WATER

1. Introduction

The most striking feature of the earth, and one lacking from the neighboring planets, is the extensive hydrosphere. Water is the solvent and transport medium, participant, and catalyst in nearly all chemical reactions occurring in the environment. It is a necessary condition for life and represents a necessary resource for humans. It is an extraordinarily complex substance. Structural models of liquid water depend on concepts of the electronic structure of the water molecule and the structure of ice. Hydrogen bonding between H_2O molecules has an effect on almost every physical property of liquid water.

Natural water systems contain numerous minerals and often a gas phase (Fig. 1). They include a portion of the biosphere and organisms, and their abiotic environments are interrelated and interact with each other. The distribution of chemical species in waters is strongly influenced by an interaction of mixing cycles and biological cycles.

Human civilization interferes more and more with the cycles that connect land, water, and atmosphere, and pollution seriously affects water quality. In order to assess the stresses caused to aquatic ecosystems by chemical perturbation, the distribution of pollutants and their fate in the environment must be investigated (see AIR POLLUTION).

2. Water Resources

Water resources are renewable but finite and scarce. Most (97.22%) of earth's water is captured in oceans. Its total volume is enormous, 1.3 billion cubic kilometers, but inadequate for human consumption because of the salt content. Approximately 2% of water is locked up in polar icecaps and glaciers. Water found in land, including surface water and groundwater, makes up less than 1% of the earth's water resources (1). Groundwater is found in aquifers, moisture-laden strata where water fills the spaces between rock particles. Although only about half of groundwater can be economically withdrawn for human use, it represents more than 97% of the usable freshwater resources. In addition, groundwater is a major source of replenishment for surface water.

3. Hydrological Cycle and Water Reservoirs

In hydrological studies, the transfer of water between reservoirs is of primary interest. The magnitudes of the main reservoirs and fluxes (volume per time) are given in Figure 2.

The oceans are subdivided into surface (100–1000-m) ocean and deep ocean. The zone separating the warmer, surface water from the lower, cooler layer (oceanic thermocline) is characterized by a density gradient that prevents mixing.

The exchange of water between the various reservoirs includes ocean mixing, evaporation, precipitation, runoff, and percolation. The exchange of water between surface and deep ocean, ie, mixing by upwelling and downwelling, and the subsequent circulation of water masses are the most important water-transport processes. About 20 times more water is added to the surface ocean by mixing than by river runoff. The ocean–atmosphere–continents system may be regarded as a great heat engine; its water cycle is driven by the sun (see SOLAR ENERGY). Evaporation uses 23% of the energy of solar radiation. The oceans provide 86% and the continents 14% of the annual total atmospheric water. The average annual amount of worldwide precipitation is 0.7 m, ranging from 0 to 0.25 m for desert areas, to 0.25–0.40 m for grasslands or open woodland, 0.40–1.25 m for dry forests, and >1.125 m for wet forest. The mean residence time for a water molecule in the atmosphere is ca 10 d.

3.1. Human Appropriation of Renewable Freshwater.

Freshwater constitutes about 2.5% of the total volume of water on earth and two-thirds of this freshwater is locked in glaciers and ice caps.

Freshwater is now scarce in many regions of the world, resulting in severe ecological degradation, limits on agricultural and industrial production, threats to human health, and increased potential for international conflict.

As emphasized by Postel and co-workers (3), only freshwater flowing through the solar-powered hydrological cycle is renewable (Fig. 2). Nonreplenishable (fossil) groundwater can be tapped, but such extraction depletes reserves in much the same way as extractions from oil wells do. The terrestrial renewable freshwater supply, $RFWS_{\text{land}}$, equals precipitation on land, P_{land}, which then subdivides into two major segments: evapotranspiration from the land, ET_{land}, and runoff to the sea, τ. Because groundwater and surface water are often hydraulically connected, soil infiltration and groundwater replenishment are included as part of this runoff component. Thus,

$$RFWS_{\text{land}} = P_{\text{land}} = ET_{\text{land}} + \tau$$

Agriculture consumes by far the most of any use category to which the accessible runoff worldwide is applied. Postel and co-workers estimate that human uses make up 26% of total terrestrial evapotranspiration and 54% of the runoff geographically and temporally accessible (3). Increased use of evapotranspiration will confer minimal benefits globally because most of the land suitable for rain-fed agriculture is already in production. New dam construction could increase accessible runoff by about 10% over the next 20 years; however, population increase during that period is projected to be more than 45%.

Use of Water in the United States. Estimates of water use in the United States indicate that about 408 billion gallons per day (Bgal/d) were withdrawn for all uses during 2000. This total has varied less than 3% since 1985 as withdrawals have stabilized for the two largest uses: thermoelectric power and irrigation. Fresh groundwater withdrawals (83.3 Bgal/d) during 2000 were 14% more than during 1985. Fresh surface-water withdrawals for 2000 were 262 Bgal/d, varying less than 2% since 1985 (4).

About 195 Bgal/d, or 48% of all freshwater and saline-water withdrawals for 2000, were used for thermoelectric power. Most of this water was derived from surface water and used for once-through cooling at power plants. About 52% of fresh surface-water withdrawals and about 96% of saline-water withdrawals were for thermoelectric-power use. Withdrawals for thermoelectric power have been relatively stable since 1985.

Irrigation remained the largest use of freshwater in the United States and totaled 137 Bgal/d for 2000. Since 1950, irrigation has accounted for about 65% of total water withdrawals, excluding those for thermoelectric power. Historically, more surface water than ground water has been used for irrigation. However, the percentage of total irrigation withdrawals from ground water has continued to increase, from 23% in 1950 to 42% in 2000. Total irrigation withdrawals were 2% more for 2000 than for 1995, because of a 16-% increase in groundwater withdrawals and a small decrease in surface-water withdrawals. Irrigated acreage more than doubled between 1950 and 1980, then remained constant before increasing nearly 7% between 1995 and 2000. The number of acres irrigated with sprinkler and microirrigation systems has continued to increase and now comprises more than one-half the total irrigated acreage.

Public-supply withdrawals were more than 43 Bgal/d for 2000. Public-supply withdrawals during 1950 were 14 Bgal/d. During 2000, about 85% of the population in the United States obtained drinking water from public suppliers, compared to 62% during 1950. Surface water provided 63% of the total during 2000, whereas surface water provided 74% during 1950.

Table 1 summarizes U.S. water use from 1950–2000 (4).

4. Hydrogeochemical Cycle

4.1. Chemical Weathering. Chemical weathering is one of the major processes controlling the global hydrogeochemical cycle of elements (5–7). In this cycle, water operates both as a reactant and as a transporting agent of dissolved and particulate components from land to sea. The atmosphere provides a reservoir for carbon dioxide and for oxidants required in the weathering reactions. The biota assists the weathering processes by providing organic ligands and acids and by supplying locally, upon decomposition, increased CO_2 concentrations.

During chemical weathering, rocks and primary minerals become transformed to solutes and soils, and eventually to sediments and sedimentary rocks. Weathering reactions consume protons and produce alkalinity.

Under natural conditions the rates of dissolution of most minerals are too slow to depend on mass transfer of the reactants or products in the aqueous phase. This restricts the case to one either of weathering reactions where the rate-controlling mechanism is the mass transfer of reactants and products in the solid phase, or of reactions controlled by a surface process and the related detachment process of reactants.

Calcareous minerals and evaporite minerals (halides, gypsum) are very soluble and dissolve rapidly and, in general, congruently, ie, yielding upon dissolution the same stoichiometric proportions in the solution as the proportions in the dissolving mineral and without forming new solid phases (Fig. 3). Their contribution to the total dissolved load in rivers can be estimated by considering the mean composition of river water and the relative importance of various rocks to weathering. Estimates (10) indicate that evaporites and carbonates contribute approximately 17% and 38%, respectively, of the total dissolved load in the world's rivers. The remaining 45% is the result of the weathering of silicates, underlining the significant role of these minerals in the overall chemical denudation of the earth's surface.

There are no unequivocal weathering reactions for the silicate minerals. Depending on the nature of parent rocks and hydraulic regimes, various secondary minerals like gibbsite, kaolinite, smectites, and illites are formed as reaction products (11).

In all cases, water and carbonic acid, the latter of which is the source of protons, are the main reactants. The net result of the reaction is the release of cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) and the production of alkalinity via $HCO^-{}_3$. When ferrous iron is present in the lattice, as in biotite, oxygen consumption may become an important factor affecting the weathering mechanism and the rate of dissolution.

These reactions, however, are complex and generally proceed through a series of reaction steps. The rate of weathering of silicates may vary considerably, depending on the arrangement of the silicon tetrahedra in the mineral and on the nature of the cations.

The Role of Weathering in Geochemical Processes in Oceanic and Global Systems. As indicated in the stoichiometric equations given above, the rate of chemical weathering is important in determining the rate of CO_2 consumption. Furthermore, the global weathering rate is most likely influenced by temperature and is proportional to total continental land area and the extent of its coverage with vegetation; the latter dependence results from CO_2 production in soils, which is a consequence of plant respiration and the decay of organic matter as well as the release of complex-forming substances (ligands), eg, dicarboxylic acids, hydroxycarboxylic acids, and phenols, ie, anions that form soluble complexes with cations that originate from the lattice or form surface complexes with the surface of oxide minerals. Regionally, the extent of weathering is influenced by acid rain.

It has been shown (12,13) that silicate weathering is more important than carbonate mineral weathering as a longterm control on atmospheric CO_2. The HCO_3^- and Ca^{2+} ions produced by weathering of $CaCO_3$ precipitate in the ocean as $CaCO_3$ through incorporation by marine organisms. The CO_2 consumed in carbonate weathering is released again upon formation of $CaCO_3$ in the ocean in a reversal reaction. Thus, globally, carbonate weathering results in no net loss of atmospheric CO_2. The weathering of calcium silicates, also produces Ca^{2+} and HCO_3^-, which form $CaCO_3$ in the sea, but only half of the CO_2 consumed in the weathering is released and returned to the atmosphere upon $CaCO_3$ formation. Thus, silicate weathering results in a net loss of atmospheric CO_2.

4.2. Circulation of Water with Rocks, Atmosphere, and Biota. Hydro- geochemical cycles couple atmosphere, land, and water. Natural waters acquire their chemical characteristics by dissolution and by chemical reactions with solids, liquids, and gases with which they have come into contact during the various parts of the hydrological cycle. Waters vary in their chemical composition, but these variations are at least partially understandable if the environmental history of the water and the chemical reactions of the rock–water–atmosphere systems are considered. Dissolved mineral matter originates in the crustal materials of the earth; water disintegrates and dissolves mineral rocks by weathering. Gases and volatile substances participate in these processes. As a first approximation, seawater may be interpreted as the result of a gigantic acid–base titration, ie, acid of volcanoes vs bases of rocks (oxides, carbonates, silicates) (14). The composition of freshwater may similarly be represented as resulting from the interaction of the CO_2 of the atmosphere with mineral rocks.

Figure 4, inspired by Siever (15), gives a simplified picture of some of the more important global biogeochemical transformations. A useful analogy would be that these are linked by a multitude of valves and switches that in effect control the system. Of particular interest are the gas regulators of the CO_2 and O_2 tanks. Both O_2 and CO_2 regulators are governed by photosynthesis and by weathering (15).

The classical geochemical material balance (16) assumes that the H^+ balance and the electron balance (oxidation state) in our environment have been established globally by the interaction of primary (igneous) rocks with volatile substances (Table 2).

In an oversimplified way, it may be stated that acids of the volcanoes have reacted with the bases of the rocks; the compositions of the ocean (which is at the first end point ($pH = 8$) of the titration of a strong acid with a carbonate) and the atmosphere (which with its $pCO_2 = 10^{-3.5}$ atm is nearly in equilibrium with the ocean) reflect the proton balance of reaction 1. Oxidation and reduction are accompanied by proton release and proton consumption, respectively. In order to maintain charge balance, the production of electrons, e^-, must eventually be balanced by the production of H^+. The redox potential of the steady-state system is given by the partial pressure of oxygen (0.2 atm). Furthermore, the dissolution of rocks and the precipitation of minerals are accompanied by H^+ consumption and H^+ release, respectively.

Atmosphere–Water Interaction. Although water is a very minor component of the atmosphere, less than 10^{-6} vol % of the atmosphere consisting of water, many important reactions occur in the water droplets of cloud, fog, and rain. The atmosphere is an oxic environment; in its water phase, gigantic quantities of reductants, such as organic substances, Fe(II), SO_2, CH_3SCH_3 (dimethyl sulfide), and nitrogen oxides, are oxidized by oxidants such as oxygen, $OH^{\cdot}$ radicals, H_2O_2, and Fe(III).

The atmosphere is an important conveyor belt for many pollutants. The atmosphere reacts most sensitively to anthropogenic disturbance because proportionally it represents a much smaller reservoir than land and water; furthermore, the residence times of many constituents of the atmosphere are smaller than those that occur in the other exchange reservoirs. Water and atmosphere are interdependent systems. Many pollutants, especially precursors of acids and photooxidants, originate directly or indirectly from the combustion of fossil fuels. Hydrocarbons, carbon monoxide, and nitrogen oxides released by thermal power plants and, above all by automobile engines, produce, under the influence of sunlight, ozone and other photooxidants.

Acid Rain. Figure 5 shows the various processes that involve atmospheric pollutants and natural components in the atmosphere. The following reactions are of particular importance in the formation of acid precipitation: oxidative reactions, either in the gaseous phase or in the aqueous phase, leading to the formation of oxides of C, S, and N (CO_2; SO_2, SO_3, H_2SO_4; NO, NO_2, HNO_2, HNO_3); absorption of gases into water (cloud droplets, falling raindrops, or fog) and interaction of the resulting acids ($SO_2 \cdot H_2O$, H_2SO_4, HNO_3) with ammonia (NH_3) and the carbonates of airborne dust; and the scavenging and partial dissolution of aerosols into water. In this case, aerosols are produced from the interaction of vapors and airborne (maritime and dust) particles; they often contain $(NH_4)_2SO_4$ and NH_4NO_3.

Deposition. The products of the various chemical and physical reactions in the atmosphere are eventually returned to the earth's surface. Usually, a useful distinction is made here between wet and dry deposition. Wet deposition, ie, rainout and washout, includes the flux of all those components that are carried to the earth's surface by rain or snow, that is, those dissolved and particulate substances contained in rain or snow. Dry deposition is the flux of particles and gases, especially SO_2, HNO_3, and NH_3, to the receptor surface during the absence of rain or snow. Deposition can also occur through fog, aerosols and droplets which can be deposited on trees, plants, or the ground. With forests, approximately half of the deposition of SO_4^{2-}, NH_4^+, and H^+ occurs as dry deposition.

The rainwater shown in Figure 5 contains an excess of strong acids, most of which originate from the oxidation of sulfur during fossil fuel combustion and from the fixation of atmospheric nitrogen to NO and NO_2, eg, during combustion of gasoline by motor vehicles. It should also be mentioned that there are natural sources of acidity, resulting from volcanic activity, from H_2S from anaerobic sediments, and from dimethyl sulfide and carbonyl sulfide that originate in the ocean. HCl results from the combustion and decomposition of organochlorine compounds such as poly(vinyl chloride). Bases originate in the atmosphere as the carbonate of wind-blown dust and from NH_3, generally of natural origin. The NH_3 comes from NH_4^+ and from the decomposition of urea in soil and agricultural environments.

The reaction rates for oxidation of atmospheric SO_2 ($0.05-0.5\ d^{-1}$) yield a sulfur residence time of several days, at most; this corresponds to a transport distance of several hundred to 1000 km. The formation of HNO_3 by oxidation is more rapid and, compared with H_2SO_4, results in a shorter travel distance from the emission source. H_2SO_4 can also react with NH_3 to form NH_4HSO_4 or $(NH_4)_2SO_4$ aerosols. In addition the NH_4NO_3 aerosols are in equilibrium with NH_3 (g) and HNO_3 (g).

In addition to the acid–base components shown in Figure 5, various organic acids are often found. Many of these acids are by-products of the atmospheric oxidation of organic matter released into the atmosphere. Of special interest are formic, acetic, oxalic, and benzoic acids, which have been found in rainwater in concentrations occasionally exceeding a few micromoles per liter.

Acid deposition degrades water quality by lowering pH levels, decreasing acid-neutralizing capacity (ANC), and increasing aluminum concentrations. Sulfate concentrations in lakes and streams have decreased over the past 20 years. However, they remain high compared to background conditions. Improvement in the acidity of lakes and streams in the northeastern United States has been limited.

