

Biological Activity in Relation to the Chemical Equilibrium Composition of Natural Waters

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For many elements, the concentration of a species in a given body of water can be predicted by abiotic chemical reactions such as protolysis, precipitation, complexation, redox, and sorption. Aquatic organisms can influence the concentration of compounds directly by metabolic uptake, transformation, storage, and release. Aquatic organisms may also cause chemical reactions by changing the concentrations of solutes which are important in abiotic equilibria. The two most important reactions of this type are changes in the pH of the water as a result of respiration and photosynthesis and the uptake and release of organic compounds. Both of these reactions can influence acid-base, precipitation, complexation, redox, and sorption reactions in natural waters.

The concentration of a particular species of an element in the aquatic environment is determined by the thermodynamics and kinetics of its chemical reactions. The concentrations of some elements present in a body of water can be predicted from abiotic chemical reactions such as protolysis, precipitation, complexation, redox, and sorption. However, the concentrations of other elements are influenced significantly by biochemical reactions. This concept has been emphasized by several authors. For example, Ruttner (56) has stated that "it is quite impossible to understand the chemistry of an aquatic biotope without taking into consideration the causal relationships in the metabolism of its community of organisms." This idea has been reiterated by Cushing (12), who lists the "quality and quantity of biota, particularly producers," among

the factors influencing ionic changes in the aquatic environment, and it is the basis for Hynes' (30) view of a lake as a trap for fertility.

Biological populations are responsible to a great extent for cycling elements in natural waters. Although temperature and hydrologic cycles profoundly influence chemical equilibria in the aquatic environment, without the constant turnover provided by the aquatic fauna and flora, reactions would proceed largely in one direction. Aquatic organisms as well may influence the chemistry of an element in natural waters by altering concentrations of ions or compounds, such as H^+ ion, which in turn may alter the position of chemical equilibria in water.

We do not wish to argue the importance of the chemical *vs.* the biological role in specific equilibrium reactions but rather to bring to attention certain studies of biological material which suggest a role in determining the chemical composition of the aquatic environment, with special reference to the fresh water environment.

For the most part, ecologists have been concerned with studying the relationship of an organism to its physical, chemical, and biological environments. Hence, much effort has been devoted to examining the effects of various chemical compounds on aquatic organisms. We are concerned here, however, with the effects of aquatic biota on the concentrations of particular ions or compounds in natural waters. Few studies of fresh waters have been conducted from the latter point of view, however, although Redfield, Ketchum, and Richards (53) have reviewed the literature on the influence of organisms on the composition of sea water.

Since every organism may affect water chemistry, each should be considered. However, although occasionally higher plants and animals become significant when their numbers are large, bacteria and microscopic plants and animals ordinarily play dominant roles. Of particular importance is the high surface area to volume ratio of microorganisms and their biochemical versatility. Biochemical versatility is characteristic especially of bacteria of the genus *Pseudomonas*, one of the dominant genera in surface waters not significantly affected by sewage pollution. Pseudomonads are noted for their resistance to antibiotic substances and their production of antagonistic agents. Individual species may cause disease in fish, spoilage of food and dairy products, degradation of petroleum products, and the mineralization of algae.

Populations of bacteria in lakes determined by plate counts generally lie in the range of 10–100 organisms per ml. (2, 60). However, counts of 10,000–100,000 may be observed by this technique, particularly in shallow bay areas. The relation between plate and direct counts may vary greatly, however, and Collins (11) has reported ratios varying from 20 to 13,400. Thus, actual bacterial populations may be much higher

than observed by direct plating techniques, often exceeding 10^6 cells per ml.

In open water, bacteria may exist freely as single cells or associated with particulate matter. The number living in a truly planktonic fashion is quite low, however, as can be seen in Table I. The surfaces of particulate matter, where organic substances are adsorbed and excreted products of other community members are available, afford the associated bacteria an opportunity to function in an enriched situation relative to the surrounding open water. Bacteria form the base of the ecological pyramid in attached communities. Colonization of surfaces may afford an opportunity to create special localized conditions, permitting solution of mineral constituents or the metabolism of certain organic materials by altering the pH, redox potential, or by preventing dispersal of extracellular enzymes.

Table I. Bacteria Populations in Water

Source	Percent of Bacteria (free-living)	Reference
Nile River	0.02-0.04	(31)
Experimental Stream		
Groundwater	0.005	(70)
Groundwater + 2% sewage	0.9	(70)
Lakes (Stuttgart Region)	10-30	(3)

The association of large numbers of bacteria with large populations of algae is evident from the data in Figure 1 (50). From work with *Chlorella pyrenoidosa* and *Thalassiosira nana*, Steemann-Nielsen (61) has suggested that during algal blooms occurring in the spring and summer, the bacterial populations actually are not associated with the surfaces of algae or with other surfaces because of the antibacterial activity of substances produced by the algae, but rather they exist in a truly planktonic state, metabolizing the excreted products of the photosynthetic organisms. Bacteria may be observed associated with the surfaces of dying algae, however. Golterman (23) showed that the mineralization of *Scenedesmus obliquus* depended on the presence of bacteria and that bacterial growth was promoted by substances released during autolysis of the algae. This author demonstrated the release of nitrogen comparable with that observed in the presence of natural bacterial populations caused by a pseudomonad which he isolated from decaying algae. Anaerobic and facultative bacteria active in the bottom sediments enriched with the remains of dead planktonic organisms influence the chemistry of natural waters, particularly those of the hypolimnion. Special conditions are created here as a result of oxygen depletion and the release of CO_2 , H_2S , and many organic compounds.

