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Redox Conditions in Natural Waters

Redox conditions in rivers, lakes, and the ocean are largely controlled by the processes of photosynthesis and bacterial decomposition of organic matter.

PHOTOSYNTHESIS

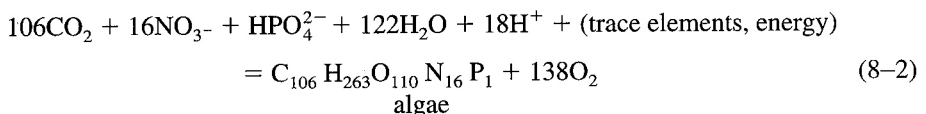
Photosynthesis is the process by which carbon dioxide (which may be derived from HCO_3^-) is converted to organic matter and oxygen:



Photosynthesis uses energy from the sun to form unstable compounds (organic matter and oxygen) from the stable compound CO_2 . In the absence of photosynthesis, the oxygen in the atmosphere would be steadily consumed by the oxidation of organic matter until no free oxygen remained (Garrels and Perry, 1974; Holland, 1978).

Carbon and oxygen are not the only elements involved in photosynthesis. Plants also require nitrogen compounds, phosphorus compounds, and a wide range of trace elements. Plants (in aquatic systems, primarily microscopic algae) will grow and multiply until all available phosphate or nitrate is used up, at which point photosynthesis ceases. In unpolluted fresh waters phosphate is normally the *limiting nutrient*; nitrate is sometimes limiting in polluted waters. The availability of particular trace elements is occasionally limiting for short periods of time, but this is rare. Photosynthesis is the ultimate source of food for all organisms in surface waters.

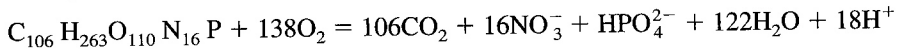
The average composition of the organic matter in plankton is approximately $\text{C}_{106} \text{H}_{263} \text{O}_{110} \text{N}_{16} \text{P}_1$ (Redfield et al., 1963), so photosynthesis can be represented by the more complex equation:



rather than the simple form of Eq. (8-1). Eq. (8-2) illustrates the enormous importance of phosphate in the carbon-oxygen balance of waters, particularly lakes. Each atom of phosphorus (as phosphate) added to a surface water results in fixation of about 106 atoms of carbon in organic matter, and when the organic matter produced from one atom of phosphorus decays, it has the potential to consume 138 molecules of oxygen.

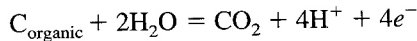
RESPIRATION AND DECAY

As long as free oxygen is available, the net results of respiration and decay are essentially the reverse of photosynthesis:

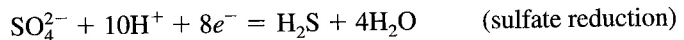
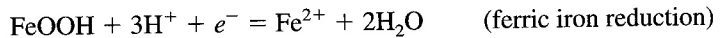
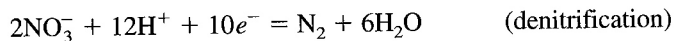


Carbon is released as CO_2 , organically combined nitrogen as NO_3^- , and organically combined phosphorus as HPO_4^{2-} . The release of CO_2 causes an increase in P_{CO_2} and hence a decrease in pH.

When molecular oxygen is not available, or when it has been used up, decay of organic matter continues by a series of reactions that represent successively lower pe levels (Fig. 8-1). The essential difference between the reactions is the *terminal electron acceptor*. Oxidation of carbon to CO_2 can be viewed (Chapter 7) as a reaction that generate electrons:



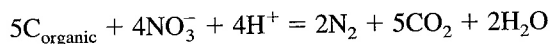
Since free electrons cannot accumulate, there must be some corresponding chemical system to accept the electrons, such as



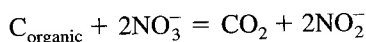
Electron acceptors are essentially "oxidizing agents," compounds capable of being reduced. From a biochemical viewpoint, it is much more realistic to think in terms of electron transfers than transfers of oxygen.

Some of the most important reactions are:

1. *Nitrate reduction.* In nitrate reduction, in a complex series of reactions bacteria use nitrate ion as the terminal electron acceptor to oxidize organic carbon to CO_2 . If molecular nitrogen is the final product, the process is called *denitrification* or *dissimilatory nitrate reduction*.