A recent study shows that 41% of the lakes in the Adirondack region of New York State are still acidic and subject to short-term pulses in acidity associated with snowmelt or rain storms. Fifteen percent of the lakes in the Catskills and New England exhibit the same characteristics. Most of the impact (83%) is due to acid deposition. The remaining problem is due to natural conditions, but these lakes have been made more acidic due to acid deposition. Recovery of these lakes and streams is hindered by a decrease in base cations and the fact that sulfur in the soil is now releasing into these bodies of water (18).

Groundwater. The uppermost part of the earth's rocks constitutes a porous medium in which water is stored and through which it moves. Up to a certain level, these rocks are saturated with water that is free to flow laterally under the influence of gravity. Subsurface water in this saturated zone is groundwater, and the uppermost part of the zone is the water table. The chemistry of the groundwater is influenced by the composition of the aquifer and by the chemical and biological events occurring in the infiltration.

A general relationship between the composition of the water and that of the solid minerals with which the water has come into contact during infiltration and in the aquifer can be expected. Biological activity, especially in the organic layer above the mineral part, has a pronounced effect on the acquisition of solutes. Because of microbial respiration, the CO_2 pressure is increased. CO_2 pressure tends to increase the alkalinity and the concentration of Ca^{2+} and other solutes.

4.3. Biochemical Cycle.

The ecological system may be considered as a unit of the environment that contains a biological organization made up of all the organisms interacting reciprocally with the chemical and physical environment. The maintenance of life in aquatic ecosystems results directly or indirectly from the steady impact of solar energy. Photosynthesis is carried out mostly by algae and water plants; it may be conceived as a disproportionation of water into an oxygen reservoir and hydrogen, which forms high energy bonds with C, N, S, and P compounds that are incorporated as organic matter in the biomass. Various organisms catalytically decompose the unstable products of photosynthesis through energy-yielding electron-transfer reactions, eg, reduction–oxidation processes and respiration. These organisms use this source of energy for their metabolic needs (7,8).

The composition of natural waters is strongly influenced by the growth, distribution, and decay of algae and other organisms. Organisms regulate the oceanic and lacustrine composition and its variation with depth. Dissolved constituents are taken up by organisms. Their remains sink under the influence of gravity and are gradually destroyed by oxidation. The superposition of this particular cycle upon the ordinary mixing cycle in the ocean or in lakes accounts for the variation in depth and distribution of chemical properties.

5. Properties

5.1. The Solvent Water.

Water is an unusual liquid. It has a very high boiling point and high heat of vaporization; ice has a very high melting point. The maximum density of liquid water is near 4°C, not the freezing point, and water thus expands upon freezing (Fig. 6, Tables 3 and 4). It has a very high surface tension. It is an excellent solvent for salts and polar molecules. It has the greatest dielectric coefficient of any liquid. These unusual properties are a consequence of the dipolar character of the H_2O molecule. Figure 7 depicts the electron cloud of the angular water molecule, resulting from the hybridization of s and p electrons to yield two bonding orbitals between the O and the two H atoms, and two nonbonding sp^3 orbitals on the oxygen. The molecule thus has high negative charge density near the oxygen atom and high positive charge density near the protons. It is a dipolar molecule.

Figure 8 shows the measured angle of 105° between the hydrogens and the direction of the dipole moment. The measured dipole moment of water is 1.844 debye (a debye unit is 3.336×10^{-30} C m). The dipole moment of water is responsible for its distinctive properties in the liquid state. The O–H bond length within the H_2O molecule is 0.96×10^{-10} m. Dipole–dipole interaction between two water molecules forms a hydrogen bond, which is electrostatic in nature. The lower part of Figure 8 (not to the same scale) shows the measured H-bond distance of 2.76×10^{-10} m or 0.276 nm.

The hydrogen-bonded structure of ice is shown in Figure 9**a**, and one of the several models proposed for the structure of water in the liquid state is shown in Figure 9**b**. In the open tetrahedral ice structure, each oxygen atom is bound to four nearby oxygen atoms by H bonds. The energy of each H bond is estimated to be about 20 kJ mol^{-1}; by comparison, covalent bond energies are typically 20 times greater. H bonds are of low energy, but they are numerous in ice and water (23).

Upon melting, ice loses its open structure with the "melting" of some fraction of the hydrogen bonds, and so the volume of the liquid water decreases, reaching a minimum at 4°C; above this temperature thermal expansion dominates the density.

In Figure 9**b** the Frank-Wen flickering cluster model envisions larger clusters of H-bonded water surrounded by noncluster waters, which nonetheless interact with neighbors by dipole–dipole forces. The lifetime of the clusters is estimated at around 100 ps, which is long with respect to the period of a molecular vibration of approximately 0.1 ps. The persistence, or the reformation, of hydrogen bonding in liquid water is a key to understanding the physical properties of water as well as its poorer solvent properties for nonpolar, hydrophobic solutes. The highly structured water linked by H bonds must be disrupted by any solute. When the solute is ionic, the attractive interactions between ion and water molecule favor dissolution. When the solute is nonpolar molecule, the structural cost to the hydrogen-bonded water makes the probability of dissolution unfavorable.

Thermodynamic and physical properties of water vapor, liquid water, and ice I are given in Tables 5–7. The extremely high heat of vaporization, relatively low heat of fusion, and the unusual values of the other thermodynamic properties, including melting point, boiling point, and heat capacity, can be explained by the presence of hydrogen bonding (8,20).

5.2. Solute Species. Dissolution of ionic and ionizable solutes in water is favored by ion–dipole bonds between ions and water. Figure 10 illustrates a hydrated sodium ion, Na^+ (aq), eg, from dissolution of NaCl in water, surrounded by six water molecules in octahedral positions. The energy of the ion–dipole bonds depends on the size of the ion and its charge. Higher charge and smaller ionic radii favor the bonding. Further away from the central ion, the water molecules are structured through additional dipole–dipole interactions. In a similar way, the Cl^- (aq) ion interacts with the solvent water to form ion–dipole bonds, with the hydrogen side (local positive charges) of H_2O pointing toward the central ion.

The dissolution of polar molecules in water is favored by dipole–dipole interactions. The solvation of the polar molecules stabilizes them in solution. Nonpolar molecules are soluble in water only with difficulty because the relatively high energy cost associated with disrupting and reforming the hydrogen-bonded water is unfavorable to the former occurring.

6. Chemical Composition

The concentrations of the principal elements in marine and freshwaters are given in Figure 11. The concentrations of biologically regulated components, ie, C, N, P, and Si, vary with depth and are markedly influenced by the growth, distribution, and decay of phytoplankton and other organisms. The concentrations of other constituents, especially the salts, ie, Cl^-, SO_4^{2-}, Mg^{2+}, and Na^+, are remarkably constant and are different from those in fresh waters. For most elements, a mass balance appears to exist between input into the sea, mostly by rivers, and its removal, mostly by sedimentation. Thus, the oceans are often assumed to be at steady state. The mean residence time, τ, (yr) of an element or constituent is defined as average time a given element spends in the ocean before being removed by sedimentation and other processes, where M is the concentration of

$$\tau = \frac{\text{total mass}}{\text{input or output}} = \frac{M}{Q}$$

a particular constituent in seawater multiplied by the volume of the ocean water, and Q is the product of the concentration of the particular element in average river water and the annual flux of river water to the ocean or the quantity of this element being removed from the water by sedimentation. Some sea salts, especially NaCl, are recycled through the atmosphere as aerosols from droplets of sea spray to the land masses, where they are washed out by rain. Chloride and sodium originating from the atmosphere, for example, contribute about one-third of the annual river flux of these elements. The other main constituents are derived principally from the weathering of rocks, and the fraction for atmospherically cycled salts is small.

The chemistry of natural waters is covered in References 8, 25, and 26. The aquatic environmental chemistry of soils is reviewed in Reference 27. The chemistry of the mineral–water interface and of aquatic environmental particles and colloids is reviewed in References 28 and 29. References 7 and 30 review the role of the hydrosphere in the biogeochemistry of global change.

The concept of residence time can also be applied to lakes where the flow through the outlet has to be considered. In lakes it is often convenient to define a relative residence time, ie, a residence time relative to that of water.

The flow of hydrothermal solutions into the oceans from hydrothermal vents, ie, springs coming from the sea floor in areas of active volcanism, and the chemical reactions occurring there by high temperature alteration of basalts are of significance in the mass balance of Mg^{2+} and K^{+}. Furthermore, during the cycling of seawater through the earth's crust along the mid-ocean ridge system, geothermal energy is transferred into chemical energy in the form of reduced inorganic compounds. These compounds are derived from the reaction of seawater with crustal rocks at high temperatures and are emitted from warm ($\leq 25°C$) and hot ($\sim 350°C$) submarine vents at depths of 2000–3000 m. Chemolithotrophic bacteria use these reduced chemical species as sources of energy for the reduction of carbon dioxide (assimilation) to organic carbon (31).

The observed oceanic residence times range from 100 yr for aluminum to ca 10^8 yr for chlorine (Figs. 9 and 10; Table 8), reflecting the great variation in geochemical reactivity; unreactive elements simply accumulate in the ocean and have large τ values. Figure 12 shows the strong correlation between the mean oceanic residence time of an element and the distribution of that element between seawater and crystal rocks (33).

The transition between rivers and oceans occurs in estuaries, which are semi-enclosed coastal bodies of water within which seawater is diluted with freshwater from land drainage. Several types of water circulation may occur (vertically mixed or stratified), depending on topography, tidal currents, and freshwater discharge. Estuaries are of great environmental concern. Many marine organisms require the estuarine environment for part of their life cycle; thus, pollution in an estuary may have long-range ecological consequences.

Estuaries with their salinity gradients and tidal movements represent gigantic natural coagulation tanks. In coagulation, colloidal particles agglomerate and are subsequently removed by sedimentation. Clay minerals, organic matter, colloidal hydroxides of iron(III), and heavy metals tend to coagulate and accumulate in the estuary. The trapping of organic matter may impart anaerobic conditions in the lower part of estuarine water.

6.1. Chemical Variety. The term species refers to the actual form in which a molecule or ion is present in solution. For example, a metal ion may occur in natural waters, as a free metal ion, ie, an aquo complex $Me(H_2O)_n^{z+}$, an inorganic or organic complex, and it may be present in dissolved or particulate, often colloidal, form. It is difficult to distinguish between the dissolved and particulate forms. The definition by pore size (0.45 μm) of membrane filter is considered questionable, and what are thought to be dissolved species may often include some or most of the colloidal forms of an element. The inorganic fraction of suspended particulate matter consists mainly of minerals formed by weathering of terrestrial rocks. The organic particulate matter is primarily composed of living organisms, their decay, and metabolic products. Inorganic trace elements may be sorbed or bonded onto them.

Dissolved inorganic species present in seawater are principally electrolytes (Table 8), uncharged species, and dissolved gases. The species patterns for cations in model seawater (pH 8.2) and freshwater have been derived from calculations based on stability constants of complexes (8,9,40). The principal species of the more important elements occurring in natural waters are given in Figure 11. The concentration and distribution of dissolved trace metals in surface marine waters has been reviewed (26,41). A few typical concentrations of dissolved heavy metals in natural waters are given in Table 9. The characterization of the carbon dioxide system in marine waters is given in Reference 42.

Metals and metalloids that form alkyl compounds, eg, methylmercury and methylarsenic acid, tributyltin, deserve special concern because these compounds are volatile and accumulate in cells; they are poisonous to the central nervous system of higher organisms. Because methylmercury or other metal alkyls may be produced at a rate faster than it is degraded by other organisms, it accumulates in higher organisms such as fish. Hg species are also reduced to elementary Hg^0 which is soluble in water but lost by volatilization to the atmosphere (43).

7. Factors Affecting Stream Water Quality

7.1. General Principles of Stream Water Geochemistry. The composition of pristine stream water can range from nearly that of rainwater, a very dilute solution containing up to a few tens of milligrams per liter of dissolved material, to concentrations of as much as several thousand milligrams per liter, which mainly are found in semiarid regions where saline springs contribute chemical constituents derived from readily soluble rock strata. In general, however, the dissolved-solids concentrations of principal streams in humid and subhumid regions of the conterminous United States have a narrower range. Analyses showing maximum and minimum concentrations for a recent 3-year period for 29 stream-sampling sites in the United States recently were published (44). Seven of these sites had maximum total dissolved-solids concentrations greater than 1000 mg/L; these high concentrations are attributable to natural saline inflows, although human activities probably intensified their effects.

Chemical analyses of stream water that have been published since the early years of this century generally include determinations for four positively charged ions (cations)—calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{2+}), and potassium (K^+)—and five negatively charged ions (anions)—bicarbonate (HCO_3^-), sulfate (SO_4^{2-}), chloride (Cl^-), fluoride (F^-), and nitrate (NO_3^-)—and uncharged dissolved silicic acid (generally reported in terms of silica, SiO_2). These are the major constituents in most natural stream water. Minor constituents, present at concentrations substantially less than 1 mg/L, include a wide variety of inorganic and organic constituents, and although these constituents commonly are the result of human activities, they are not considered in detail in this article because few reliable measurements were made until the 1970s. Short-term trends for these constituents have been evaluated using statistical techniques (45).

Chemical Reactions that Govern Stream Composition. Weathering is a general term for mechanical and chemical alteration of rock minerals that are exposed to the atmosphere and circulating water at and near the land surface.

Chemical reactions that occur during weathering produce both water-soluble and nonwater-soluble products; those that are water soluble are transported from the reaction site in surface runoff or in moving groundwater. To a certain extent, at least, the concentrations of dissolved elements would be expected to reflect the relative abundance of the elements in the rocks exposed at the reaction site. Such a broad generalization has some validity for silicon (Si) and the four elements that form the major cations of most natural stream water. These five elements are among the eight most abundant elements, with oxygen being the most abundant, in igneous and sedimentary rocks of the Earth's outer crust. The other two of the most abundant elements—aluminum (Al) and iron (Fe)—form oxides or hydroxides of very low solubility during normal rock weathering and, therefore, generally are not present in large amounts in stream water. On the other hand, major anions in stream water display a more complex relation to rock composition. In the average stream water sample, the five most abundant anions represent the nonmetallic elements carbon, sulfur, chlorine, fluorine, and nitrogen. Also, oxygen is included in three of the anions of these elements.

Oxygen is by far the most abundant element in crustal rocks, composing 46.6% of the lithosphere (46). In rock mineral structures, the predominant anion is O^{2-}, and water (H_2O) itself is almost 90% oxygen by weight. The nonmetallic elements fluorine, sulfur, carbon, nitrogen, chlorine, and phosphorus are present in lesser amounts in the lithosphere. These elements all play essential roles in life processes of plants and animals, and except for phosphorus and fluorine, they commonly occur in earth surface environments in gaseous form or as dissolved anions.

In a very broad general sense, then, the major cationic constituents of stream water tend to reflect the composition of associated rocks and the relative resistance of the rock minerals to weathering. The anions, which must be present in these water solutions in electrochemical balance with the cations, tend to reflect the influence of various chemical and biochemical processes that have broken down the rock minerals as well as the chemical, biochemical, and physical processes taking place in the aquatic and surrounding environments. The predominance of bicarbonate anions in most stream water is related to cycling of carbon dioxide (CO_2) from air and to biological processes in soil. Dissolution of carbon dioxide in water produces carbonic acid (H_2CO_3) that attacks rock minerals. Bicarbonate anions are formed in solutions participating in such reactions in amounts equivalent to the amount of cations that are released.

Sulfur and nitrogen participate in biologically mediated oxidation reactions producing hydrogen ions (H^+) that become available for weathering of rock minerals. For example, pyrite (FeS_2) can be converted to dissolved ferrous iron and sulfate as a result of oxidation of sulfur by dissolved oxygen, and the hydrogen ion is a major by-product. Carbonate or sulfate in sedimentary rocks (eg, limestone and gypsum) can be taken directly into solution and can add substantially to the bicarbonate and sulfate contents in water that is in contact with such rocks.

Chlorine plays a less significant role in chemical weathering processes than do sulfur and carbon. Most geochemists believe that much, or most, of the chloride in stream water in coastal areas is derived from sea salt that is carried landward or deposited by rainfall. Farther inland, however, a major part of the chloride loads in streams is the result of human activities.