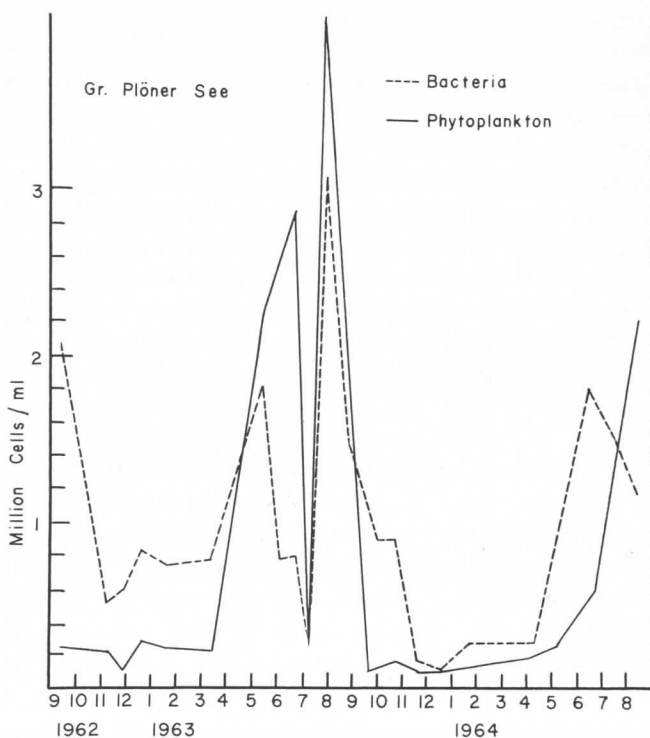


Figure 1. Total bacteria and phytoplankton at 1 meter below the surface in the Grossen Plöner See in 1962–1964 (50)

The algal populations differ from most bacteria present by being largely autotrophic. These organisms concentrate nitrogen, phosphorus, sulfur, and many mineral substances in water bodies, obtaining carbon from dissolved CO_2 and energy from sunlight. The algae exist as phytoplankton and as epiphytic, epipelic, and epilithic populations. Population levels may be influenced or controlled by temperature, enrichment, predation, and concentrating factors such as winds and currents. The distribution of phytoplankton is subject to many influences related to the morphometry of the water body, stratification, wind, current, and local availability of nutrient substances. The actively photosynthesizing population is restricted to the euphotic zone or must be carried into the euphotic zone for a period sufficient to permit a net gain of energy through photosynthesis during the day. Below the euphotic zone, in the profundal, the photosynthetic plankton enrich and support the metabolic activity of heterotrophic bacteria. The attached populations of the

epiphytic, epipelagic, and epilithic communities are restricted to the littoral zone where light penetrates to the bottom.

Rivers, ponds, small and large lakes represent quite different environments for algal populations, and these must be considered in interpreting the effects of algae on the chemistry of natural waters.

Direct Effects of Biota on Water Chemistry

In a grossly oversimplified model, an aquatic microorganism may be treated as a reaction site at which compounds are sorbed and are influenced by the organism. The sorbed compounds are transformed enzymatically into different compounds and are stored and/or released to the surrounding water. Biochemical literature shows that few, if any, elements are not influenced to some degree in natural waters by the aquatic biota. Therefore, in those waters where the rate of supply of an element controls its concentration—i.e., where no precipitation and little or no abiotic sorption occurs—aquatic organisms may control the concentration of the element in solution. The most obvious examples of direct control occur for those elements that are major constituents of cellular materials—e.g., carbon, nitrogen, and phosphorus. Also directly influenced by the aquatic biota are those elements which form principal components of the hard parts of many organisms, such as calcium in molluscs, silicon in diatoms, and certain testaceans (such as *Euglypha*). Studies by Lund *et al.* (41, 42) have demonstrated an inverse relationship between *Asterionella*, *Fragilaria*, and *Tabellaria* populations and the concentration of silicon in solution in Lake Windermere (Figure 2). These authors have observed decreases in the silicon concentration associated with large diatom populations. It appears, therefore, that diatoms may exert a significant influence on the silicon concentration in lakes. In Lake Windermere, the rate of uptake of silicon by diatoms exceeds the rate of supply of the element through geochemical processes and the rate of regeneration of the element upon death of the algae. Certain bacteria have been reported to enhance solution of aluminosilicates, coincidentally freeing other associated elements. Tesic and Todorovic (63) have suggested that such species are of the *Bacillus circulans* group, but they emphasize the need for study to determine whether these represent specific silicate bacteria and whether silicon and aluminum represent essential elements in the life of these bacteria. In this regard, Parés (51) has suggested bacterial involvement in the solution of many metals, either in the pure form or as ores.