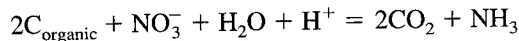
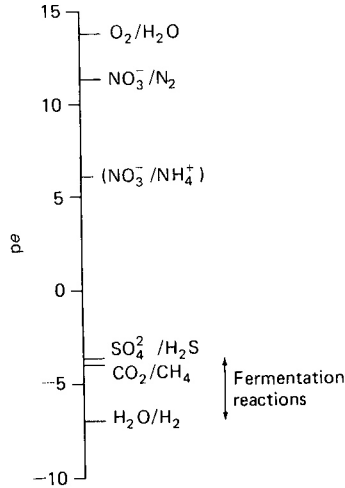


The importance of this reaction is that it converts nitrate, an essential nutrient, into biologically inert molecular nitrogen; it is important in the nutrient balance of lakes and rivers. Many bacteria reduce nitrate only as far as nitrite:

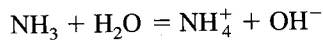


whereas other bacteria reduce nitrate all the way to ammonia:

FIGURE 8-1 Approximate pe values at which various redox reactions occur in water at pH 7 and 25°C.

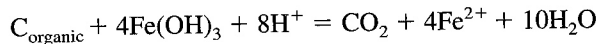


Ammonia may also be released from the decomposition of the amino acids in proteins. Ammonia that is released by microbial processes reacts with water



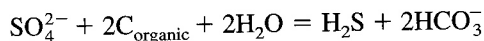
to form ammonium ion, NH_4^+ , causing a net rise in pH. The rise in pH may cause precipitation of calcium as a carbonate or as a soap (the calcium salt of a fatty acid) (Berner, 1969, 1971), which may be important in the formation of concretions.

2. Ferric iron reduction. Reduction of ferric oxyhydroxides (and sometimes manganese oxyhydroxides) is an important process in groundwater systems where the oxyhydroxides are present. It is relatively less important in surface waters because the mass of oxyhydroxide available is usually quite small. Stoichiometrically, the reaction is



The Fe^{2+} produced may remain in solution, it may precipitate as FeCO_3 (siderite) or, if iron reduction is followed by sulfate reduction, it may precipitate as a sulfide such as pyrite (FeS_2). Iron reduction is commonly microbially mediated.

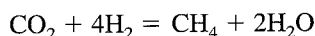
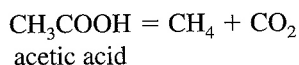
3. Sulfate reduction. In sulfate reduction, bacteria use SO_4^{2-} as a terminal electron acceptor in the oxidation of organic matter to CO_2 . Sulfide species are the final reduction product, although various sulfur species such as thiosulfate may be produced as intermediates. The overall stoichiometry of the reaction is



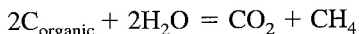
If the pH is above 7, HS^- will form rather than H_2S . If the pH is below 6, CO_2 will form rather than HCO_3^- . If any reactive iron compounds are present, the sulfide species will react with them to form solid sulfides. Sulfate-reducing bacteria are capable of utilizing only relatively simple organic molecules such as formate, acetate, lactate and a range of other compounds containing up to about 20 carbon atoms (and also hydrogen) (Chapelle, 1993; Hansen, 1993). They are thus typically dependent on fermentative bacteria (see below) to produce these simple molecules.

There are many consequences of ferric iron and sulfate reduction. H_2S and HS^- are highly toxic to most organisms, so the biota in the environment are strongly affected. Conversion of iron oxides to sulfides generally causes a color change from red or brown to black or gray. Species (e.g., heavy metals and phosphate ion) that were adsorbed onto ferric oxyhydroxides (see Chapter 9) will be released to solution, and many heavy metals (e.g., Cu, Zn, Mo, Pb, and Hg) that are relatively soluble in oxidizing waters (provided that the pH is not too high) are highly insoluble (as sulfides) in the presence of dissolved sulfide species.

4. *Fermentation reactions and methanogenesis.* When no external electron acceptors are available, organisms use a wide variety of organic transformations as a source of energy in fermentation reactions. The reactions are fundamentally transformation of complex molecules such as carbohydrates into simple compounds such as CO_2 , formate, acetate, and hydrogen. Measurable hydrogen concentrations are commonly present in fermentative systems. Associated with these fermentative organisms are another group of microorganisms that use the products of fermentation to derive energy by reactions involving methane formation such as



The overall result of fermentation and methanogenesis is thus to convert organic matter into methane and CO_2 . It can be represented in a very simplified way as