The final composition of stream water is the product of the weathering reactions and related processes outlined above. However, the chemical processes are influenced and controlled by an intricate combination of environmental factors that are characteristic for each drainage system. Therefore, the composition of the bedrock in an area and the residual material left at the surface as soil and subsoil exert a strong influence on the chemical composition of runoff from the area. The reactions of water with this material are the ultimate geological control and are the source of soluble weathering products.

Most igneous and metamorphic rocks are composed predominantly of aluminosilicate minerals, including feldspar such as albite ($NaAlSi_3O_8$) or anorthite ($CaAl_2Si_2O_8$) and crystalline forms of silica such as quartz (SiO_2). Various mixed metal-plus-silicon oxides such as olivine [$(Mg,Fe)_2(SiO_4)$] and pyroxene [$Mg_2(SiO_3)_2$] can be major constituents in darker colored igneous rocks that are relatively low in total silicon.

Rocks that were deposited as sediment can consist of unaltered fragments of a precursor rock body and are represented by sandstone and conglomerate. The finer grained sedimentary rocks, such as shale or siltstone, also can contain some unaltered particles but also usually have high proportions of slightly soluble alteration products, such as clay minerals, formed during weathering of resistant silicate minerals. Such rocks are classified as hydrolyzates. Another class of sedimentary rock of major importance is the precipitates, such as limestone and dolomite, which are predominantly composed of calcium carbonate and calcium plus magnesium carbonate, respectively. Evaporites are sedimentary rocks produced by extensive evaporation of water from weathering solutions. Common examples are gypsum and anhydrite, primarily composed of calcium sulfate, or halite (rock salt), primarily composed of sodium chloride. Obviously the more readily soluble minerals of evaporite or precipitate rocks can dissolve rapidly when exposed to circulating water. Carbonates also can act as cementing material between the mineral grains of resistate and hydrolyzate rocks.

The extent to which minerals are attacked and dissolved from igneous and metamorphic terranes depends in large part on the availability of reaction sites on solid surfaces and the length of time the solution–solid contact is maintained. The effects of weathering are controlled by kinetic factors, such as the rates of the chemical reactions and the general rates of water and sediment movement, and biological factors that include the effects of biotic growth in the weathering zone. Also, the hydrologic properties of the drainage system (precipitation, evaporation, runoff, slope of the area), the relative permeability of rocks and soils, and the degree to which the surface drainage system is coupled to the groundwater reservoirs are important modulating forces. In rocks that contain more soluble minerals such as calcite, the degree to which solids are dissolved and carried off in the runoff is more likely to be governed by chemical thermodynamic factors, and in carbonate systems a state of chemical equilibrium could be closely approached.

Mineral dissolution reactions of importance generally require a continuous supply of hydrogen ions in the incoming solution. To some degree, reacting hydrogen ions are supplied from the water itself, which always includes, to some extent, water molecules that have broken apart (dissociated) into hydrogen and hydroxide ions. Under standard conditions (25°C and 1 atm pressure), the effective concentration (activity) of hydrogen ions in pure water is $10^{-7.00}$ mol/L. (A mole of a chemical element is a quantity in grams numerically equal to the atomic weight. For hydrogen, $10^{-7.00}$ moles/L is equivalent to 0.1 μg/L.)

The pH scale commonly used to express acidity is defined as the negative base-10 logarithm of the activity of hydrogen ions in a solution. At neutrality under the conditions defined in the preceding paragraph, the pH therefore will be 7.00. A change of 1 pH unit represents a 10-fold change in hydrogen ion activity. The activity of a dissolved ion is exactly equal to its concentration only in very dilute solutions. This topic has been discussed and explained more extensively elsewhere (47).

In natural systems the most effective sources of hydrogen ions generally are chemical reactions involving dissolved constituents. An important source is carbon dioxide gas, which is present in weathering solutions as a result of contact with air; it is produced in larger quantities by plant root respiration and decay of soil organic matter and by the metabolic processes of various organisms in water and sediment. Equation 1 shows that some of the carbon dioxide that dissolves forms carbonic acid (note that in the following equations the arrows indicate the direction in which the reaction normally proceeds; reactants are on the left side and products on the right; double arrows indicate that reactions can proceed in either direction):

$$CO_2 + H_2O \rightleftarrows H_2CO_3 \tag{1}$$

Equation 2 shows that the acid dissociates to form bicarbonate ions and hydrogen ions:

$$H_2CO_3 \rightleftarrows HCO_3^- + H^+ \tag{2}$$

and carbonate anions can be formed in a second dissociation step:

$$HCO_3^- \rightleftarrows CO_3^{2-} + H^+ \tag{3}$$

The H^+ that is supplied by reactions in Eqs. 2 and 3 can react with silicate minerals such as the sodium-bearing form of feldspar:

$$\underset{\text{albite}}{2\ NaAlSi_3O_8} + \underset{\text{hydrogen}}{2\ H^+} + \underset{\text{water}}{9\ H_2O} \rightarrow \underset{\text{kaolinite}}{Al_2Si_2O_5(OH)_4} + \underset{\text{silicic acid}}{4\ H_4SiO_4(aq)} + \underset{\text{sodium}}{2\ Na^-} \tag{4}$$

to produce the clay mineral kaolinite, undissociated silicic acid (H_4SiO_4 which also can be written as SiO_2), and sodium ions. This is essentially an irreversible process (note the single arrow) in that albite is not readily synthesized from the reaction products under ordinary natural weathering conditions, and the reaction will continue to proceed to the right as long as reactants are available.

The hydrogen ion flux that is provided by carbonic acid dissociation also can attack calcite ($CaCO_3$):

$$CaCO_3 + H^+ \rightleftarrows HCO_3^- + Ca^{2+} \tag{5}$$

This reaction is relatively fast and readily reversible so that in drainage basins in carbonate-dominated terranes the stream water commonly will have near-equilibrium concentrations of hydrogen, bicarbonate, and calcium ions. At equilibrium, the rates of forward and reverse processes represented in equation 5 are equal.

In effect, the forward progress of reactions such as is shown in equations 4 and 5 will be controlled by the availability of hydrogen ions, but the final result, as indicated by the chemical composition of stream water from any given drainage basin, will be influenced by a complicated set of interrelated physical factors that influence the volume and rate of water movement, ecologic and climatic factors that control the type and density of plant and bacterial growth and soil development, and the human development of water and land resources. Thus, the geochemistry of stream water in any given drainage basin is unique to that basin. The historical record of water chemistry in a specific basin cannot be interpreted without giving proper attention to the way various hydrologic and other environmental factors in the basin have influenced the chemical composition of the water. An extensive body of research on the topic of global stream water geochemistry is summarized in Ref. 48.

Effects of Human Activities. A considerable part of the currently existing motivation for organized long-term water quality studies has been public concern that human activities in many drainage basins have induced destructive changes in stream water quality. From examples cited in this article, such effects can indeed be documented. Also, in some basins water quality management has succeeded in correcting some of the human-caused deterioration and is substantially restoring the quality of the water. The concept of sustainability is relevant, and the development goal for drainage systems is to maintain suitable water quality while permitting levels of water use that will sustain the basin's existing and reasonable future economic development.

Human activities that alter stream flow characteristics and thus cause water quality changes include the building of structures that impound or regulate rates of stream flow, diversion of water from one drainage basin to another, irrigation of land adjacent to streams, and lowering of tributary groundwater tables by pumping from wells. Waste disposal, directly or indirectly, into streams also influences water quality by adding chemicals and suspended matter. Disposal of untreated organic waste into streams was common in urban and rural areas of the nation until the early twentieth century. Besides pathogenic bacteria in the waste, large amounts of organic chemicals and suspended material depleted the dissolved oxygen of receiving waters and killed much of the aquatic biota in some streams. Thus, the concentration of dissolved oxygen in stream water also is considered a contamination index. Normally, the dissolved-oxygen content is near the saturation level that can be calculated for water that is in contact with air at ambient temperature, but oxidizable material in solution, especially organic waste, can substantially deplete the dissolved-oxygen content.

Additionally, phosphate (PO_4^{-3}) concentrations are indicative of contamination from waste sources. Phosphate is a constituent of domestic and industrial waste, in part, because of the widespread use of phosphate compounds as detergent additives.

Land use changes and related developments also can affect stream water quality. Examples include urbanization, clearing of forests, various agricultural practices, such as use of fertilizers and pesticides and return flow of drainage water from irrigated fields, and industrialization. Urbanization and industrialization lead to various side effects. Mining for coal and metals generally contaminates water during and after the mining activity. The smelting of ores to recover metals and the burning of coal to generate power release pollutants into the air, and eventually some of these pollutants find their way into water supplies. Metal ores, coal, and other organic fuels commonly contain, or are associated with, reduced sulfur. Oxidation of the sulfur by burning the fuel and smelting the ores and oxidation in the mines or in waste dumps when sulfides are exposed to air constitute major sources of sulfur in stream water. High metal concentrations commonly are found in streams draining metal-mining areas, and sodium chloride and calcium chloride are dispersed widely by salt and sand mixtures used to melt ice from highways.

7.2. Circulation Rates of Elements.

The concept of cycling of individual elements, in part coupled to the hydrologic cycle, has been developed and quantified over the past half century. Besides the total quantities of the elements present in various reservoirs—bedrock (the lithosphere), soils, all forms of living matter (the biosphere), the oceans, the atmosphere, and fresh water—the rates of exchange and mechanisms of movement from one reservoir to another are considered in the cycle. This concept is highly relevant in developing a frame of reference for evaluating possible environmental effects of energy technology.

A simplified diagram representing the various reservoirs and transport mechanisms and pathways involved in the cycles of nutrient elements at and above the surface of the Earth is given in Figure 13. The processes are those considered to be the most important in the context of this article, but others of lesser significance can be postulated. For some of the elements, notably carbon, sulfur, chlorine, and nitrogen, considerable research has been done to evaluate (quantitatively) the amount of the various elements in the reservoirs and the rates of transfer.

Carbon. Most of the Earth's supply of carbon is stored in carbonate rocks in the lithosphere. Normally the circulation rate for lithospheric carbon is slow compared with that of carbon between the atmosphere and biosphere. The carbon cycle has received much attention in recent years as a result of research into the possible relation between increased atmospheric carbon dioxide concentration, most of which is produced by combustion of fossil fuel, and the "greenhouse effect," or global warming now referred to as "climate change". Extensive research has been done on the rate at which carbon dioxide might be converted to cellulose and other photosynthetically produced organic compounds by various forms of natural and cultivated plants. Estimates also have been made of the rate at which carbon dioxide is released to soil under optimum conditions by various kinds of plant cover, such as temperature-zone deciduous forests, cultivated farm crops, prairie grassland, and desert vegetation.

The efficiency of the weathering of rocks in using carbonic acid produced in the carbon cycle is affected by various hydrologic, environmental, and cultural controls. The fact that the principal anion in fresh surface water worldwide almost always is bicarbonate attests to the overriding importance of this process. Exceptions are systems in which evaporite minerals are available for dissolution by groundwater or where human activities are major sources of sulfate or chloride inflow.

Quantitative estimates of the magnitude of the carbon cycle, based mainly on a compilation in Ref. 50, suggest that the total amount of carbon dioxide converted to organic matter during a year might be as great as 7–9 tons/acre in midlatitude deciduous forests and about a tenth that amount in native grassland. Cultivated farm crops presumably convert somewhat more carbon dioxide per unit area than might be expected in native grassland. Respiration of carbon dioxide by plant roots is at a rate equal to about 25% of the total carbon dioxide used by the plants, and the potential supply of carbon dioxide from vegetation for weathering rock is about 1.65 tons/acre/yr on the average, over the whole land area of the Earth (50). This is equivalent to about 1060 tons/mi^2/yr of carbon dioxide. If all this carbon dioxide were dissolved in water and the resulting carbonic acid reacted with silicate minerals to maintain near-neutral pH, the annual bicarbonate yield could be as great as 1500 tons/mi^2. A drainage basin in a limestone terrane theoretically could produce bicarbonate at an even higher rate, as the reaction between dissolved carbon dioxide and solid carbonate minerals produces two bicarbonate ions per reacting dissolved carbon dioxide molecule.

As might be expected, the average rates of bicarbonate yield in drainage basins of the world are far below these numbers, as only a relatively small proportion of the carbon dioxide released in soil is likely to participate in rock weathering. A general indication of the role of dissolved carbon dioxide in weathering processes in streams can be obtained by calculating the average annual bicarbonate yield from average concentration of dissolved bicarbonate, average water discharge, and drainage basin area. Examples of this type of calculation can be obtained from published literature. Ref. 51 studied 56 drainage basins in the conterminous United States and Hawaii to determine the relative importance of stream temperature, human population density, atmospheric precipitation, and predominant type of bedrock (limestone, sandstone, or crystalline) as controls of constituent yield. Of the 19 limestone basins, the Kalamazoo River at Saugatuck, Michigan, had the maximum annual bicarbonate yield, which was about 324 tons/mi^2. However, in the other basins, annual bicarbonate yields were substantially lower—15 had less than 225 tons/mi^2, and the average yield for the 19 limestone basins was 114 tons/mi^2.

In general, bicarbonate yields reported in Ref. 51 were much smaller for basins in crystalline (noncarbonate) rock terranes than for those in limestone or sandstone terranes. Other investigators have reported relatively large bicarbonate yields for certain igneous terranes. For example, Ref. 52 reports large bicarbonate yields from igneous drainage basins in the Pacific Northwest. Among studies referred to is a study for a basin having an active glacier in the northern Cascade Mountains of Washington (53). In this basin, the annual bicarbonate yield was near or slightly greater than 100 tons/mi^2.

The high bicarbonate yield in some of the Pacific Northwest streams could be the result of glacial action and mechanical erosion of rock material in basins having steep slopes that produce large amounts of relatively freshly fractured and fine-grained sediment that would participate readily in dissolution and alteration reactions. The rate at which such reactions would proceed is a function of net surface area of sediment available per unit volume of runoff and the length of time such material was exposed to water in the runoff process. Therefore, the efficiency of solvent erosion under conditions in the Pacific Northwest region could be considerably increased by such factors.

The chemical analyses tabulated in this article identify “alkalinity” as a property of the water rather than a simple constituent. Alkalinity has been more broadly defined as “capacity for acid neutralization” (54,55). Common practice in water analysis is to report alkalinity in terms of bicarbonate and carbonate concentrations, although other ionic species also may contribute by reacting with the titrating acid.

Sulfur. The cycle of sulfur in weathering environments is affected by a more diverse set of reactions than for carbon. As is the case with carbon, most of the Earth’s supply of sulfur is stored in the lithosphere (47). Although some sulfur actually is taken up by vegetation, the growth and decay of plants does not tie up large proportions of the total sulfur supply. The element’s geochemical behavior in the environment is summarized in Ref. 56. In igneous and metamorphic rocks, sulfur generally is present in the chemically reduced sulfide form (S^{2-}) and commonly is associated with metals. Polysulfide minerals in which the nominal valence of sulfur is between -2 and 0 also are common. An example is pyrite (FeS_2), which commonly occurs in association with coal seams and other sediments laid down under conditions where free oxygen was not available.

In weathering environments where oxygen is continuously available, negatively charged reduced forms of sulfur are converted to positively charged oxidized forms such as sulfate (SO_4^{2-}) in which the sulfur is in the fully oxidized (S^{6+}) state. Oxidation and reduction reactions of sulfur commonly are bacterially mediated. The calcium sulfate minerals gypsum ($CaSO_4{\cdot}2H_2O$) and anhydrite ($CaSO_4$) are common constituents of evaporite rocks, and in semiarid regions where such rocks are near the land surface, stream water can contain substantial concentrations of sulfate. However, streams in humid regions generally carry relatively low concentrations of sulfate unless human activities have intervened. Weathering reactions that involve oxygen are important in the development of soils, especially in humid and subhumid climates. Commonly, oxygen is in relatively short supply at shallow depths in the soil zone, having been depleted by oxidation of organic matter. In wetland soil and submerged sediments, oxygen can be in very short supply and sulfur is in reduced form. However, as noted in Refs. 57 and 58, the sulfur in aerated soil is principally a component of organic compounds. In any event, any reduced species of sulfur may be converted to sulfate by oxidation when wetlands are drained or soils are converted from their natural state to agricultural cropland. All these processes can increase the availability of sulfate for transport by streams and cause increased sulfate loads in areas affected by development.