The effect of biological activity on the chemistry of an element or compound in natural waters is interdependent upon (1) population of a particular group of organisms, (2) the lifetime of the organisms, (3) the

rate of regeneration of the element upon death of the organisms, (4) concentration of the compound in the water, and (5) the biochemistry of the organisms. Each of these factors is considered below. Particular species of elements may be influenced by the organisms present, and these are not necessarily the species determined by the usual analytical procedures.

Numbers and Types of Organisms. The numbers of a particular group of organisms in a natural water represent a response to the environment and may be limited by factors such as concentrations of essential nutrients and toxic or inhibitory substances, reproduction rates, competition for available nutrients, predation, disease rate, and physical factors (light, temperature, pressure). The concentrations of certain elements may be reduced as a result of biological activity to such an extent that populations are limited (42), whereas the concentrations of other elements may be decreased significantly and yet never limit biological activity. It is extremely difficult, however, if not impossible at the present time, to determine the factors that limit the population of particular organisms in natural waters, as has been demonstrated during current research on the role of nitrogen and phosphorus in the eutrophication of natural waters.

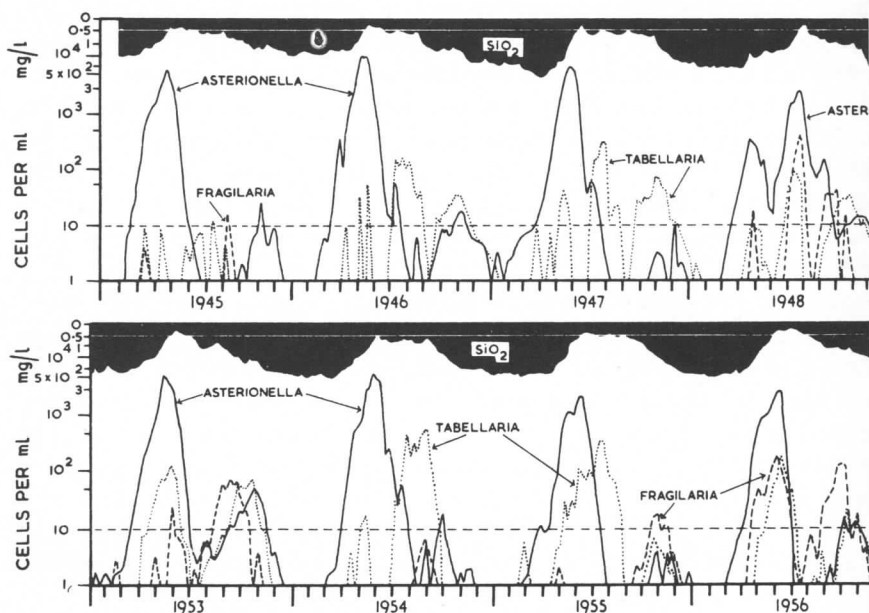
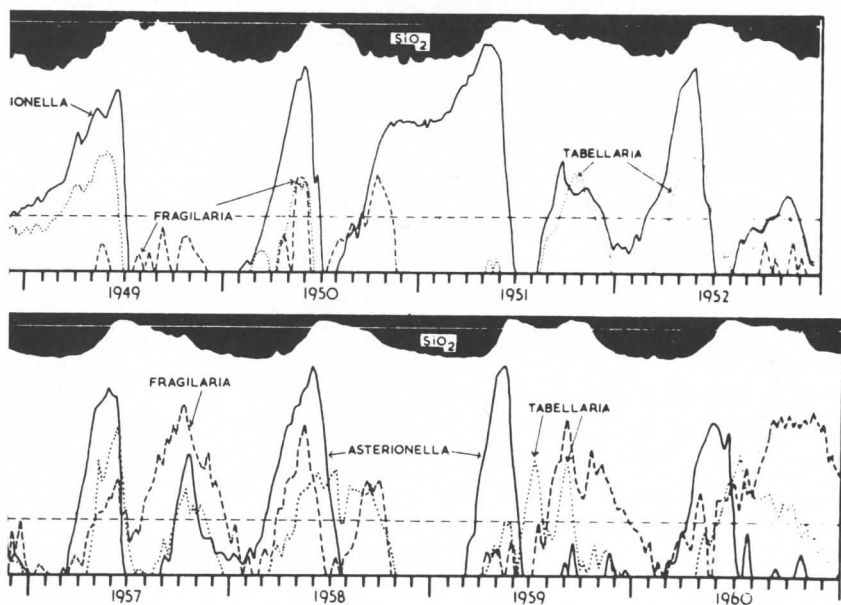


Figure 2. Periodicity of *Asterionella formosa* Hass., *Fragilaria Crotonensis* and fluctuations in the concentration of dissolved silica, in 0-5-meter water

The role of photosynthesis in the carbon cycle is familiar, and the indirect effects on the chemistry of natural waters caused by removing or adding CO_2 during photosynthesis and respiration (particularly of photosynthetic microorganisms) are discussed below. A direct effect of these microorganisms, however, is selective removal of the light carbon and oxygen isotopes from the water, resulting in an enrichment of the heavy isotopes in the water body and of the light isotopes in the sediments (although enrichment of the sediments depends also upon the amount of marl deposited). Deevey and his associates (13, 14) have demonstrated the fractionation of carbon and oxygen in Linsley Pond, Conn., and Green Lake, N. Y.