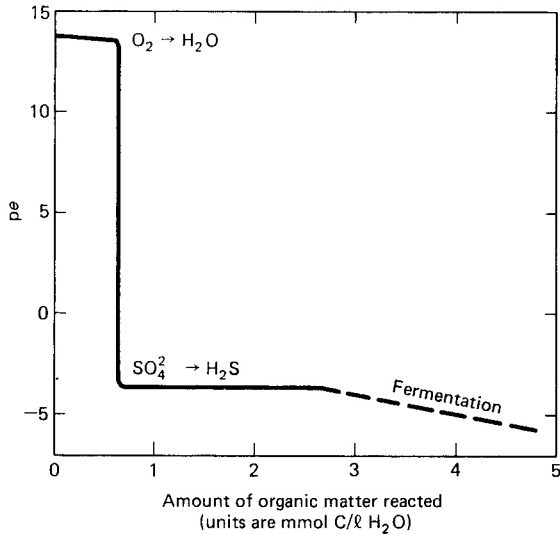
whose equilibrium p_e is shown in Fig. 8-1. Fermentation reactions typically generate hydrogen as a biochemical intermediate and can drive the p_e down to the H_2 - H_2O boundary.

Fundamentally, the various anaerobic decay reactions represent mechanisms by which microorganisms use decomposition of the products of photosynthesis as a source of energy. Since the bacteria derive energy from the reactions, their function is essentially to catalyze the conversion of thermodynamically unstable systems to more stable systems. In general, each reaction is mediated by a specific type of bacterium, and the reactions occur more or less in succession, with the reactions that yield most energy to the bacteria occurring earliest. Sulfate reduction does not occur until all molecular oxygen has been used up, and methane generation generally does not occur significantly until all sulfate has been used up. The succession is not strict, and there is commonly some overlap between the ranges of activities of the different microorganisms. Molecular oxygen is toxic to many anaerobic bacteria, so nitrate and sulfate reduction do not generally occur until all oxygen has been removed from the system.

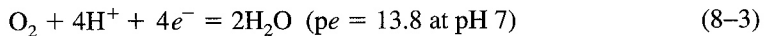
REDOX BUFFERING

In addition to p_e (redox level or redox intensity), *redox buffering* (or redox capacity) is an important concept. A system is buffered or poised with respect to redox processes if oxidizable or reducible compounds are present that prevent a significant change in p_e in response to additions of small amounts of strong oxidizing or reducing agents. Fig. 8-2 shows schematically how p_e might change as organic matter decomposes in a typical surface water. It is assumed that the water was initially in equilibrium with atmospheric oxygen, but no additional oxygen is added as the organic matter decomposes.

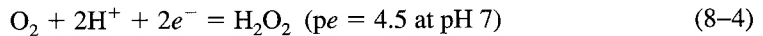
FIGURE 8-2 Change in pe of a fresh water (dissolved $O_2 = 10 \text{ mg/l}$, dissolved $SO_4^{2-} = 96 \text{ mg/l}$) as a function of the amount of organic matter decomposed. Reactions involving nitrogen compounds may provide a small amount of buffering between the O_2/H_2O and the SO_4^{2-}/H_2S levels. pH is assumed constant at 7.0.



As long as free oxygen is present, pe remains high. There has been some disagreement in the literature as to the “correct” pe of oxygenated water. The overall reduction of oxygen



generally does not occur as a single step, but as a series of separate reactions, two of the most important of which are



and



Breck (1974) argued that reaction (8-5) was much slower than reaction (8-4), and hence pe was essentially controlled by reaction (8-4). The effective pe for oxygenated waters would then be 4.5 (at $pH \ 7$), rather than the value of 13.8 predicted by reaction (8-3). Stumm (1978) disagreed, pointing out that some natural redox systems seemed to respond as if reaction (8-3) determined pe , and some as if reaction (8-4) controlled pe . Stumm concluded that the use of a single pe to characterize oxygenated waters is meaningless because the various redox couples in natural waters are not in equilibrium with each other. Since a single pe for all redox systems cannot be defined, it is probably best to think of pe as being “high” without specifying an exact number. For general discussion purposes, it is as logical to use the value defined by the O_2-H_2O couple as any other.

As soon as all free oxygen is consumed, pe drops abruptly to the value where sulfate reduction takes place (the amount of nitrate in an unpolluted water is usually too small for denitrification to be a significant buffer). pe remains essentially constant until all sulfate is reduced and then decreases gradually as various fermentation reactions take place. We would expect the pe values in natural waters to be generally in one of the buffered ranges because values in the unbuffered range are unstable; any trace of oxygen or reactive organic matter should shift the pe from an unbuffered range into a buffered range. The only place where we

would expect an “unbuffered” p_e to persist is in a region where p_e is controlled by diffusion between an anaerobic water (e.g., interstitial water in sediments) and an aerobic water (e.g., oxygenated lake or ocean water).