Geochemical studies of sulfate in streams have been approached in various ways. For example, Ref. 59 is a review of literature on sources of sulfate in the dissolved loads of streams, especially in areas where development effects are likely to be strong. It was concluded that for North America as much as 60% of the average yield of sulfate carried to the ocean is related to human activities. This study assigned a higher proportion of the total yield of sulfate in European streams to human sources, but for other continents it was thought the effects of human activities to be relatively minor.

Some of the compounds produced in the sulfur cycle are gases. For example, combustion of fossil fuels, especially coal, produces sulfur dioxide gas (SO_2), which is further oxidized in the atmosphere to sulfur trioxide (SO_3) that combines with water to form sulfuric acid (H_2SO_4). Reduction of sulfate in anaerobic soils and sediment produces hydrogen sulfide (H_2S) gas that also is reoxidized to sulfate in the presence of air. As a result, precipitation from the atmosphere is a major source of sulfate in streams in parts of North America and Europe. The estimate for human sources includes both sulfur dioxide and hydrogen sulfide reaction pathways (59). A compilation by the U.S. Environmental Protection Agency (60), summarizing research on acidic deposition, quoted estimates and measurements of "excess sulfate" yields in precipitation and in lakes and streams in the northeastern United States and southeastern Canada. Among measured data cited was a wet-plus-dry annual sulfate deposition rate for a site in the Adirondacks that ranged from about 8.2 to 16 tons/mi^2. Although a wide range of values was observed, these rates probably can be considered reasonable for much of the eastern half of the United States. The term "excess sulfate" is defined as the amount "over and above that supplied by sea salt cycling." Ref. 51 estimates that, on average, 60% of the sulfate yield observed for the stream basins he studied was assignable to atmospheric sources.

Another source of sulfur in the global hydrologic cycle that is not related to human activities is gaseous emission of hydrogen sulfide and sulfur dioxide from volcanoes and other geothermal sources. Although effects of these emissions can be locally intense, they generally are thought to be much less significant on a global scale than the human sources.

Sulfate concentration in streams and changes over time and is one of the principal indices of human influences on stream water composition. Differences and similarities in sulfate yields help in attaining a reasonable perspective on the importance of various hydrologic and geochemical characteristics of individual drainage systems.

Chlorine. Nearly all chlorine compounds are readily soluble in water. As a result, the major reservoir for this element in Figure 13 is the ocean (47). Chloride, as noted earlier, is naturally present at low levels in rain and snow, especially over and near the oceans. Widespread increases in chloride concentration in runoff in much of the United States can be attributed to the extensive use of sodium chloride and calcium chloride for deicing of streets and highways. Ref. 61 points out the importance of the increased use of deicing salt as a cause of increased chloride concentrations in streams of the northeastern United States and the role of this factor in the chloride trends in Lake Ontario. Increases in chloride concentration also can occur as a result of disposal of sewage, oil field brines, and various kinds of industrial waste. Thus, chloride concentration trends also can be considered as an index of the alternation of streamwater chemistry by human development in the industrialized sections of the world. Although chlorine is an essential element for animal nutrition, it is of less importance for other life forms.

Nitrogen. About three-fourths of the Earth's nitrogen is present in the atmosphere as nitrogen gas. Because of its importance as an essential element in plant and animal nutrition, nitrogen, in its various oxidation states and its yield and concentration, is of considerable interest in studies of human influences on stream water composition. Certain small- and medium-sized streams in the intensively developed agricultural areas of the United States have been strongly affected by nitrogen-bearing runoff from fertilized soil. However, because of its use by aquatic vegetation, the amount and form of nitrogen tend to be seasonally variable, and especially for larger streams, it is more difficult to use than sulfate or chloride as an index of human effects on water composition. Although nitrate concentrations are reported in some of the streams, no attempt at interpretation of the nitrogen chemistry is made here; however, Ref. 62, using mainly U.S. Geological Survey (USGS) data, evaluates nitrogen trends since 1905 in the Mississippi River at St. Francisville, Louisiana.

8. Stream Water Quality Trends

The first comprehensive nationwide study of the chemical composition of surface water in the United States was begun by the USGS in 1905. This program received cooperative support from state agencies in Illinois, Minnesota, Kansas, California, Oregon, and Washington and entailed collection of daily samples of water at or near gaging station sites on principal streams for a period of about one year. The daily samples were combined into 10-day composites, which were filtered to remove suspended material and analyzed for principal dissolved constituents using standard "wet-chemical" procedures. As a result of decreased funding and related factors, this work was substantially curtailed after 1907; however, the studies did produce compilations of analyses for about 100 stream-sampling sites east of the 100th Meridian (63) and for about another 55 sites in the western part of the country (64). Somewhat more detailed reports for each of the six cooperating states also were issued in the USGS Water-Supply Paper series, and Clarke (65) used many of the analyses from the program in his summary of the composition of river and lake waters of the United States.

From about 1914 to 1940 studies of river water quality were carried on at only a few sites in the United States. A revival of interest began in the 1940s, however, and by the 1960s, a much larger number of sampling sites were in operation than had existed at the height of the 1905–1907 program. The available historical data base for most U.S. sampling stations has no water quality measurements for the 1910–1940 period.

Stream water quality commonly varies greatly in response to water discharge; thus, a single year of record is not adequate for reliable extrapolation, and in any exacting comparison of historical data, this factor needs to be taken into account. From the beginning, it has been a general policy in the USGS surface water quality program to locate sampling sites at or near gaging stations where records of stream flow are obtained. Until about 1970, many of the USGS water quality records were based on daily sampling, generally with determinations of specific electrical conductance (an indicator of total cation and anion concentration) on each sample, but with extensive analyses performed only on composited daily samples. Composites usually contained 10 daily samples. However, where stream discharge and other factors caused substantial day-to-day changes in specific conductance, the composite period was shortened to prevent mixing of chemically dissimilar samples and to give a clearer indication of the stream chemistry variability. Annual averages of these analyses, weighted by time or discharge, were used to summarize the records. After 1970, complete analyses were done on single samples collected at various time intervals ranging from semimonthly to quarterly, and analyses of composite samples were no longer made. Analytical procedures changed from time to time as improved instrumentation and techniques became available.

In 1974, the National Stream Quality Accounting Network (NASQAN) program was established to develop a baseline water chemistry data set that was long-term and systematically collected throughout the United States. Originally there were 500 collection stations, but later budget cuts limited the stations to ca 275 in 1994. Data were collected at uniform intervals without concern for the hydrological patterns of high or low flow, and therefore, a fairly representative description of conditions on any given day was provided.

For the first five years after a major redesign in 1995 the NASQAN program focused on the water quality of the major rivers in the United States: the Mississippi (including the Missouri and the Ohio); the Columbia; the Colorado; and the Rio Grande. An extended range of chemicals, including pesticides and trace elements, were measured in tandem with stream discharge.

In 2001, the program entered a five-year study that included decreasing the data collection in the two basins at the Colorado and the Columbia and redirected its sampling to the Yukon. The redirection is aimed are providing a baseline on organic carbon dynamics in response to melting of permafrost in the Arctic (66).

The United States Geological Survey National Water Quality Assessment (NAWQA) program recently reported on the water quality of major river basins and aquifers in the U.S. and determined that the waters are generally suitable for irrigation, drinking water supply, and home and recreational uses (67). Major challenges that continue to affect streams and ground water include point and non-point sources of pesticides, nutrients, metals, and gasoline-related compounds. Human activities on water resources such as effects associated with agriculture and urban development are also being monitored. Contaminant levels change from season to season among the various watersheds due to the differences in land management strategies.

Some of the findings from the recent reports include the following:

1. Changes in land management can improve stream quality. In the Yakima River Basin of Washington, varying the irrigation techniques (switching to sprinkler and drip irrigation) has led to a reduction in runoff from farms, which reduces suspended sediment, total phosphorus, dissolved nitrates and organochlorine compounds in streams.

2. Ground water quality responds to changes more slowly than surface water.
3. Urbanizing watersheds show positive and negative changes in water quality. Data from around the U.S. show decreasing concentrations of lead, PCBs, and DDT, and an increase in polycyclic aromatic hydrocarbons, which are identified with increased motor vehicle traffic.
4. Low levels of urbanization can affect aquatic ecosystems.
5. The influence of natural features can be substantial. For example, mercury concentrations are affected by the amount of wetlands and the presence of sulfur, carbon, organic matter, and dissolved oxygen in the soils and water. Concentrations of mercury were higher in Boston, Maine, and New Hampshire. Mercury in fish was higher in the forested watersheds because of the larger amount of wetlands.
6. Analyses detected very low levels of pesticides and volatile organic compounds (VOCs) in river basins and aquifer systems across a wide range of landscapes and land uses.
7. Some contaminants occur naturally even in pristine areas. Elevated concentrations of phosphorus in streams are derived from igneous and marine sedimentary rocks. Elevated concentrations of arsenic most likely result from sedimentary rocks in contact with geothermal water.

8.1. Specific Watersheds in the United States. The United States Geological Survey's website (usgs. gov) gives access to 1.5×10^6 sites in the United States. "Surf your Watershed" gives specific information on the impact of human activities, quality and quantity of water, habit quality for fish and birds, and forecasting.

Major studies are presented for Chesapeake Bay, Mojave Desert, Platte River, San Francisco and Delta, and South Florida.

9. Analytical Methods

Since 1970, new analytical techniques, eg, ion chromatography, have been developed, and others, eg, atomic absorption and emission, have been improved (68–72). Detection limits for many chemicals have been dramatically lowered. Many wet chemical methods have been automated and are controlled by microprocessors which allow greater data output in a shorter time (73). Isolation of samples is maintained by pumping air bubbles into the flow line. Flow-injection analysis has also become popular, and a theoretical comparison of it with the segmented flow analyzer has been made (74,75). Several books are available regarding automated chemical analysis (76,77) (see ANALYTICAL METHODS; also BIOTECHNOLOGY).

Although simple analytical tests often provide the needed information regarding a water sample, such as the formation and presence of chloroform and other organohalides in drinking water, require some very specialized methods of analysis. The separation of trace metals into total and uncomplexed species also requires special sample handling and analysis (78).

A list of all water analyses would be extremely long since, under some conditions and with enough time, water can solubilize everything to some extent. Fortunately, a great deal can be learned about a water supply by carrying out a few physical and chemical tests. These simple tests might be all that are needed to characterize a water supply for many purposes, and it is usually the purpose for which the water is to be used that determines the type and extent of testing. The methods described in this article are intended primarily for freshwater analysis and may not be suitable for the analysis of saline water. In addition, there are several books, manuals, and annual review articles available that detail water analysis for different substances and uses (79–84).

9.1. Physical Properties *Temperature.* Water temperature is an important parameter in calculations of oxygen solubility, calcium carbonate saturation and stability, and various forms of alkalinity, as well as in determining basic hydrobiological characteristics. The temperature should be taken *in situ* for accuracy, and a standard mercury thermometer with readings to the nearest 0.1°C should be used. It should be calibrated against a precision thermometer certified by the National Bureau of Standards. A thermistor is preferable when attempting to measure temperature at different depths and for automated monitoring and surveillance, and should be similarly calibrated (see TEMPERATURE MEASUREMENT).

Specific Conductance. The specific conductance depends on the total concentration of the dissolved ionized substances, ie, the ionic strength of a water sample. It is an expression of the ability of the water to conduct an electric current. Freshly distilled water has a conductance of 0.5–2 μS/cm, whereas that of potable water generally is 50–1500 μS/cm. The conductivity of a water sample is measured by means of an a-c Wheatstone-bridge circuit with a null indicator and a conductance cell. Each cell has an associated constant which, when multiplied by the conductance, yields the specific conductance.

The concentration of dissolved ionic substances can be roughly estimated by multiplying the specific conductance by an empirical factor of 0.55–0.9, depending on temperature and soluble components. Since specific conductance is temperature dependent, all samples should be measured at the same temperature. Alternatively, an appropriate temperature-correction factor obtained by comparisons with known concentrations of potassium chloride may be used. Instruments are available that automatically correct conductance measurements for different temperatures.

Color. Many water samples have a yellow to brownish-yellow color which is caused by natural substances, eg, leaves, bark, humus, and peat material. Turbidity in a sample can make the measurement of color uncertain and is usually removed by centrifugation prior to analysis. The color is usually measured by comparison of the sample with known concentrations of colored solutions. A platinum–cobalt solution is used as the standard, and the unit of color is that produced by 1 mg/L platinum as chloroplatinate ion. The standard is prepared from potassium chloroplatinate (K_2PtCl_6) and cobalt chloride ($CoCl_2 \cdot 6H_2O$). The sample may also be compared to suitably calibrated special glass color disks.

Three special tristimulus light filters are available which, when combined with a specific light source and a filter photometer, can be used to obtain color data (83). Although this method provides added precision and accuracy, it is seldom worth the extra effort required (see COLOR).

Turbidity. Turbidity in natural water is caused by the presence of suspended matter which scatters light. The suspended material is usually clay or silt, finely divided organic and inorganic material, or microorganisms. It is measured either visually or by a nephelometric method. The former is based on the light path through a sample that just causes the image of the flame of a standard candle to disappear. Longer light paths are indicative of lower turbidities. Suspensions of clay are used as standards and results are reported in Jackson turbidity units (JTU). The lowest turbidity value that can be measured using this method is 25 JTU.

The nephelometric method involves illuminating the sample in a turbidimeter and measuring the amount of light scattered at 90° to the incident beam. The higher the intensity of scattered light, the greater the sample turbidity. A formazan polymer suspension is used as the standard and results are reported in nephelometric turbidity units (NTU). The greater precision, sensitivity, and wider applicability of this method make it preferable to the visual method.

Taste and Odor. The measurement of taste and odor is somewhat subjective and depends on the personal judgements of individuals. Panels of not less than five observers, and preferably more than ten, are used. The sample is diluted with odor-free water until a ratio at which the odor is just perceptible is determined; this ratio is called the threshold odor number (TON). A similar method is used to detect a distinct taste in water (see FLAVOR CHARACTERIZATION).

Dissolved Solids. Dissolved solids are materials that pass through a glass-fiber filter and remain after evaporation and drying at 180°C.

Suspended Solids. Suspended solids are determined by filtering a known volume of water through a glass-fiber filter and weighing the filter before and after filtration. The filter is dried at 105–110°C, and the weight difference is equal to the suspended solids.

pH. The pH of most natural waters is 4–9 and should be measured *in situ* since it is subject to change once a sample has been isolated. It can be measured either colorimetrically or potentiometrically. The former method relies on color-indicator papers which are impregnated with pH-sensitive dyes. The potentiometric method requires the use of a pH-sensitive glass electrode, which is generally interference-free at pH 4–9. The electrode should be calibrated frequently against standard buffer solutions of known pH (see HYDROGEN-ION ACTIVITY).

9.2. Principal Mineral Constituents and Gases. *Alkalinity.* The alkalinity of a water sample is its acid-neutralizing capacity. Bicarbonate and carbonate ions are the predominant contributors to alkalinity in most waters, and their chemical equilibria generally maintain the pH of 5–9. The presence of enough hydroxide ion to affect the alkalinity determination in natural waters is rare. Silica, borate, or phosphate do contribute to the overall alkalinity if present in large enough quantities.

The alkalinity is determined by titration of the sample with a standard acid (sulfuric or hydrochloric) to a definite pH. If the initial sample pH is >8.3, the titration curve has two inflection points reflecting the conversion of carbonate ion to bicarbonate ion and finally to carbonic acid (H_2CO_3). A sample with an initial pH <8.3 only exhibits one inflection point corresponding to conversion of bicarbonate to carbonic acid. Since most natural-water alkalinity is governed by the carbonate–bicarbonate ion equilibria, the alkalinity titration is often used to estimate their concentrations.

Acidity. Acidity is the base-neutralizing capacity of a sample of water. It is determined by titration of the sample with standard base to pH 8.3 (phenolphthalein end point). Generally, a sample is not reported as acidic unless its initial pH is <4.5. The acidity may be the result of free acids, eg, HCl or H_2SO_4, or the hydrolysis of certain metal cations.

The free-acid content is determined by titration of a cold solution to pH 4.5. The total acidity is determined by titration to pH 8.3 in a boiling solution. Some natural-water samples might be complex, and the best determination of acidity results from visual inspection of the plotted titration curve.