Return of Elements to the Biological Cycle. The amount of an element bound in biological material and possible limits imposed on developing populations as a result of depletion in the water mass depend on the residence time of the element in the biomass and organism remains after death. Numerous studies have shown that the turnover rates of many elements are quite rapid so that the average residence time in the biomass is short. Phosphorus, for example, is released rapidly in water following death of the organisms (55). On the other hand, the return of the silicon composing diatom tests may be slow. As viewed by the water



Kitton, *Tabellaria flocculosa* (EHR) Grun. Var. *Asterionelloides* (Grun.) Knuds. column of the northern basin of Windermere from 1945-1960, inclusive (41)

chemist, the turnover time of an element is important since it determines the availability of the element for strictly chemical reactions as well as the availability for biological use. Those elements with long turnover times will remain as part of the particulate matter in the water and therefore will tend to accumulate in the sediments.

Concentration of Element. The role that the biota may play in the chemistry of natural waters requires considering the concentration of the element in the water relative to the amount of the element accumulated per unit weight of cell material. A population of organisms that has a high requirement for certain elements that occur in low concentrations in the water will tie up relatively large amounts of the element in the cell material and thereby significantly reduce the concentration in solution (*—e.g.*, the depletion of dissolved silicon by diatom populations in Lake Windermere). Ideally, some insight into this relationship could be gained by determining the numbers of organisms present in a body of water. The average composition of the organisms could be used to estimate the amount of the element present in the biomass. This relationship is complicated by the heterogeneous distribution and composition of organisms and the fact that they frequently will store up to 10 or more times their metabolic needs. The luxury consumption of phosphate by algae is well documented (35). Additional complications arise from apparent interactions between solutes which affect the uptake of nutrients by microorganisms. The so-called “phosphate sparing factor” (29) is an example of a solute interaction by which algae seem able to grow in laboratory cultures at lower phosphate concentrations, provided a little organic matter from natural water is added to the culture. The mechanism of this relationship is not understood.

Biochemistry of the Element. The biochemical function of an element in biological organisms may be significant in determining the concentration and forms of the element in the water. For example, organic compounds that are utilized during heterotrophic growth and metabolism are removed from water, transformed in part into cellular material, and partly excreted as CO_2 . The net result is that an element in one form—*e.g.*, organic compound—is removed from the water, some of it is stored for a period of time, while the remainder is rapidly released to the environment in another oxidation state or chemical form. The reverse process occurs during photosynthesis and chemolithotrophic growth. During daylight, photosynthetic organisms remove CO_2 from the water and reduce it to carbohydrate *via* the Calvin-Benson cycle. Some investigators have reported that approximately 50% of the CO_2 fixed by algae appears as dissolved organic compounds in a short time (19).

Chemolithotrophic organisms can oxidize inorganic substances such as H_2S , elemental sulfur, or reduced nitrogen compounds, obtaining

energy for growth. The iron bacteria provide a controversial example of cellular biochemical effects. It has been suggested that some members of this group can derive energy from the oxidation of ferrous to ferric iron (69). Other members appear to metabolize organic compounds that "hold" iron in suspension. The iron is released and deposited in the bacterial sheath as $\text{Fe}(\text{OH})_3$. Oborn (47, 48) has recently reviewed the literature on the influence of organisms on the chemistry of iron and manganese.

Nitrogen's chemistry is controlled largely by biochemical reactions in natural waters. Although it has been suggested that the Van Slyke reaction (by which nitrite reacts with ammonia or amino acids to produce nitrogen gas) may take place in natural waters, Brezonik and Lee (5, 6) have shown that in natural waters this reaction proceeds at a significant rate only at pH of 3 or less. The oxidation and reduction of nitrogen compounds (nitrogen cycle) are all the result of enzymatic processes. Some of the transformations of nitrogen compounds in natural waters are brought about by specific organisms: *Nitrosomonas* oxidizes ammonia to nitrite, and *Nitrobacter* oxidizes nitrite to nitrate. Rheinheimer (54) attributed relatively high nitrite concentrations in the River Elbe during the summertime to a difference in the rates of nitrite and nitrate formation. More recently Bock (4) has studied the effects of light on *Nitrosomonas europaea* and *Nitrobacter winogradskyi* and found that *N. winogradskyi* was more light sensitive than *Nitrosomonas*, indicating a possible explanation.

The biochemical reduction of sulfate to sulfide by bacteria of the genus *Desulfovibrio* in anoxic waters is a significant process in terms of the chemistry of natural waters since sulfide participates in precipitation and redox reactions with other elements. Examples of these reactions are discussed later in this paper. It is appropriate now, however, to mention the enrichment of heavy isotopes of sulfur in lakes. Deevey and Nakai (13) observed a dramatic demonstration of the isotope effect in Green Lake, a meromictic lake near Syracuse, N. Y. Because the sulfur cycle in such a lake cannot be completed, depletion of $^{32}\text{SO}_4$, with respect to $^{34}\text{SO}_4$, continues without interruption, and ^{32}S sulfide is never returned to the sulfate reservoir in the monimolimnion. Deevey and Nakai compared the lake to a reflux system. H_2S -enriched ^{32}S diffuses to the surface waters and is washed out of the lake, leaving a sulfur reservoir depleted in ^{32}S . The result is an ^{34}S value of +57.5% in the monimolimnion.

