or sediments, the total concentration of dissolved inorganic carbon species (C_T) must remain constant, even if the relative concentrations of individual carbonate species change in response to environmental conditions:

$$[CO_2(aq)] + \left[HCO_3^-\right] + \left[CO_3^{2-}\right] = C_T = \text{constant} \tag{1.15}$$

Many reactions in aquatic systems are sufficiently fast that they reach equilibrium (i.e., there is no net reaction in either direction) over a time scale that is relevant to the perturbation of the system, for example, by biological processes, chemical weathering, or anthropogenic inputs. The important reaction of formation of bicarbonate from CO_2 in solution reaches equilibrium within minutes

$$CO_2(aq) + H_2O \rightleftarrows HCO_3^- + H^+$$

At equilibrium the concentrations of reactants and products obey the *mass law equation*:

$$\frac{[HCO_3^-]\,[H^+]}{[CO_2]} = K_{a1} \tag{1.16}$$

where K_{a1} is an *equilibrium constant* that depends on temperature. Note that, in this case, the equilibrium constant has dimensions of mol L^{-1} and that the solvent, H_2O, is not included explicitly in the mass law equation.

Equilibrium can also describe the relation between the mean concentrations of chemical species in solution and in the gas phase over some time scale. For example, when averaged over a period longer than a day the concentration of CO_2 in surface water is often proportional to its partial pressure in the atmosphere, P_{CO_2}:

$$CO_2(g) \rightleftarrows CO_2(aq)$$

$$\frac{[CO_2(aq)]}{P_{CO_2}} = K_H \tag{1.17}$$

where P_{CO_2} is expressed in atm (1 atm = 101.3 kilopascals) and the Henry's law constant, K_H, quantifies the solubility of the gas in mol L^{-1} atm^{-1} (=M atm^{-1}).

Partial pressures of gases in the atmosphere are proportional to their mole fraction, n_{gas}/n_{total}, following Dalton's law:

$$P_{CO_2} = \frac{[n_{CO_2(g)}]}{n_{total}} P_{atm} \tag{1.18}$$

where n_{CO_2}/n_{total} is the mole fraction of CO_2. and the atmospheric pressure, P_{atm}, is equal to the sum of the partial pressures of all the gases in dry air:

$$P_{atm} = P_{N_2} + P_{O_2} + P_{Ar} + P_{CO_2} + \cdots \tag{1.19}$$

It is, however, often the case that the partitioning of CO_2 between the gas phase and aqueous solution is not at equilibrium. This calls for a *kinetic* description of the transfer of CO_2 between the atmosphere and surface waters.

$$CO_2(g) \rightleftarrows CO_2(aq)$$

As shown in Figure 1.14, the net daily consumption of CO_2 by photosynthesis in sunlit surface waters in the summer exceeds its production by respiration in the dark, while the reverse occurs in the winter. The net result is an annual cycle of the weekly mean CO_2 concentration in the water, which is undersaturated in the summer compared with atmospheric CO_2 and supersaturated in the winter. While CO_2 equilibrium between the atmosphere and the water surface would be a good assumption for the mean condition over a year ($P_{CO_2} \sim 400$ μatm), a kinetic description of the changes in CO_2 concentration is necessary on a shorter time scale. This is made possible by a mathematical expression of the rate of transfer of CO_2 across the air–water interface. (Note that, over a time scale of hours or less, a diurnal cycle is superimposed on the seasonal cycle as a result of the day–night light cycle.)

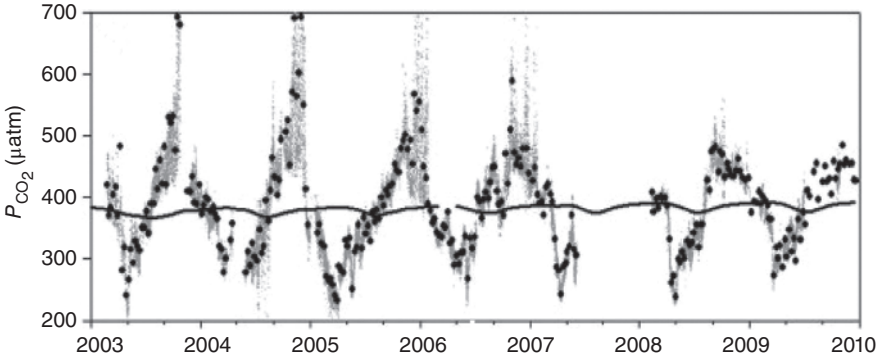

Figure 1.14 Seasonal cycle of CO_2 in the bay of Brest over several years (bi-weekly means of P_{CO_2}). Source: Bozec et al. [12] with permission of ELSEVIER.

Another type of reaction that is often not at equilibrium in natural systems is mineral dissolution, which accounts for most of the solutes in freshwaters. Groundwaters are typically acidic as result of the respiration of soil microorganisms which produces high CO_2. Dissolution of soil minerals consumes this acidity and releases cations and silica into the infiltrating water (e.g., reaction 1.11). If the dissolution reactions were at equilibrium, the composition of groundwater should reach a constant composition independent of the contact time. Field observations, however, show a linear increase in SiO_2 concentrations as a function of apparent groundwater age (Figure 1.15). This observation is consistent with a constant rate of mineral dissolution

$$\frac{d[SiO_2]}{dt} = \text{constant} \tag{1.20}$$

where the constant term would incorporate a kinetic rate coefficient and the surface areas of the mineral surface (where the dissolution reaction takes place). As long as the mineral surface is not depleted during the reaction (and equilibrium is not approached), the solute concentration increases linearly with reaction time.

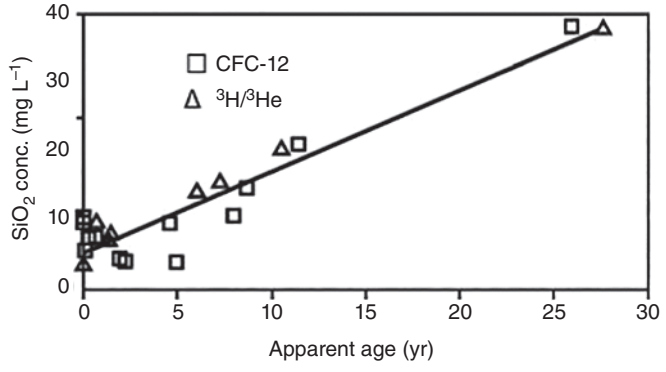

Figure 1.15 SiO_2 vs. groundwater age. Concentrations of SiO_2 in groundwater as a function of groundwater age calculated from CFC-12 and $^3H/^3He$. Similar patterns were observed for Ca and Na. Source: Adapted from Burns et al. [13].

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