Hardness (Calcium and Magnesium). The term *hardness* has its origins in the household laundry use of water. Some waters were considered harder to use for laundering because they required more soap to produce suds. The hardness of water was then taken to be a measure of the capacity of the water to cause the precipitation of soap. This is actually a result of the reaction of soap with calcium or magnesium ions. Thus, water hardness is generally a measure of the total concentration of calcium and magnesium. The portion of hardness that disappears with boiling is temporary or carbonate hardness and is primarily caused by calcium and magnesium bicarbonates. They precipitate as their carbonates by the loss of carbon dioxide during boiling. The hardness remaining after boiling is the permanent or noncarbonate hardness. Other cations, eg, strontium or barium, also contribute to hardness, but their concentration is usually insignificant (see DISPERSANTS; DETERGENCY).

Calcium and magnesium can be titrated readily with disodium ethylenediaminetetraacetate, with Eriochrome Black T as the indicator. The solution is buffered at pH 10.0. Certain metal ions interfere with this procedure by causing fading or indistinct end points. Cyanide, sulfide, or hydroxylamine can be used to eliminate or minimize the interferences.

Hardness can also be calculated by summation of the individually determined alkaline earths by means of atomic absorption analysis. Basic samples must be acidified, and lanthanum chloride must be added to minimize interferences from phosphate, sulfate, and aluminum. An ion-selective electrode that utilizes a liquid ion exchanger is also available for hardness measurement; however, this electrode is susceptible to interferences from other dissolved metal ions.

Magnesium, calcium, barium, and strontium can also be determined by ion chromatography with *m*-phenylenediamine in perchloric acid as the eluent. Ion chromatography by conductimetric detection has been described, and applications to environmental waters have been discussed (68,85,86).

Sodium and Potassium. Sodium and potassium can be determined by either atomic emission or absorption. Large concentrations of sodium can interfere with the potassium determination in either of these methods. Excess sodium can be added to both the potassium standards and samples to minimize any variations in the samples. Proper positioning of the flame helps reduce sodium interference in atomic absorption.

Chloride. Chloride is common in freshwater because almost all chloride salts are very soluble in water. Its concentration is generally 10^{-4} to 10^{-3} *M*. Chloride can be titrated with mercuric nitrate. Diphenylcarbazone, which forms a purple complex with the excess mercuric ions at pH 2.3–2.8, is used as the indicator. The pH should be controlled to ±0.1 pH unit. Bromide and iodide are the principal interferences, whereas chromate, ferric, and sulfite ions interfere at levels greater than 10 mg/L. Chloride can also be determined by a colorimetric method based on the displacement of thiocyanate ion from mercuric thiocyanate by chloride ion. The liberated SCN^- reacts with ferric ion to form the colored complex of ferric thiocyanate. The method is suitable for chloride concentrations from 10^{-6} to 10^{-3} *M*.

Ion chromatography can be used to determine chloride concentrations of 2–1000 ppb with a carbonate–bicarbonate eluent (86). Fluoride, nitrite, phosphate, bromide, nitrate, and sulfate do not interfere and can be measured simultaneously with a total analysis time of <30 min.

An ion-selective electrode is available for chloride analysis; chloride can be measured potentiometrically at 10^{-6}–1 *M*. Iodide and sulfide are the principal interferences.

Sulfate. Mine drainage may contribute to high sulfate concentrations resulting from pyrite oxidation. High concentrations may exhibit a cathartic action. Sulfate concentrations of 10^{-5} to 10^{-3} *M* can be titrated in an alcoholic solution with standard barium chloride and using Thorin as an indicator. Barium reacts with Thorin to form a deep red complex. The sample should be kept at pH 2–5, and the sample must be passed through a strong cation-exchange column prior to the titration. This is done to remove any multivalent cations which would also form intensely colored complexes with Thorin. High concentrations of sulfate can be determined by gravimetric analysis. The sulfate precipitates as barium sulfate. The ion-chromatographic response to sulfate is linear from 2 to 10^4 ppb (86).

Nitrate and Nitrite. Nitrate is usually present in trace quantities in surface waters but occasionally occurs in high concentrations in some groundwaters. If present in excessive amounts, it can contribute to the illness infant methemoglobinemia. Nitrate is an essential nutrient for many photosynthetic autotrophs. Nitrite is an intermediate in the reduction of nitrate as well as in the oxidation of ammonia; it is also used as a corrosion inhibitor in some industrial processes.

Nitrite can be determined by reaction with sulfanilamide to form the diazo compound, which couples with *N*-(1-naphthyl)ethylenediamine dihydrochloride to form an intensely colored red azo dye. Nitrate can be determined in a similar manner after reduction to nitrite. Suitable reducing agents are cadmium filings or hydrazine. This method is useful at a nitrogen concentration of 10^{-7}–10^{-4} *M*.

Nitrate can also be measured potentiometrically with an ion-selective electrode at 10^{-5}–10^{-1} *M* (87,88). This method is suggested as a screening method for determining the approximate nitrate concentration (83). Ion chromatography can be used for nitrate concentrations of 2 to 10^4 ppb (86).

Fluoride. A fluoride concentration of ca 1 mg/L is helpful in preventing dental caries. Fluoride is determined potentiometrically with an ion-selective electrode. A buffer solution of high total ionic strength is added to the solution to eliminate variations in sample ionic strength and to maintain the sample at pH 5–8, the optimum range for measurement. (Cyclohexylenedinitrilo)tetraacetic acid (CDTA) is usually added to the buffer solution to complex aluminum and thereby prevent its interference. If fluoroborate ion is present, the sample should be distilled from a concentrated sulfuric acid solution to hydrolyze the fluoroborate to free fluoride prior to the electrode measurement (89,90).

Several colorimetric procedures for fluoride are available, but it is usually desirable to distill the sample from concentrated sulfuric acid prior to analysis to eliminate interferences. One method is based upon bleaching a dye formed by the reaction of zirconium and sodium 2-(*p*-sulfophenylazo)-1,8-dihydroxy-3,6-naphthalenedisulfonate (SPADNS reagent) (91).

Phosphate. Phosphorus occurs in water primarily as a result of natural weathering, municipal sewage, and agricultural runoff. The most common form in water is the phosphate ion. A sample containing phosphate can react with ammonium molybdate to form molybdophosphoric acid ($H_3P(Mo_3O_{10})_4$). This compound is reduced with stannous chloride in sulfuric acid to form a colored molybdenum-blue complex, which can be measured colorimetrically. Silica and arsenic are the chief interferences.

Some water samples contain phosphorus forms other than phosphate, eg, polyphosphate, hexametaphosphate, and organic phosphates. These forms can be hydrolyzed to phosphate in hot sulfuric acid solution and determined by the preceding method. The more refractory organic phosphates require digestion in a sulfuric acid–ammonium persulfate solution. Ion chromatography can also be used to measure ${PO^{3-}}_4$ at 2 to 10^4 ppb (84).

Boron and Borates. Boron is an essential element for plant growth; however, concentrations >2 mg/L are harmful to some plants. Natural-water concentrations of boron are usually well below this value, although higher concentrations can occur as a result of industrial waste effluents or cleaning agents.

Two colorimetric methods are recommended for boron analysis. One is the curcumin method, where the sample is acidified and evaporated after addition of curcumin reagent. A red product called rosocyanine remains; it is dissolved in 95 wt % ethanol and measured photometrically. Nitrate concentrations >20 mg/L interfere with this method. Another colorimetric method is based upon the reaction between boron and carminic acid in concentrated sulfuric acid to form a bluish-red or blue product. Boron concentrations can also be determined by atomic absorption spectroscopy with a nitrous oxide–acetylene flame or graphite furnace. Whole-water recoverable boron can be determined by the use of inductively coupled plasma-mass spectrometry (92).

Silica. The silica content of natural waters is usually 10^{-5} to (5×10^{-4}) M. Its presence is considered undesirable for some industrial purposes because of the formation of silica and silicate scales. The heteropoly-blue method is used for the measurement of silica. The sample reacts with ammonium molybdate at pH 1.2, and oxalic acid is added to reduce any molybdophosphoric acid produced. The yellow molybdosilicic acid is then reduced with 1-amino-2-naphthol-4-sulfonic acid and sodium sulfite to heteropoly blue. Color, turbidity, sulfide, and large amounts of iron are possible interferences. A digestion step involving $NaHCO_3$ can be used to convert any molybdate-unreactive silica to the reactive form. Silica can also be determined by atomic absorption with a nitrous oxide–acetylene flame or by atomic emission involving either a d-c or inductively coupled argon plasma source.

Oxygen. The solubility of atmospheric oxygen in water depends primarily on pressure, temperature, and salt content. The most reliable results for oxygen measurement are obtained from fresh samples. The longer the time lag between sampling and measurement, the greater the chance that the dissolved oxygen concentration diminishes because of chemical or biological activity in the sample. The Winkler titration has been the preferred method for dissolved oxygen determination for many years. Several modifications of the basic method have been made to minimize interferences (83). The basis of this analysis is the quantitative oxidation of alkaline manganous hydroxide by the oxygen in the sample. Upon acidification in the presence of excess iodide, an amount of iodine equivalent to the dissolved oxygen is released. The iodine can then be titrated with standard sodium thiosulfate.

Considerable care is required in the collection of samples for dissolved-oxygen analysis. The errors associated with sampling can be minimized by an *in situ* method. Membrane-covered dissolved-oxygen electrodes are ideally suited to this purpose. These electrodes can be either polarographic or galvanic. The electrodes are protected by an oxygen-permeable polymeric membrane, which provides a rigorously defined diffusion barrier against solution impurities. For the polarographic type, an external voltage must be applied to the working or sensing electrode and must be sufficient to reduce molecular oxygen. With the galvanic type, two solid metal electrodes are used, such that the reduction of oxygen occurs spontaneously and no external voltage source is necessary. In both cases and under steady-state conditions, the resulting current is proportional to the dissolved-oxygen concentration in solution. The use and operation of dissolved-oxygen electrodes are thoroughly described in several publications (93,94).

9.3. Minor Mineral Constituents and Gases. *Metals.* The method of choice for metal analysis generally depends upon the concentration as well as the number of metals to be analyzed per sample and, to a lesser degree, the number of samples. When there is a large number of metals per sample, an emission spectroscopy method is preferred because of its simultaneous multielement capabilities. This technique has become much more popular for water analysis because of the development of a argon plasma as an emission source. This source combines the advantages of the flame with the high temperature of an electric arc or spark. The plasma can be generated either through an induction process or by a direct current. When coupled with a polychromator in a direct-reading fashion, this method can be used to measure up to 60 elements in approximately 1 min (95–97). Limits of detection for many elements are comparable to or better than flame atomic absorption and, in some cases, to graphite-furnace atomic absorption.

Atomic absorption spectroscopy is more suited to samples where the number of metals is small, because it is essentially a single-element technique. The conventional air–acetylene flame is used for most metals; however, elements that form refractory compounds, eg, Al, Si, V, etc, require the hotter nitrous oxide–acetylene flame. The use of a graphite furnace provides detection limits much lower than either of the flames. A cold-vapor-generation technique combined with atomic absorption is considered the most suitable method for mercury analysis (98).

Nonmetals. *Arsenic.* Total arsenic concentration can be determined by reduction of all forms to arsine (AsH_3) and collection of the arsine in a pyridine solution of silver diethyldithiocarbamate. Organoarsenides must be digested in acidic potassium persulfate prior to reduction. The complex that forms is deep red, and this color can be measured spectrophotometrically. Reduction is carried out in an acidic solution of $KI{-}SnCl_2$, and AsH_3 is generated by addition of zinc.

Atomic absorption spectroscopy is an alternative to the colorimetric method. Arsine is still generated but is purged into a heated open-end tube furnace or an argon–hydrogen flame for atomization of the arsenic and measurement. Arsenic can also be measured by direct sample injection into the graphite furnace. The detection limit with the air–acetylene flame is too high to be useful for most water analysis.

Whole-water recoverable arsenic can be determined by the use of inductively coupled plasma-mass spectrometry (92).

Selenium. Selenium is determined by atomic absorption after the organoselenides are broken down with acidic persulfate and all forms of selenium have been converted to H_2Se. The reduction is brought about in acidic solution of $KI{-}SnCl_2$ or borohydride, and H_2Se is generated by addition of zinc. The dihydrogen selenide is purged into an open-end tube furnace or argon–hydrogen flame for atomization and measurement. Selenium can also be determined by direct sample injection into the graphite furnace.

Cyanide. Industrial processes frequently discharge significant concentrations of cyanide, which can be extremely toxic at very low levels. Cyanide compounds are classified as either simple or complex. It is usually necessary to decompose complex cyanides by an acid reflux. The cyanide is then distilled into sodium hydroxide to remove compounds that would interfere in analysis. Extreme care should be taken during the distillation as toxic hydrogen cyanide is generated. The cyanide in the alkaline distillate can then be measured potentiometrically with an ion-selective electrode. Alternatively, the cyanide can be determined colorimetrically. It is converted to cyanogen chloride by reaction with chloramine-T at $pH < 8$. The CNCl then reacts with a pyridine barbituric acid reagent to form a red-blue dye.

Bromide and Iodide. The spectrophotometric determination of trace bromide concentration is based on the bromide catalysis of iodine oxidation to iodate by permanganate in acidic solution. Iodide can also be measured spectrophotometrically by selective oxidation to iodine by potassium peroxymonosulfate ($KHSO_5$). The iodine reacts with colorless leucocrystal violet to produce the highly colored leucocrystal violet dye. Greater than 200 mg/L of chloride interferes with the color development. Trace concentrations of iodide are determined by its ability to catalyze ceric ion reduction by arsenous acid. The reduction reaction is stopped at a specific time by the addition of ferrous ammonium sulfate. The ferrous ion is oxidized to ferric ion, which then reacts with thiocyanate to produce a deep red complex.

Both of these halides can also be determined potentiometrically with an appropriate ion-selective electrode. Sulfide and cyanide both interfere with the electrode response.

Gases. Hydrogen Sulfide. Sulfide ion from 10^{-7} to 1 M can be measured potentiometrically with an ion-selective electrode. Mercuric ion interferes at concentrations $>10^{-7} M$. The concentration of hydrogen sulfide can be calculated knowing the sample pH and the pK_a for H_2S.

Ammonia. The most reliable results for ammonia are obtained from fresh samples. Storage of acidified samples at 4°C is the best way to minimize losses if prompt analysis is impossible. The sample acidity is neutralized prior to analysis. Ammonia concentrations of 10^{-6}–0.5 M can be determined potentiometrically with the gas-sensing, ion-selective electrode. Volatile amines are the only known interferents.

The most common colorimetric technique involves a reaction between ammonia and a reagent containing mercuric iodide in potassium iodide (Nessler reagent) to form a reddish-brown complex. Turbidity, color, and hardness are possible interferences that can be removed by preliminary distillation at pH 9.5.

9.4. Organic Materials. *Nonspecific Organics. Biochemical Oxygen Demand.* The biochemical oxygen demand (BOD) test is an empirical determination of the oxygen requirement of a sample. It is most often applied to wastewaters, industrial effluents, and polluted waters. The decrease in the dissolved oxygen concentration resulting primarily from biological action is measured after storage for 5 d at 20°C.

If the sample has very low initial dissolved oxygen, it must be aerated; if it has a very high BOD, it may be necessary to dilute the sample. The dilution water is a phosphate buffer containing magnesium sulfate, calcium chloride, and ferric chloride. The percentage dilution must usually be determined by trial and error, although rough estimates may be made depending on sample type (83).

The dissolved oxygen concentrations are determined immediately and after five days. The method for dissolved measurement involves either a modified Winkler titration or a membrane-covered oxygen electrode. The difference between initial and final dissolved oxygen multiplied by the dilution factor is the BOD value.

Chemical Oxygen Demand. The chemical oxygen demand (COD) test measures the oxygen equivalent of the organic matter in a sample that is susceptible to oxidation by a strong oxidant (83). The sample is refluxed with a known amount of potassium dichromate in sulfuric acid for 2 h. Silver sulfate is added to catalyze the oxidation of straight-chain compounds, and mercuric sulfate is added to the sample prior to refluxing to react with chloride ion and prevent its oxidation. The amount of unreacted dichromate is then titrated with standard ferrous ammonium sulfate.

Organic Carbon. The total organic carbon (TOC) in a water sample is determined by injecting a microliter sample into a heated, packed tube in a stream of oxygen. The water is vaporized and carbon is converted to carbon dioxide, which is detected with a nondispersive infrared analyzer. Nitrogen is bubbled through the acidified sample prior to injection to remove inorganic carbon and other volatiles.