The sulfide produced by sulfate reducers may be oxidized by several sulfur bacteria. Common among these are members of *Beggiatoales* and *Thiobacteriaceae*, as well as photosynthetic bacteria of *Thiorhodaceae* and *Chlorobacteriaceae*, which are common in eutrophic lakes in which the hypolimnion is depleted in oxygen. An example is the development

of photosynthetic sulfur bacteria, particularly *Chromatium* spp., between the anaerobic and aerobic zones of Lake Windermere (11). Butlin and Postgate (7) examined four lakes in the Libyan Desert which were saturated with CaSO_4 but were low in organic matter. From three of these lakes, 200 tons of raw sulfur (50% sulfur) were removed yearly. The three productive lakes produced massive crops of the purple sulfur bacterium, *Chromatium* and the green sulfur bacterium, *Chlorobium*, whereas the fourth, which produced no elemental sulfur, did not. In laboratory experiments, Butlin and Postgate were able to establish symbiotic growth of sulfate reducers and *Chromatium*. The photosynthetic bacteria, in addition to oxidizing sulfide to elemental sulfur, provided organic matter for growing sulfate reducers.

The biochemical activity of an organism may be regulated by environmental factors. Fitzgerald and Nelson (18) have shown recently that planktonic algae grown in water containing a surplus of phosphorus do not possess alkaline phosphatase activity. However, if the same organisms are deprived of orthophosphate, they do develop it. The measure of alkaline phosphatase activity shows promise as a tool for determining whether or not algae have grown in the presence of limiting or surplus phosphorus concentrations in natural waters.

Another way in which organisms affect the chemistry of natural waters is by accelerating the rate of a reaction that normally proceeds by nonenzymic processes. Hydrolysis of pyrophosphate and tripolyphosphate to orthophosphate has been shown to proceed at a slow rate in the absence of microorganisms in natural waters. However, in the presence of microorganisms, the rate is greatly accelerated (9, 10, 57).

A reaction of considerable importance in water pollution is the production of high acidity waters in coal mines. The acidity of these waters seems to be the result of oxidation of pyritic compounds. Although the oxidation mechanism is not understood, several investigators feel that microorganisms accelerate this reaction rate (25).

In summary, there are few, if any, elements whose aqueous environmental chemistry is not directly influenced and/or controlled by biochemical reactions. In addition to the direct influence, microorganisms may also be significant in the chemistry of elements in natural waters by altering the composition of the water with respect to other elements or compounds. For the purpose of this discussion, this type of reaction will be termed indirect. Examples of these reactions are discussed below.

Indirect Effects of the Aquatic Biota in Water Chemistry

In general, the indirect influence of aquatic organisms on the chemistry of elements in natural waters is the result of assimilation or excretion of compounds that react chemically with the element in the water. The

changes in the amount of CO_2 in the water that accompany respiration and photosynthesis deserve special consideration since many reactions are influenced by pH.

Indirect Effects as a Result of CO_2 Changes. **ACID-BASE.** Since respiration and photosynthesis cause changes in the carbon dioxide content of the water and since the carbonic system determines the pH of most natural waters, large populations of organisms may influence the pH markedly. The diurnal variation of pH in the euphotic zone is commonly ± 0.5 pH units and in eutrophic lakes the epilimnion may have a pH that is several units higher than the hypolimnion (39). The surface variations are caused largely by the activity of photosynthetic organisms, and the pH gradient in eutrophic lakes by anaerobic metabolism of bacteria in the profundal. The magnitude of the pH effects attributable to the biota is determined by the numbers, types, and activity of the organisms present, as well as sunlight, turbidity, buffer capacity, pH, and turbulence. It is probable also that the magnitude of pH changes is greater at cell surfaces and that resulting reactions are more intense at these surfaces.

In addition to changing the pH of the water, the uptake and release of CO_2 alter the buffer capacity of the water. The effect upon buffer capacity is the result of two factors: (1) the dependence of buffer capacity on the hydrogen ion concentration, and (2) the dependence of buffer capacity on the total concentration of weak acid and conjugate base in solution (67, 68). The precipitation of CaCO_3 in natural waters reduces the buffer capacity to a value lower than that predicted on the basis of pH change and respiratory or photosynthetic changes in CO_2 content of the water.

DEGREE OF PROTOLYSIS. The most obvious effect of a pH change is the degree of protolysis of the acids present in solution. The distribution of carbonic species (CO_2 , HCO_3^- , and CO_3^{2-}), phosphates, sulfide, hydrous oxides of iron and aluminum, and organic acids is determined by pH. Since many chemical reactions (precipitation and complexation) take place between the conjugate base and some other element, a change in the degree of protolysis may result in a change in the extent of these reactions.