In this discussion we have considered only redox reactions involving organic matter and the solutes in water. In groundwaters and waters in effective contact with sediments, redox reactions involving solid phases may also buffer p_e . Fig. 8-3 shows how Fig. 8-2 might be modified to include such reactions. The lengths of the various horizontal segments in Fig. 8-3 are arbitrary, as it is hard to generalize on the distribution and reactivity of specific minerals in sediments.

Some of the effects of bacterial decomposition of organic matter in marine sediments are shown in Figs. 8-4 and 8-5. Fig. 8-4 shows profiles of dissolved nitrate, manganese, and iron in a core from the eastern equatorial Atlantic (Froelich et al., 1979). First nitrate is reduced (denitrification), then manganese oxides are reduced to Mn^{2+} , and then iron oxides are reduced to Fe^{2+} . There was no reduction of sulfate in the core studied (sulfate reduction probably occurred at greater depth in the sediment), reflecting the relatively low organic matter content of the sediment. Fig. 8-5 shows the interstitial water chemistry in a core containing abundant organic matter from a near-shore environment off North Carolina (Martens and Goldhaber, 1978). Sulfate is completely reduced to sulfide in the top 40 cm, and methane is generated in the deeper part of the core. The high concentrations of ammonia and phosphate illustrate the release of inorganic nutrients accompanying the decomposition of organic matter. The profiles indicate that the nutrient elements are diffusing upward into the overlying water. These processes have been synthesized into a general model by Van Cappellen and Wang (1996).

Although organic matter is the common reducing agent in natural waters, lowering of p_e can also be brought about by oxidation of minerals containing ferrous iron or reduced sulfur species. Solutions emerging from basalt at oceanic spreading centers contain high concentrations of dissolved iron and manganese, or sometimes high concentrations of sulfide. Presumably, these solutions represent seawater, the p_e of which has been lowered by reaction with ferrous minerals in the basalt. Some springs emerging from ultramafic rocks (rocks composed largely of Mg-Fe silicates) on land actually produce bubbles of hydrogen gas from the reduction of water by ferrous minerals (Barnes et al., 1972).

FIGURE 8-3 Change in p_e of a fresh water in contact with sediment as a function of the amount of organic matter decomposed. The lengths of the various horizontal segments are arbitrary, depending on the amounts of specific solid phases available for reaction. pH is assumed constant at 7.0.

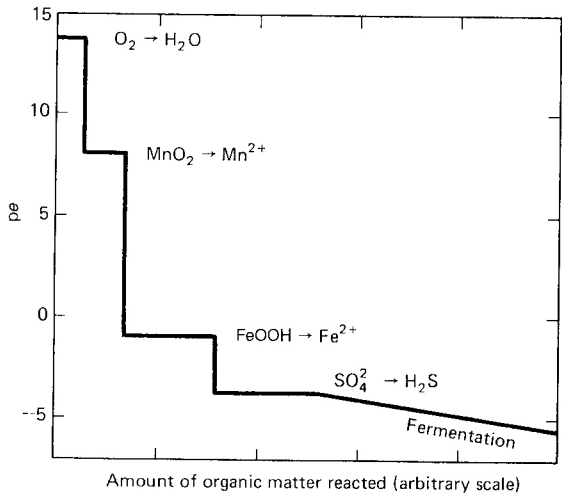


FIGURE 8-4 Profiles of nitrate, dissolved manganese, and dissolved iron in interstitial water from a sediment core from the eastern equatorial Atlantic (Froelich et al., 1979).