An analytical method has been developed for the determination of dissolved organic carbon concentration in water samples. This method includes the results of tests used to validate the method and the quality control practices used for organic carbon analysis. Prior to the analysis, water samples are filtered to remove suspended particulate matter. A Shmiadzu total organic carbon analyzer is used to analyze samples by high temperature catalytic oxidation. The analysis is usually completed within 48 hours of sample collection. The laboratory reporting level is 0.22 mg/L (99).

Detergents. The most widely used surfactant in synthetic detergents is the readily biodegradable linear alkyl sulfonate (LAS). Since the detergent industry began using this ingredient, the occurrence of foaming incidents has all but disappeared (see SURFACTANTS). The methylene-blue method is used to measure LAS in addition to alkyl sulfates and alkyl poly(ethoxyl sulfate)s. The blue salt that forms is extracted with chloroform and measured colorimetrically. There are many organic and inorganic interferences associated with this method and, since a large number of surfactants react with methylene blue, the test is designated as one for methylene-blue-active substances. If this test shows a significant amount of surfactant, confirmation of the LAS should be made by other methods, eg, thin-layer chromatography followed by infrared spectroscopy (100).

Oil and Grease. Industrial processes contribute most of the grease and oil found in water. Oil and grease can cause problems in wastewater-treatment processes as well as prevent the use of the sludge as fertilizer. The amount of oil and grease can be determined by extraction of an acidified sample with an organic solvent followed by evaporation of the solvent and weighing the residue. During the last part of the solvent evaporation, the sample must not be overheated to prevent the loss of low boiling oils.

Specific Organics. Large quantities of specific organic materials are used annually in industrial and agricultural applications, and these compounds or their degradation products are present in surface and groundwaters. The volume of publications dealing with analytical methodology for specific organics is enormous. The development of glass capillary columns has improved the application of gas–liquid chromatographic (glc) separations. In addition, the application of the mass spectrometer (ms) as a detector for gas–liquid chromatography has made the positive identification of peaks possible. High performance liquid chromatography (hplc), which involves various detectors, can be used to measure hydrophilic and hydrophobic organic compounds in water.

Various methods for the glc monitoring of EPA Consent Decree Priority Pollutants in water have been described (101) (see REGULATORY AGENCIES). The determination of organic pollutants in water by glc and ms methods has also been detailed (102,103). Nonvolatile organic compounds in drinking water have been determined by hplc (104) (see WATER, POLLUTION).

Pesticides. Chlorinated hydrocarbon insecticides are determined with an electron-capture detector following extraction with an organic solvent (83). If polychlorinated biphenyls (PCBs) are known to be present or if the extract contains so many pesticides that separation by glc is difficult, the extract should be passed through a Florisil column. Elution of the column with different solvents allows certain group separations of the pesticides. The following organochlorinated pesticides and PCBs have been determined by the method: lindane, heptachlor, heptachlor epoxide, aldrin, dieldrin, *p,p′*-1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane (*p,p′*-TDE), *p,p′*1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (*o,p′*-DDT), *o,p′*-DDT, *p,p′*-1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene (*p,p′*-

DDE), endrin, *p,p*′-methoxychlor, α-endosulfan, β-endosulfan, *cis*-chlordane, *trans*-chlordane, Aroclor 1248, Aroclor 1254, and Aroclor 1260. Quantitation is by comparison of chromatograms with standard concentrations of pure compounds treated in an identical manner. The phenoxy acid herbicides (2,4-dichlorophenoxy)acetic acid (2,4-D), silvex, and (2,4,5-trichlorophenoxy)acetic acid (2,4,5-T) can be determined by electron-capture detection after extraction and conversion to the methyl esters with BF_3-methanol. The water sample must be acidified to pH ≤ 2 prior to extraction with chloroform.

Identification of the pesticides is based on retention time on at least two dissimilar glc columns. A nonpolar and a relatively polar packing are generally used, for example, OV-17 and a mixture of QF-1 and DC-200.

Organophosphorus pesticides are determined with a flame photometric detector, which is sensitive only to compounds containing phosphorus or sulfur (83). The water sample is extracted with benzene, and the solvent is concentrated to a small volume prior to glc analysis. The following organophosphates are determined by this method: ethyl guthion, guthion, trithion, ruelene, diazinon, disyston, ethion, imidan, malathion, methyl parathion, methyl trithion, parathion, thimet, and trolene (see INSECT CONTROL TECHNOLOGY).

High performance liquid chromatography with electrochemical detection has been used to determine 2–7 ppb of carbamate pesticides in water (105). The investigated pesticides were aminocarb, asulam, *sec*-butyl phenylmethylcarbamate (BPMC), carbaryl, carbendazim, chlorpropham, desmedipham, and phenmedipham.

Methods of analysis for acetamide, triazine, and phenylurea herbicides and their degradation products have been reported. The analysis detects these compounds in natural water samples by solid-phase extraction and liquid chromatography/mass spectrometry. Special consideration was given in the development of these tests to prevent degradation during analysis (106,107).

Trihalomethanes. Wherever chlorine is used as a disinfectant in drinking-water treatment, trihalomethanes (THMs) generally are present in the finished water. The THMs usually formed are trichloromethane (chloroform), bromodichloromethane, dibromochloromethane, and tribromomethane (bromoform). There are four main techniques for the analysis of THMs: headspace, liquid–liquid extraction (lle), adsorption–elution (purge–trap), and direct aqueous injection. The final step in each technique involves separation by gas–liquid chromatography with a 2 mm ID coiled glass column containing 10 wt % squalene on chromosorb-W-AW (149–177 μm (80–100 mesh)) with detection generally by electron capture.

The purge–trap method is the most widely accepted method for THMs as well as for other purgeable organohalides (108). The purgeable organics are stripped from the water sample with a stream of inert gas and are adsorbed in a porous polymer trap. The compounds are thermally desorbed from the trap into a gas chromatograph. All of the lle methods involve extraction of a small volume of water with a much smaller volume organic solvent (109). An aliquot of the extract is then gas-chromatographed. Different lle techniques have been evaluated to be as sensitive and accurate as the purge–trap methods (109,110).

Gasoline Oxygenates. Methyl-*tert*-butyl ether (MTBE), methyl *tert*-pentyl ether (TAME), diisopropyl ether (DIPE), and ethyl-*tert*-butyl ether (ETBE) are members of a group of chemicals commonly known as fuel oxygenates. MTBE replaced lead as an octane enhancer in 1979. The use of MTBE is now being challenged. Ethanol is replacing MTBE in some cases. A laboratory method for analysis of small concentrations of these oxygenates has been reported. These oxygenates can be detected in water by purge- and trap-capillary-column gas chromatography. Long-term method detection levels range from 15 to 83 nanograms/L (112).

9.5. Radioactive Materials. Radioactivity in environmental waters can originate from both natural and artificial sources. The natural or background radioactivity usually amounts to $\leq$100 mBq/L. The development of the nuclear power industry as well as other industrial and medical uses of radioisotopes (qv) necessitates the determination of gross alpha and beta activity of some water samples. These measurements are relatively inexpensive and are useful for screening samples. The gross alpha or beta activity of an acidified sample is determined after an appropriate volume is evaporated to near dryness, transferred to a flat sample-mounting dish, and evaporated to dryness in an oven at 103–105°C. The amount of original sample taken depends on the amount of residue needed to provide measurable alpha or beta activity.

Alpha counting is done with an internal proportional counter or a scintillation counter. Beta counting is carried out with an internal or external proportional gas-flow chamber or an end-window Geiger-Mueller tube. The operating principles and descriptions of various counting instruments are available, as are techniques for determining various radioelements in aqueous solution (83,111). A laboratory manual of radiochemical procedures has been compiled for analysis of specific radionuclides in drinking water (113). Detector efficiency should be determined with commercially available sources of known activity.

9.6. Bacteria. A bacteriological examination of water is primarily carried out to determine the possible presence of harmful microorganisms. Testing is actually done to detect relatively harmless bacteria called *colon bacilli*, commonly called the coliform group, which are present in the intestinal tract of humans and animals. If these organisms are present in a water in sufficient number, then this is taken to be evidence that other harmful pathogenic bacteria may also be present.

One standard test used to determine the presence of the coliform group is called the multiple-tube fermentation technique (sometimes called the presumptive test). If this test indicates the presence of these bacteria, then a confirmed test must be done. If only negative colonies or no colonies develop during this test, it is considered negative; otherwise, a completed test must be undertaken. Positive results obtained in the completed test are evidence for the presence of coliform bacteria. Testing methods have been given by the APHA, and the detailed procedures contained therein should be consulted (83).

Another standard test, which is much simpler and more convenient, is the membrane filter technique. A suitable volume of sample is filtered through a sterile, 0.45-μm membrane filter. The filter is placed in a petri dish containing a specific growth medium (M-Endo nutrient broth, M-Endo medium) and incubated for 24 h at 35°C. If after this time the colonies show the characteristic green sheen, this is taken as positive evidence for the presence of the coliform group (see WATER, SEWAGE).

Micro-organisms can be detected by the use of biomembranes and potassium permanganate (114).

Fecal Coliforms. Fecal coliforms are those originating from the intestines of warm-blooded animals. Fecal coliforms can be determined by a multiple-tube procedure, which must be applied to a positive presumptive test for optimum recovery of fecal coliforms (83). Incubation must be at $44.5 \pm 0.2^{\circ}$C for 24 ± 2 h. Gas production during incubation is positive evidence of fecal coliform pollution.

A membrane filter technique can also be used to determine the presence of fecal coliforms, and this procedure is said to be 93% accurate (83). A sample is passed through a membrane filter, and this filter is placed in a petri dish containing an enriched lactose medium. The dishes are incubated at $44.5 \pm 0.2^{\circ}$C for 24 h. Following the incubation period, the fecal coliform colonies appear blue.

Both multiple-tube and membrane-filter methods are also available for testing for the fecal streptococcal group (83). These assays can be used to provide supplementary data regarding the bacteriological quality of water. Other fecal indicators should also be used concurrently because of the survival characteristics of the fecal streptococci.

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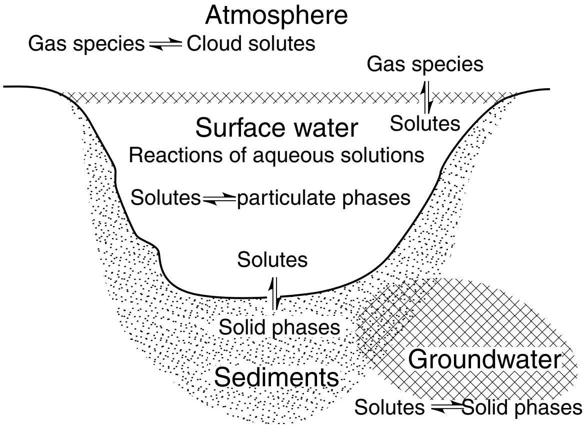


Fig. 1. Natural water environments. Water links essential cycles of the atmosphere with those of the sediments.

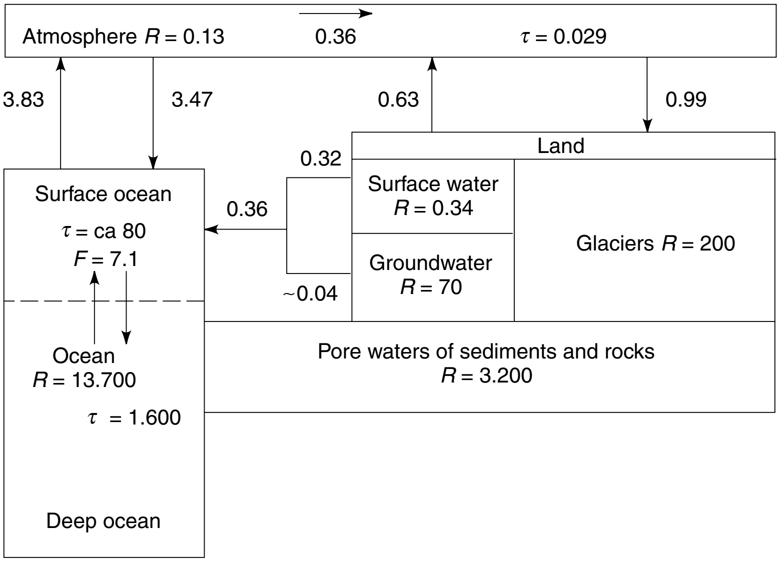


Fig. 2. The principal reservoirs in the hydrological cycle R, reservoirs in units of 10^{14} metric tons (10^5 km^3); F, fluxes in units of 10^5 km^3/yr; τ, residence time, yr: R/F = volume/input−output. Fluxes (flows) are approximate. For range of estimates, see Ref. 2.

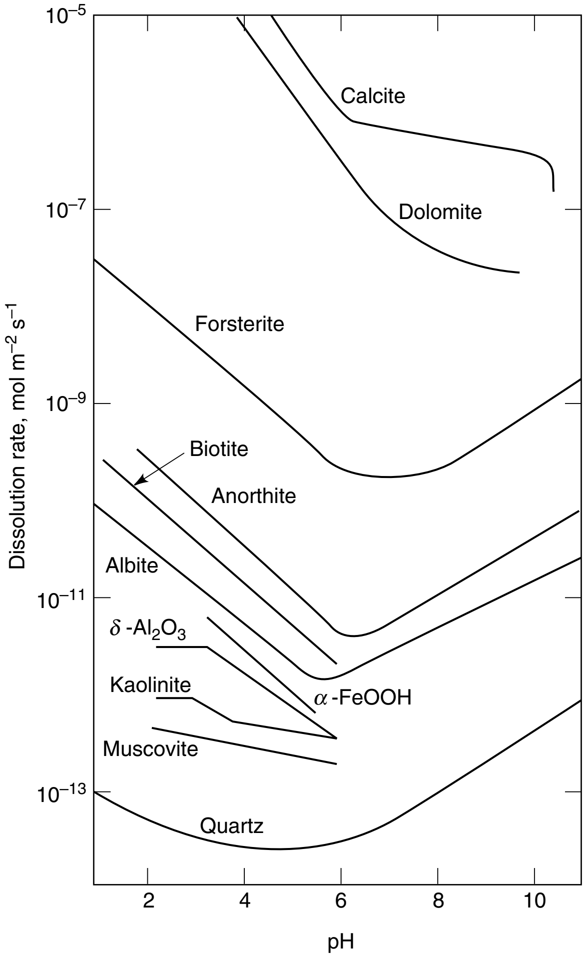


Fig. 3. Dissolution rate of different minerals as a function of pH at 25°C (8,9).