PRECIPITATION REACTIONS. A change in the pH of a natural water may result in the precipitation from solution of those species that are at or near saturation if one of the precipitating species enters into acid-base reactions. The classical example is the photosynthetic precipitation of calcium carbonate. During photosynthesis, aquatic plants may remove sufficient CO_2 to raise the pH to the value at which the concentration of carbonate times that of calcium exceeds the solubility product for calcium carbonate. If nucleation occurs, calcium carbonate will be precipitated.

Bacteria have been reported to enhance the precipitation of CaCO_3 in sea water. Recently, Oppenheimer (49) has demonstrated an increase in the formation of aragonite in aged-filtered sea water enriched with 0.1% NaNO_3 and 0.67% NaHCO_3 when inoculated with washings from oolytic deposits. Greenfield (24) studied the influence of a marine pseudomonad on the precipitation of CaCO_3 from artificial sea water enriched with 1% peptone. Bacterial cells became enriched in calcium and magnesium with respect to the surrounding medium. Crystals of aragonite were formed in the presence of the bacteria but not in uninoculated controls. Single bacterial cells formed the nuclei of individual crystals, and Greenfield proposed that the bacterial surfaces—particularly the surfaces of dead cells—provided a concentrated calcium source. Raising the pH to values above that observed in the medium did not cause precipitation in the controls.

In addition to the removal of calcium and carbonate from solution, it is highly probable that other elements, such as Sr^{2+} , Pb^{2+} , and Zn^{2+} , are coprecipitated with CaCO_3 . Normally, it would be expected that CaCO_3 precipitated during periods of high photosynthetic activity would be redissolved at night when pH is lower. However, Chave (8) has reported that CaCO_3 particles from the sea become coated with organic compounds that prevent solution of these particles in unsaturated water.

COMPLEXATION. A change in the pH of a natural water may change the degree of complexation of a species in solution since many complexing agents are also conjugate bases of weak acids and the stability of many complexes depends on pH. A change in pH may cause a change in degree of protolysis of the acid and therefore a change in the amount of complexing agent in solution. Since little is known about the nature of the complexing compounds in natural waters, it is impossible to estimate the significance of this effect.

REDOX REACTIONS. Changes in pH may significantly affect the rate of redox reactions. Stumm and Lee (62) have found that the rate expression for the reaction of dissolved oxygen and ferrous iron is:

$$-\frac{d(\text{Fe(II)})}{dt} = k(\text{Fe(II)})(\text{O}_2)(\text{OH}^-)^2$$

From this equation, it is evident that an increase of 1 pH unit will cause the rate of reaction to be increased 100 times. The rate of oxygenation of manganese(II) has been shown (46) to be pH dependent, the rate likewise increasing by a factor of 100 for each increase of 1 pH unit. The rate constant for the latter reaction is such that at the concentrations of manganese(II) and oxygen normally found in natural waters and in the pH range of 7–8, the reaction is quite slow. It is possible that the oxida-

tion of manganese in natural waters occurs at the surface of algae during photosynthesis and at the surface of CaCO_3 crystals.

In addition to influencing the rate of a reaction, pH may also control the products where alternate or sequential pH-dependent reactions take place. An example of this type of reaction is the chlorination of phenol. Lee and Morris (37) have shown that the chlorination of phenol proceeds by the stepwise substitution at the 2, 4, and 6 positions of the aromatic ring. The rate of each of these reactions depends on the product of phenate or chlorophenate anion and the hypochlorous acid concentrations. Since each phenolic compound has a slightly different acid dissociation constant, the species of chlorophenols that are formed depend on the pH of the solution.

SORPTION. The sorption of a solute by particulate matter in natural waters may be highly pH dependent. Hydrogen ions may influence sorption by (1) competing for sorption sites, (2) modifying sorption sites, and (3) changing the degree of protolysis of the sorbing species. Since charged chemical species normally are more strongly sorbed at ionic sites (whereas uncharged species and large molecules are sorbed at van der Waals sites) and since both the nature of the sorption site and the sorbate may be altered by pH changes, the amount of sorption of a weak acid may be a function of water pH. The sorption of manganese(II) on freshly precipitated MnO_2 has been shown (46) to be influenced markedly by pH. They found that a fraction of a pH unit change around pH 7–8 could significantly change the amount of sorbed Mn(II) . They proposed that this effect was caused by a change in the nature of sorption sites with pH. Studies should be conducted to determine whether or not sorption of Mn(II) on MnO_2 would behave similarly in the natural aquatic environment. If the laboratory results of Morgan and Stumm (46) are applicable to natural waters, several of the transition metals may show diurnal changes in the amount in solution as a result of diurnal pH changes.

The amount of sorption that occurs in natural waters may be influenced by pH by changing the amount of particulate matter present and the form of the precipitate. For example, if there is a diurnal precipitation and solution of CaCO_3 , then the amount of compounds sorbed by this precipitate would exhibit a diurnal cycle.

FLOCCULATION. The precipitation of hydrous metal oxides—*e.g.*, iron and aluminum, may greatly influence the concentration of solutes in natural waters (64). Various studies have shown that the degree of incorporation of many solutes depends on the pH at which flocculation takes place (44).