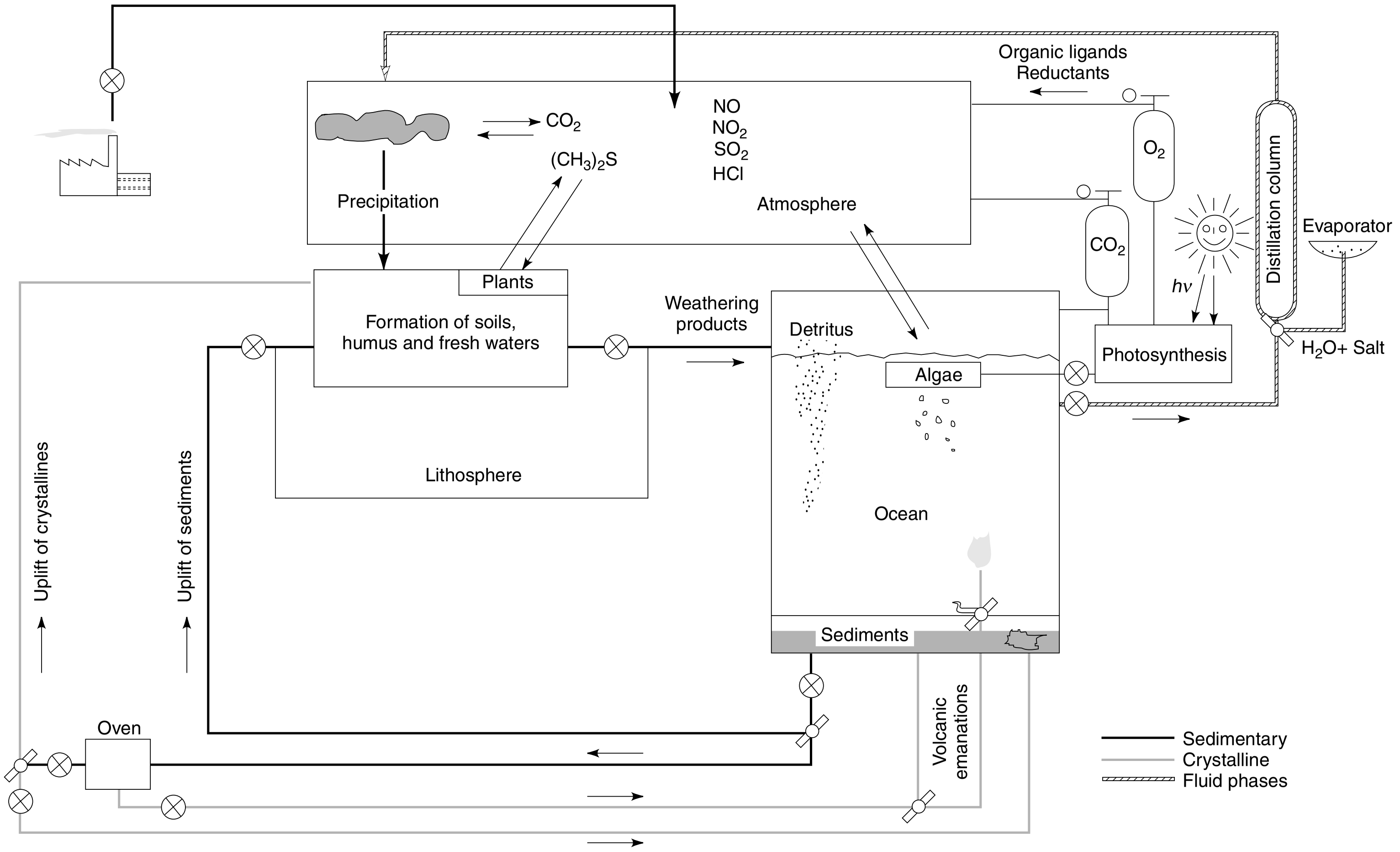


Fig. 4. Steady-state model for the earth's surface geochemical system. The interaction of water with rocks in the presence of photosynthesized organic matter continuously produces reactive material of high surface area. This process provides nutrient supply to the biosphere and, along with biota, forms the array of small particles (soils). Weathering imparts solutes to the water, and erosion brings particles into surface waters and oceans.

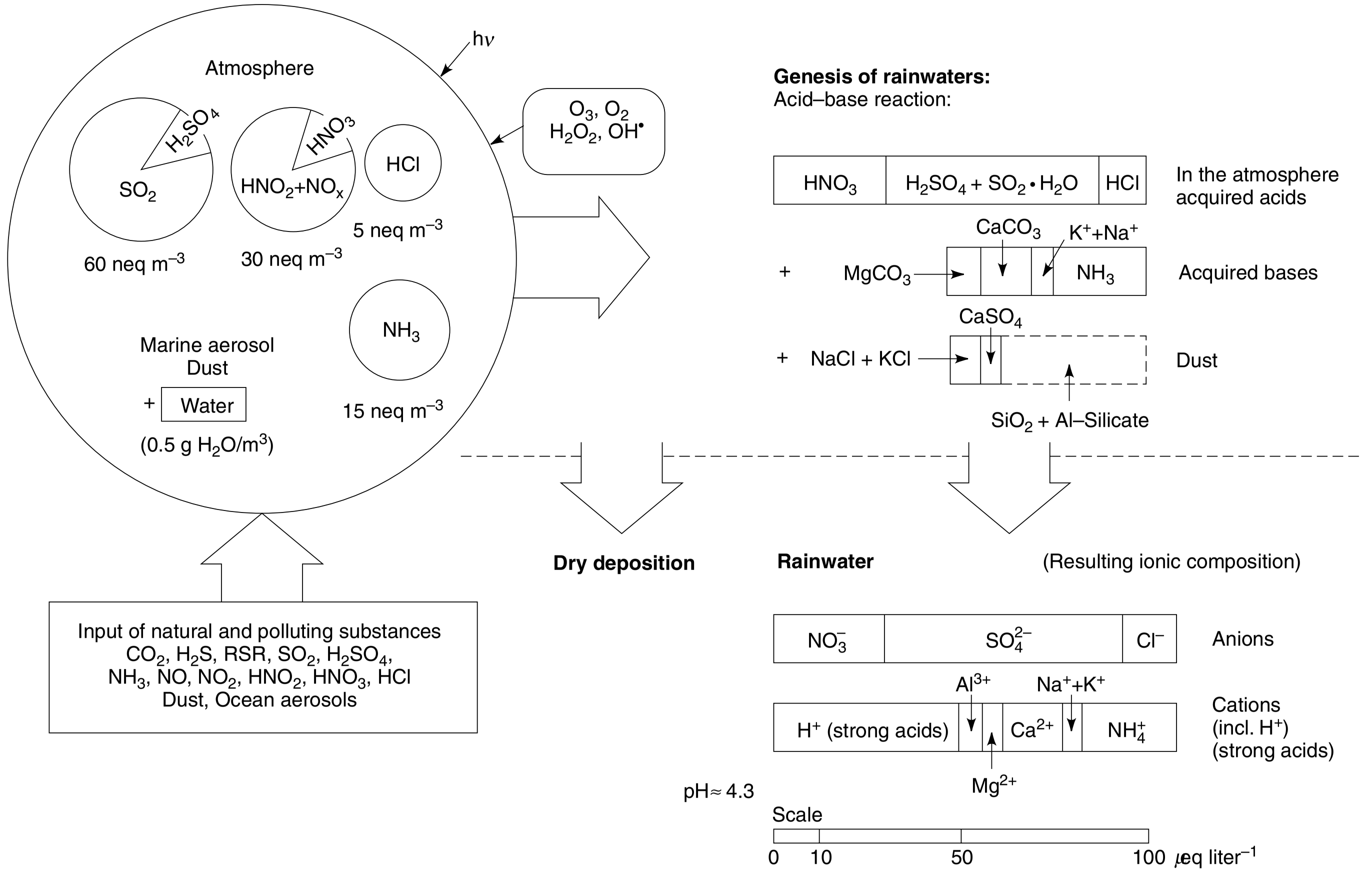
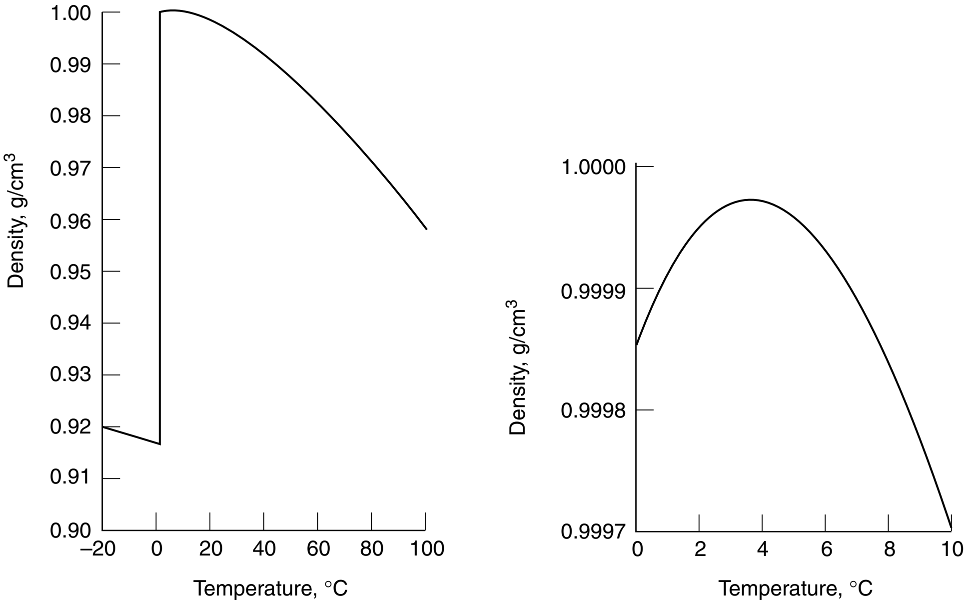


Fig. 5. Genesis of acid rain (17). From the oxidation of C, S, and N during the combustion of fossil fuels, there is a buildup in the atmosphere (gas phase, aerosol particles, raindrops, snowflakes, and fog) of CO_2 and the oxides of S and N, which leads to acid–base interaction. The importance of absorption of gases into the various phases of gas, aerosol, and atmospheric water depends on a number of factors. The genesis of acid rain is shown on the upper right as an acid–base titration. The data given are representative of the environment in the vicinity of Zürich, Switzerland.



(**a**) (**b**)

Fig. 6. (**a**) The density of ice and liquid water at 101.3 kPa (1 atm) as a function of temperature, and (**b**) the density in the domain of its maximum (19).

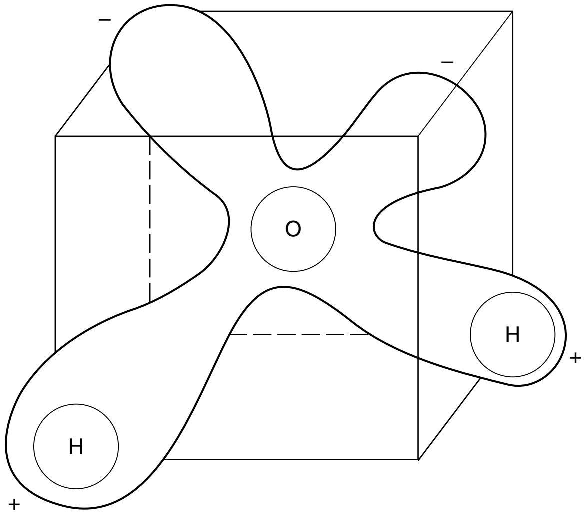


Fig. 7. Electron cloud depiction for the H_2O molecule (21).

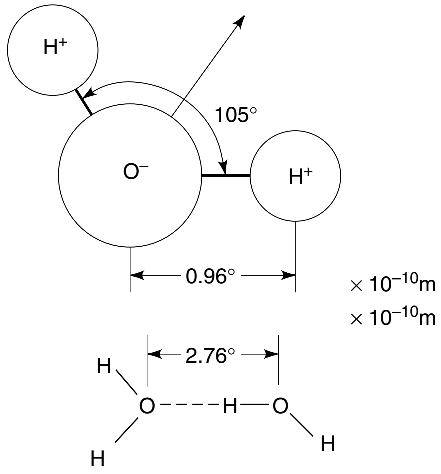


Fig. 8. Structure of the angular water molecule and the hydrogen bond (21).

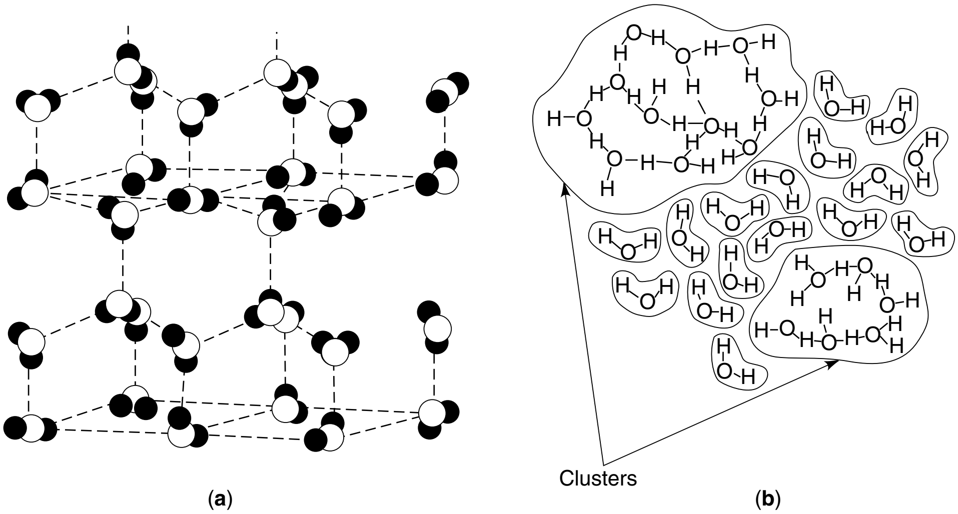


Fig. 9. (**a**) Hydrogen-bonded open tetrahedral structure of ice (22); (**b**) Frank-Wen flickering cluster model of liquid water (23).

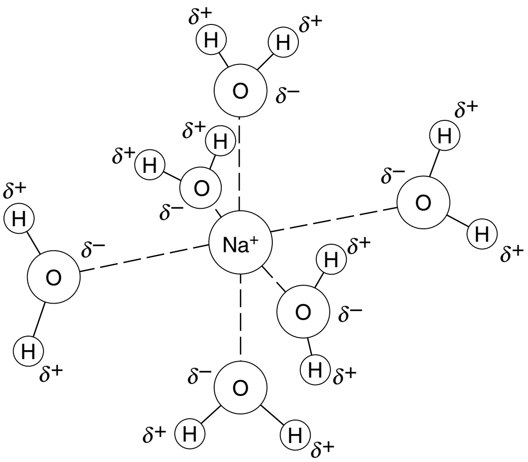
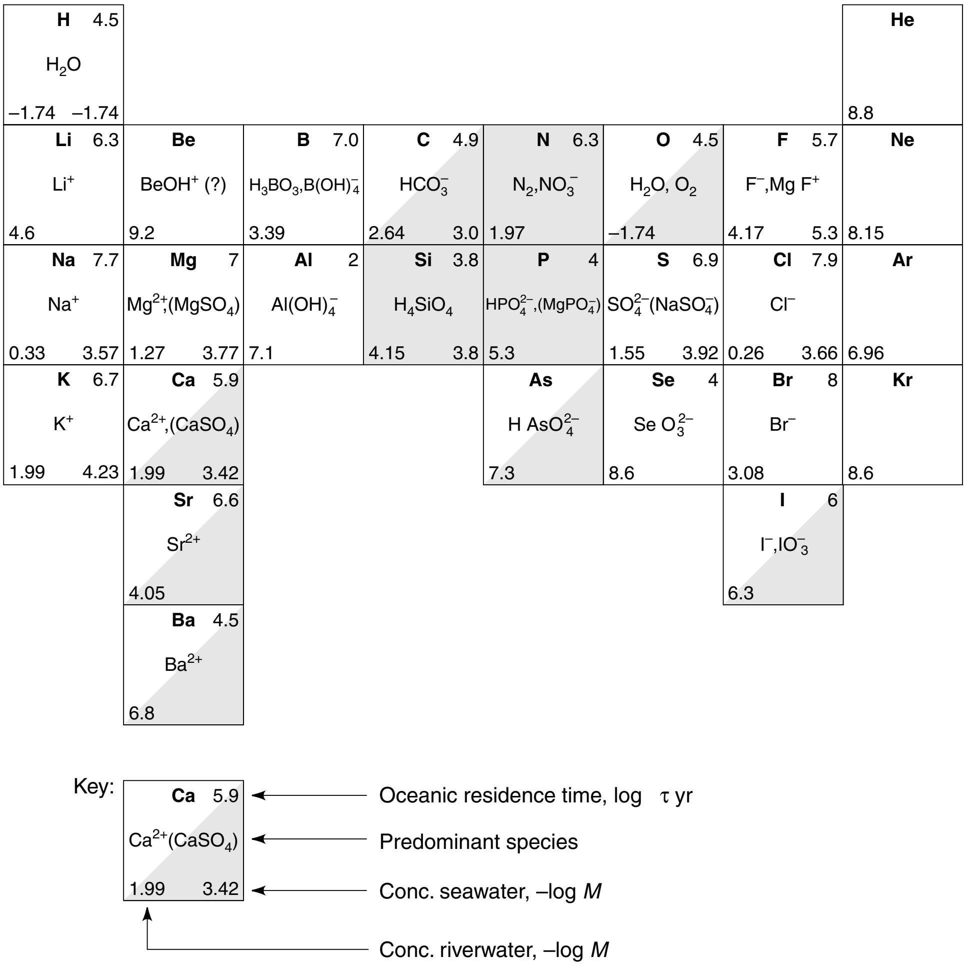


Fig. 10. Hydrated sodium ion, Na^+, in aqueous solution (22). The H_2O molecules form ion–dipole bonds to the central metal ion. The waters are in octahedral coordination to the sodium ion.