Indirect Effects Other Than CO_2 Changes. In addition to altering the pH of natural waters, biological organisms may excrete and sorb

compounds, particularly organic compounds, which enter into chemical reactions with other compounds in solution. There is little doubt but that a substantial part of the organic matter present in natural waters is produced by organisms in the water and to some extent in the watershed.

The nature of the organic compounds in natural waters has been the subject of considerable study (15, 40, 52, 65, 66). Only a few general comments are pertinent here. The fact that the greater part of the organic matter present in natural waters is nonliving is often overlooked by workers in water chemistry. Parsons (52) reported that in the euphotic zone of the sea, the relative proportions of organic matter are:

soluble organics	100
detritus	10
phytoplankton	2
zooplankton	0.2
fish	0.002

where the soluble organic matter is arbitrarily set at 100. According to Parsons (52), Duursma has reported an average dissolved organic carbon approximately 1 mg./liter near the surface of the North Atlantic Ocean. In many fresh waters, approximately 10 times this amount is normally found. Unpublished studies by Lee have shown that the concentration of dissolved organic carbon in Lake Mendota, Madison, Wis. is about 10 mg./liter and that of filterable solids about 2 mg./liter. The filterable solids in the surface waters are composed of approximately 10^6 phytoplankton cells/liter and 10^7 detritus (nonliving) particles/liter. The origin of this organic matter is believed to be the excretory and degradation products of plants and animals. In addition to aquatic organisms, terrestrial sources must be considered. Mackereth's (43) studies on the composition of lake sediments have shown that the sedimentary carbon probably reflects changes in the lake watershed rather than lake productivity. Also the organic matter in water may be significantly increased by domestic and industrial pollution.

Numerous studies have been conducted on the nature of the dissolved and particulate organic matter in natural waters. In general, these studies have shown that the composition of the bulk of the organic matter is undefined. Many of the laboratory studies on the nature of the dissolved organic matter in natural waters are of limited value owing to possible alteration of the compounds by the concentration and analytical methods used. The selectivity of the methods used to concentrate the solute to analytically detectable levels presents another problem in many analytical procedures used to study trace compounds in natural waters. Concentration procedures such as freezing, flocculation, sorption columns, and solvent extraction, have been shown to be selective for certain types of compounds (32, 34, 38). Extreme care must be exercised to insure

that compounds found in concentrates of natural waters existed in the original sample.

Since the nature of the organic matter present in natural waters is not known, it is impossible to state with certainty the reactions that these compounds may influence or cause in natural waters.

ACID-BASE. The pH of natural waters is determined primarily by the carbonate equilibria. However, organisms may produce amounts of organic matter or ammonia sufficient to influence the pH and buffer capacity of the waters. It would be of interest to determine titration curves of high organic, high color, low alkalinity waters leached from some marshes. It is possible that these waters contain sufficient amounts of organic acids to be significant.

SOLUBILITY. Little is known about precipitation and dissolution of solutes in natural waters as a result of biological activity other than pH change. Possibly organic compounds excreted by organisms may form complexes with precipitates which would increase the concentration in solution. Evans (16) discussed the possible role that ATP, nucleic acids, and nucleotides may perform in solubilizing various minerals. Further study is needed before the significance of these reactions can be evaluated. Metallic ions also may be precipitated if the complexing organic substances holding them in solution are utilized as metabolic substrates by bacteria. Excessive blooms of algae in lakes are sometimes controlled by adding copper sulfate. In high alkalinity waters, copper is rapidly precipitated as a basic carbonate. To prevent its precipitation, copper may be added as a copper citrate complex. However, it has been found that the citrate is rapidly metabolized, and the copper is precipitated (17). Possibly this type of reaction may be significant in natural waters where dissolved organic matter could act as chelating agents forming complexes with metal ions, particularly iron.

Certain bacterial activities, such as denitrification and sulfate reduction, may be accompanied by CaCO_3 precipitation, apparently as a result of increases in the pH of the solution. However, it appears that some bacteria will precipitate CaCO_3 in amounts in excess of those which would be predicted by the pH change (24). The mechanism of this precipitation is not understood. As mentioned previously, the organic matter in natural waters appears to coat CaCO_3 particles and prevent their solution in undersaturated water (8). Kitano and Hood (33) have reported that the polymorphic form of calcium carbonate precipitated is influenced by certain organic compounds. Goldberg (22) has noted that the concentration profile of barium in the sea is similar to that of many nutrient elements. He suggested that the sulfate formed during the biochemical oxidation of organic sulfur compounds could lead to a subsequent formation of insoluble BaSO_4 within the decomposing biomass. As

this mass sinks and decomposes, entrapped BaSO_4 is released to the unsaturated water.

COMPLEXATION. Organic compounds excreted by aquatic organisms may result in the formation of complexes with transition metals in natural waters. Hood and Slowey (28) presented evidence indicating that appreciable amounts of copper in waters from the Gulf of Mexico exist in soluble complexes with organic matter. Since fresh waters, in general, contain larger amounts of dissolved organic matter, it is possible that copper and other transition metals exist as organic complexes. However, the demonstration of such complexes in natural waters must await further study.

One of the major difficulties encountered in studying complexes in natural waters is the inability to distinguish between compounds in true solution and those associated with particulate matter. This differentiation requires that some operational definition of "soluble" be adopted. A criterion based on the passage of the compound through a $0.45\text{-}\mu$ pore size filter may lead to gross errors. Shapiro's (58) studies on the "holding capacity" of organic matter extracted from natural waters for iron and other metals have shown that iron and organic matter interact to form particles that will pass through a $0.45\text{-}\mu$ pore, but are retained by $0.1\text{-}\mu$ pores. It should be pointed out that complexation need not result in the formation of a soluble compound. Possibly ligand atoms which could form complexes with solutes are present on the "surfaces" of particulate matter present in natural waters. Such a reaction normally would be considered sorption.

Another example of an organometallic complex that has been found in natural waters is vitamin B_{12} . The stability constant of the cobalt in B_{12} must be large since both cobalt and B_{12} exist in natural waters at less than $1\text{ }\mu\text{gram/liter}$.

SORPTION. One of the most important reactions involving organic matter present in natural waters is sorption. Biological organisms contribute organic matter that enters into these reactions and the detritus particles on which sorption of solutes may take place. There can be little doubt that the detritus particles influence the distribution of organic and inorganic compounds in natural waters. In addition, microorganisms may cause adhesion of particles forming aggregates as in soil [see review of Harris *et al.* (26)].

In addition to particulate organic matter, many natural waters contain large amounts of inorganic particulate matter which provide sorption sites for organic matter in water. Many rivers carry large amounts of suspended solids, especially during periods of high discharge. In lakes and oceans, turbidity currents may represent the transport of large amounts of suspended matter which is usually predominantly inorganic.

Bader (2) found that various clay minerals have large sorption capacities for dissolved organic compounds.

The sorbed organic substances can influence the distribution of other compounds in solution by changing the nature of the sorption sites. Fruh and Lee (20) have shown that the rate and extent of sorption of cesium by a stratified mica is influenced by inorganic and organic species in solution. In general, various organic compounds will compete for sorption sites, and the more strongly bound compounds will displace those with less affinity for the sites. In addition to competing for sites, the sorbed organics may activate or form new sites. Studies in the senior author's laboratory have shown that parathion is weakly sorbed by clay minerals. However, if these clay minerals are exposed to organic matter from natural waters, the amount of parathion sorbed will be increased. Similar reactions may occur with other organic and inorganic compounds. Shapiro's (58) studies on "holding power" of organics have shown that organics may control the particle size of precipitates.

A special case of sorption is the accumulation of surface-active compounds at the air-water interface. Surface-active compounds could affect the rates of gas transfer in natural waters. Mancy and Okun (45) have reported that surface-active compounds can markedly retard rates of gas transfer from air to water at low turbulence; however, these same compounds may increase the rate of gas solution at high turbulence.

REDOX REACTIONS. Aquatic organisms may alter the particular oxidation state of some elements in natural waters during activity. One of the most significant reactions of this type is sulfate reduction to sulfide in anoxic waters. The sulfide formed from this reaction can initiate several chemical reactions that can radically change the types and amounts of elements in solution. The classical example of this reaction is the reduction of ferric iron by sulfide. The resultant ferrous iron and other transition metals may precipitate with additional sulfide formed from further biochemically reduced sulfate. Iron reduction is often accompanied by a release of precipitated or sorbed phosphate. Gardner and Lee (21) and Lee (36) have shown that Lake Mendota surface sediments contain up to 20,000 p.p.m. of ferrous iron and a few thousand p.p.m. of sulfide. The biochemical formation of sulfide is undoubtedly important in determining the oxidation state and amounts of several elements in natural waters.

Organic matter in natural waters may enter into redox reactions with certain compounds in solution. Hem (27) has shown that tannic acid will reduce ferric iron to ferrous iron. Shapiro (59) has found ferric iron is reduced to ferrous iron in natural water samples boiled in acid. These reactions may proceed at slow rates in natural waters.

Organic materials in natural waters also may play an important part in redox reactions by complexing metal ions. Complex formation alters the free energy change of redox reactions. In general, a complexed metal ion will be a stronger oxidizing agent than the free species. Complexation of metals by organic compounds in natural waters could alter the redox potentials sufficiently to change the oxidation state of transition metals in natural waters relative to that which would be predicted based on the free species.

Summary

While the aqueous environmental chemistry of an element is determined by the thermodynamics and kinetics of its chemical reactions, and the amounts and forms of a particular element in pure water systems can possibly be predicted by chemical equilibria, in natural waters, aquatic organisms (particularly microorganisms) may significantly affect the concentrations of many elements. As in soil, the cycling of elements is largely the result of biological activity, and the many factors affecting the numbers or activity of organisms alter reaction rates and equilibrium concentrations. Effects of the aquatic biota upon the equilibrium composition of natural waters may be a direct result of biological activity, or they may result indirectly from changes in the pH, redox potential, or chemical composition of the water.

Although few investigations have led to reliable estimates of the actual influence of the biota upon the chemistry of natural waters and although much additional investigation is needed before the extent of biological influence upon chemical equilibria and involvement in geochemical cycles can be appreciated fully, it is clear that biota have dominant roles in water chemistry.

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