H 4.5 H_2O −1.74 −1.74							**He** 8.8
Li 6.3 Li^+ 4.6	**Be** $BeOH^+$ (?) 9.2	**B** 7.0 $H_3BO_3,B(OH)_4^-$ 3.39	**C** 4.9 HCO_3^- 2.64 3.0	**N** 6.3 N_2,NO_3^- 1.97	**O** 4.5 H_2O, O_2 −1.74	**F** 5.7 F^-,Mg F^+ 4.17 5.3	**Ne** 8.15
Na 7.7 Na^+ 0.33 3.57	**Mg** 7 Mg^{2+},($MgSO_4$) 1.27 3.77	**Al** 2 $Al(OH)_4^-$ 7.1	**Si** 3.8 H_4SiO_4 4.15 3.8	**P** 4 HPO_4^{2-},($MgPO_4^-$) 5.3	**S** 6.9 SO_4^{2-}($NaSO_4^-$) 1.55 3.92	**Cl** 7.9 Cl^- 0.26 3.66	**Ar** 6.96
K 6.7 K^+ 1.99 4.23	**Ca** 5.9 Ca^{2+},($CaSO_4$) 1.99 3.42			**As** H AsO_4^{2-} 7.3	**Se** 4 Se O_3^{2-} 8.6	**Br** 8 Br^- 3.08	**Kr** 8.6
	Sr 6.6 Sr^{2+} 4.05					**I** 6 I^-,IO_3^- 6.3	
	Ba 4.5 Ba^{2+} 6.8						

Fig. 11. Elements in natural waters, their form of occurrence, and concentration. Elements whose distribution is significantly affected by biota are shaded; P, N, and Si (fully shaded) are often depleted in surface waters. Species in parentheses are the main ion pairs in seawater. Data are uncorrected for atmospheric recycling of marine salts.

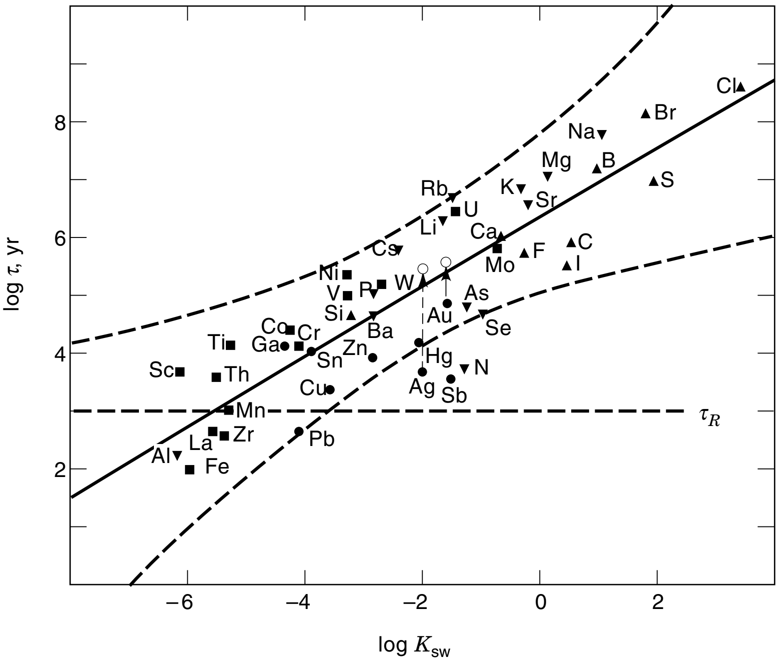


Fig. 12. The relationship between the mean oceanic residence time, τ, yr, and the seawater–crustal rock partition ratio, K_{sw}, of the elements; adapted from Ref. 32. ▼, Pretransition metals; ■, transition metals; •, B-metals; ▲, nonmetals. Open symbols indicate τ-values estimated from sedimentation rates. The solid line indicates the linear regression fit, and the dashed curves show the Working-Hotelling confidence band at the 0.1% significance level. The horizontal broken line indicates the time required for one stirring revolution of the ocean, τ_R.

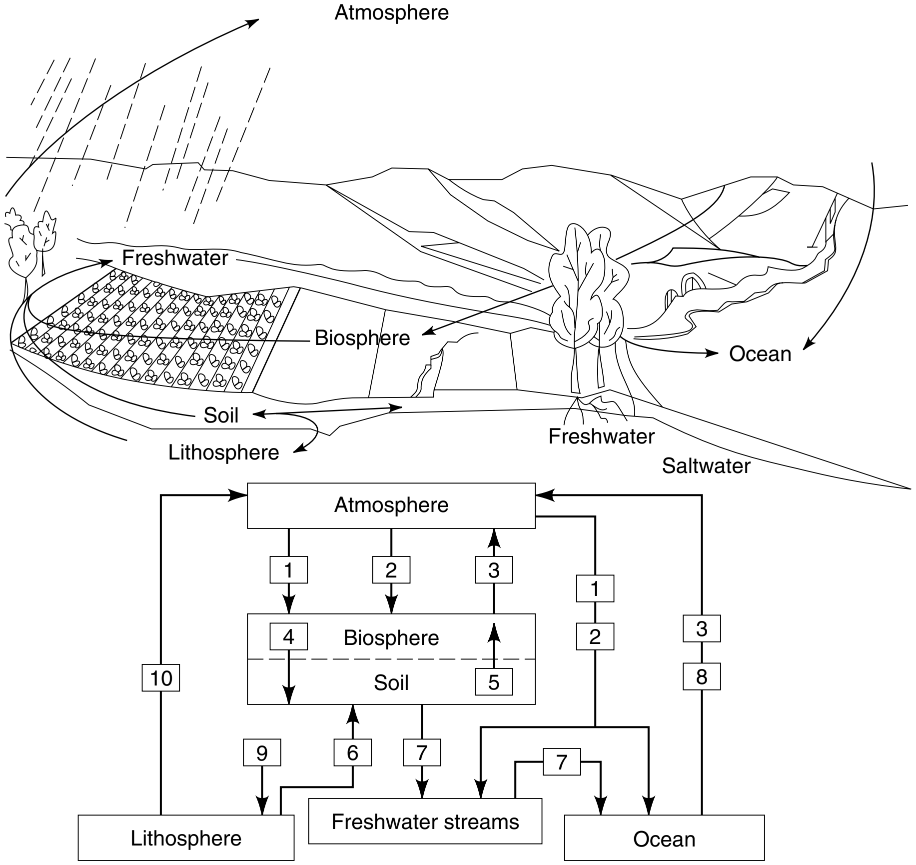


Fig. 13. Generalized cycle of the various reservoirs and transport mechanisms and pathways involved in the circulation of nutrient elements. The numbered arrows represent processes by which elements transfer among the reservoirs. Processes shown are those considered to have the most important influence on stream water quality. (Modified from Ref. 49.)

Table 1. **Estimated Use of Water in the United States in 2000**[a]

	Year											Percentage change
	1950[b]	1955[c]	1960[d]	1965[c]	1970[c]	1975[c]	1980[c]	1985[c]	1990[c]	1995[c]	2000	1995–2000
population, in millions	150.7	164.0	179.3	193.8	205.9	216.4	229.6	242.4	252.3	267.1	285.3	+7
offstream use:												
total withdrawals	180	240	270	310	370	420	440	399	408	402	408	+2
public supply	14	17	21	24	27	29	34	36.5	38.5	40.2	43.3	+8
rural domestic and livestock:												
self-supplied domestic	2.1	2.1	2.0	2.3	2.6	2.8	3.4	3.32	3.39	3.39	3.59	+6
livestock and aquaculture	1.5	1.5	1.6	1.7	1.9	2.1	2.2	4.47[e]	4.50	5.49	[f]	–
irrigation	89	110	110	120	130	140	150	137	137	134	137	+2
industrial:												
thermoelectric power use	40	72	100	130	170	200	210	187	195	190	195	+3
other industrial use	37	39	38	46	47	45	45	30.5	29.9	29.1	[g]	–
source of water:												
ground:												
fresh	34	47	50	60	68	82	83	73.2	79.4	76.4	83.3	+9
saline	[h]	0.6	0.4	0.5	1.0	1.0	0.9	0.65	1.22	1.11	1.26	+14
surface:												
fresh	140	180	190	210	250	260	290	265	259	264	262	−1
saline	10	18	31	43	53	69	71	59.6	68.2	59.7	61	+2

[a] Ref. 4.

[b] 48 States and District of Columbia, and Hawaii.

[c] 50 States and District of Columbia, Puerto Rico, and U.S. Virgin Islands.

[d] 50 States and District of Columbia, and Puerto Rico.

[e] From 1985 to present this category includes water use for fish farms.

[f] Data not available for all States; partial total was 5.46.

[g] Commercial use not available; industrial and mining use totaled 23.2.

[h] Data not available.

Table 2. **Geochemical Material Balance**

Igneous rocks +	Volatile substances	$\rightleftharpoons$	Seawater +	Atmosphere	+ Sediments
silicates carbonates oxides	CO_2 H_2O SO_2 HCl		pH = 8	$pO_2 = 0.2$ atm $pCO_2 = 0.0003$ atm	carbonates silicates

Table 3. **Thermodynamic Constants for Phase Changes of H_2O**[a]

Property	Fusion[b]	Vaporization[b]	Sublimation[c]
temperature, K	273.15	373.15	273.16
isopiestic heat capacity change Δc_p, J/(mol°C)[d]	37.28	−41.93	
enthalpy change ΔH, kJ/mol[d]	6.01	40.66	51.06
entropy change ΔS, J/(mol°C)[d]	22.00	108.95	186.92
volume change ΔV, cm^3/mol	−1.621	3.01×10^4	
internal energy change ΔE, kJ/mol[d]	6.01	37.61	48.79

[a] Ref. 19.
[b] At 101.3 kPa (1 atm).
[c] At ice–liquid–vapor triple point.
[d] To convert J to cal, divide by 4.184.

Table 4. **Physical and Chemical Properties of Liquid Water**[a]

Property	Comparison with other substances	Importance to environment
density	maximum density at 4°C, not at freezing point; expands upon freezing (both properties unusual)	in lakes prevents freezing up and causes seasonal stratification
melting and boiling points	abnormally high	permits water to exist as a liquid at earth's surface
heat capacity	highest of any liquid except ammonia	moderates temperature by preventing extremes
heat of vaporization	one of the highest known	important to heat transfer in atmosphere and oceans; moderates temperature extremes
surface tension	very high	regulates drop formation in clouds and rain
absorption of radiation	large in infrared and ultraviolet regions; less in visible regions	important control on biological activity (photosynthesis) in water bodies and on atmospheric temperature
solvent properties	excellent solvent for ionic salts and polar molecules because of dipolar nature	important in transfer of dissolved substances in hydrological cycle and in biological systems

[a] Ref. 20.

Table 5. **Selected Properties of Water Vapor**[a,b]

Property	Value
molecular weight	18.015
heat of formation, kJ/mol[c] at 100°C	242.49
viscosity, mPa·s(=cP) at 20°C	96×10^{-6}
velocity of sound, m/s at 100°C	405
diffusion coefficient, cm^2/s at 100°C in air	0.380
specific volume, cm^3/g at 100°C	1729.6
specific heat, J/(g·K)[c] at 100°C	2.078
thermal conductivity, W/(cm·K) at 110°C	2.44×10^{-4}

[a] Ref. 24.

[b] At 101.3 kPa (1 atm).

[c] To convert J to cal, divide by 4.184.

Table 6. **Selected Properties of Liquid Water**[a,b]

Property	Value
heat of formation, kJ/mol[c] at 25°C	285.890
ionic dissociation constant, M^2 at 25°C	10^{-14}
heat of ionization, kJ/mol[c] at 25°C	55.71
apparent dipole moment, C·m[d]	6.24×10^{-30}
viscosity, mPa·s(=cP) at 25°C	0.8949
velocity of sound, m/s at 25°C	1496.3
density, g/cm^3 at 25°C	0.9979751
at 0°C	0.99987
freezing point, °C	0.0
boiling point, °C	100.0
isothermal compressibility, over the range of 0.1–1 MPa,[e] nPa^{-1} at 25°C	0.45
specific heat at constant volume, J/(g·K)[c] at 25°C	4.17856
thermal conductivity, W/(cm·K) at 20°C	0.00598
temperature of maximum density, °C	3.98
dielectric constant, at 17°C and 60 MHz	81.0
electrical conductivity, S/cm at 25°C	$<10^{-8}$

[a] Ref. 24.

[b] At 101.3 kPa (1 atm).

[c] To convert J to cal, divide by 4.184.

[d] To convert C·m to D, divide by 3.336×10^{-30}.

[e] To convert MPa to atm, divide by 0.101.

Table 7. **Selected Properties of Ice**[a,b]

Property	Value
heat of formation, kg/mol at 0°C	292.72
Young's modulus of elasticity, MPa[c] at −10°C	967
density, g/cm^3 at 0°C	0.9168
coefficient of cubical thermal expansion, cm^3/(g·°C) at 0°C	120×10^{-6}
coefficient of linear thermal expansion, °C^{-1} at 0°C	52.7×10^{-6}
isothermal compressibility, nPa^{-1} at 0°C	0.12
specific heat, J/(g·K) at 0°C	2.06
thermal conductivity, W/(m·K)	210
dielectric constant, at −1°C and 3 kHz	79

[a] Ref. 24.

[b] At 101.3 kPa (1 atm).

[c] To convert MPa to psi, multiply by 145.

Table 8. **Major Composition of Seawater**

Constituent	Seawater at $S = 35$,[a]	(g kg^{-1})÷Chlorinity[b]	(mol kg^{-1})÷Chlorinity	Residence time in oceans, logτ, years[c]
Na^+	10.77	0.556	0.0242	7.7
Mg^{2+}	1.29	0.068	0.0027	7.0
Ca^{2+}	0.4121	0.02125	0.000530	5.9
K^+	0.399	0.0206	0.000527	6.7
Sr^{2+}	0.0079	0.00041	0.0000047	6.6
Cl^-	19.354	0.9989	0.8282	7.9
SO_4^{2-}	2.712	0.1400	0.0146	6.9
HCO_3^-	0.1424	0.00735	0.00012	4.9
Br^-	0.0673	0.00348	0.000044	8
F^-	0.0013	0.000067	0.0000035	5.7
B	0.0045	0.000232	0.0000213	7.0
	$Z = 35$	$Z = 1.82$	$Z = 0.058$	

[a] Salinity, S(‰), is defined as the weight in grams of the dissolved inorganic matter in 1 kg of seawater after all Br^- and I^- have been replaced by the equivalent quantity of Cl^- and HCO_3^- and CO_3^{2-} are converted to oxide. In over 97% of the seawater in the world, the salinity S is between 33‰ and 37‰. The total number of grams of major constituents (sea salt), g_T, for 1 kg of solution is related to the chlorinity by $g_T = 1.81578$ Cl (‰). Salinity S (‰), is defined as $S() = 1.80655$ (Cl ‰); thus $g_T = 1.00511$ S (‰).

[b] The chlorinity, Cl (‰), is determined by the titration of seawater with $AgNO_3$. It was defined as the chlorine equivalent of the total halide concentration in g kg^{-1} seawater; it is now defined as the mass in grams of Ag necessary to precipitate the halogens (Cl^- and Br^-) in 328.5233 g of seawater. It has been adequately demonstrated that the relative composition of the major (greater than 1 m kg^{-1} seawater) components of seawater is nearly constant. By measuring one constituent of seawater, the composition of other components can be characterized. The constituent normally selected is the chlorinity, Cl (‰).

[c] Residence times were computed by $\tau = M/Q$, where M for a particular constituent is equal to its concentration in seawater times the mass of the oceans, and Q is equal to the concentration of the constituent in average river water times the annual flux of river water to the ocean.

[d] The results given for HCO_3^- are actually values of the carbonate alkalinity expressed as though it were all HCO_3^-.

Table 9. **Representative Concentration of Some Dissolved Heavy Metals in Natural Waters**

	Metal, nM				
Area or source	Cu	Zn	Cd	Pb	Reference
East coast U.S. rivers	17	13	0.095	0.11	34
Mississippi River	23	3	23		35
Amazon River	24	0.3–0.8	0.06		35
Lake Constance	5–20	15–60	0.05–0.1	0.2–0.5	36
Lake Michigan	10	9	0.17	0.25	37
Lago Cristallina[a]	5	30	0.5	3	38
Pacific Ocean	0.5–5	0.1–10	0.01–1	0.005–0.08	39
rainwater[b]	10–300	80–900	0.4–7	10–200	38

[a] Alpine lake at 2200-m altitude in the southern Swiss Alps. Its dissolved Al(III) concentration at pH6 = 600 nM.

[b] As measured near Zürich, Switzerland.