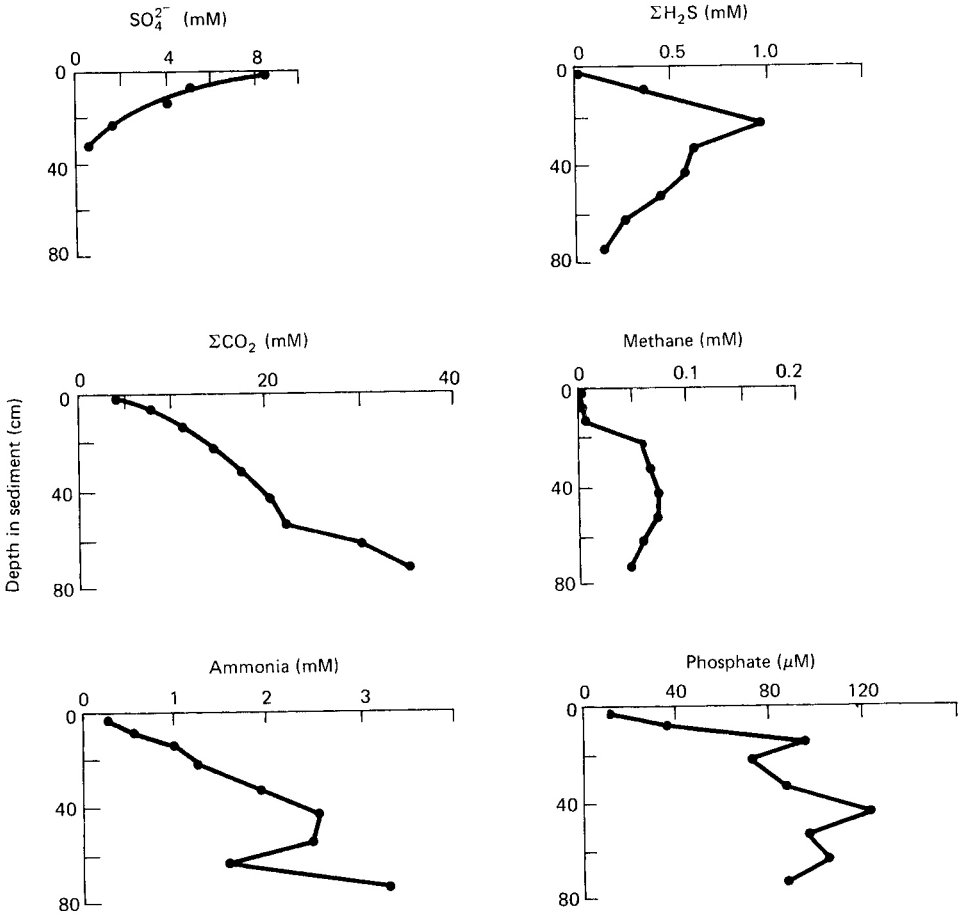
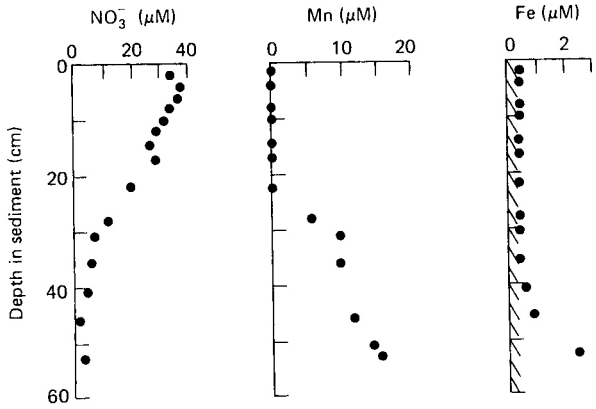


FIGURE 8-5 Profiles of dissolved species in interstitial water from a sediment core from an estuary in North Carolina (Martens and Goldhaber, 1978).

LAKES

Redox conditions in lakes are determined by the balance between the decomposition of organic matter, normally from photosynthesis in the lake, and the supply of oxygen by circulation or vertical mixing of the water. The circulation in lakes is largely controlled by density differences, which are generally a consequence of temperature differences. The density of pure water as a function of temperature is shown in Fig. 8-6. Note that the maximum density occurs at 4°C, not at 0°C.

A typical vertical temperature profile for a lake in a temperate climate in summer is shown in Fig. 8-7 (tropical lakes are discussed below). The upper layer or *epilimnion* is warm as a result of solar radiation. The temperature within the epilimnion is fairly uniform because the surface zone is stirred by wave action. Immediately below the epilimnion is the *metalimnion* or *thermocline* zone, a region in which temperature decreases rapidly with depth. Below the metalimnion is a mass of uniformly cold water, the *hypolimnion*. In real lakes, the situation may be complicated by the presence of more than one metalimnion, and, of course, very shallow lakes and ponds will consist of an epilimnion only. The situation shown in Fig. 8-7 represents stable stratification. Warm, low-density water floats above cold, high-density water, and the density contrast results in little mixing or exchange of solutes between epilimnion and hypolimnion.

At the end of summer, the temperature of the epilimnion starts to decrease. When it reaches a value close to that of the hypolimnion (about 4°C in deep lakes in cold-winter climates), the density contrast between epilimnion and hypolimnion disappears. Storms, or even normal winds, cause complete mixing between the epilimnion and hypolimnion, an event called the *fall turnover*. If surface temperatures become even colder, stable stratification may again develop, with water (and ice) at about 0°C overlying more dense water at 4°C. This stratification breaks down at the *spring turnover*, when the surface layers again warm to 4°C. Lakes that turn over twice a year are called *dimictic*; those that turn over once a year are called *monomictic*.

FIGURE 8-6 Density of pure water at 1 atm as a function of temperature.

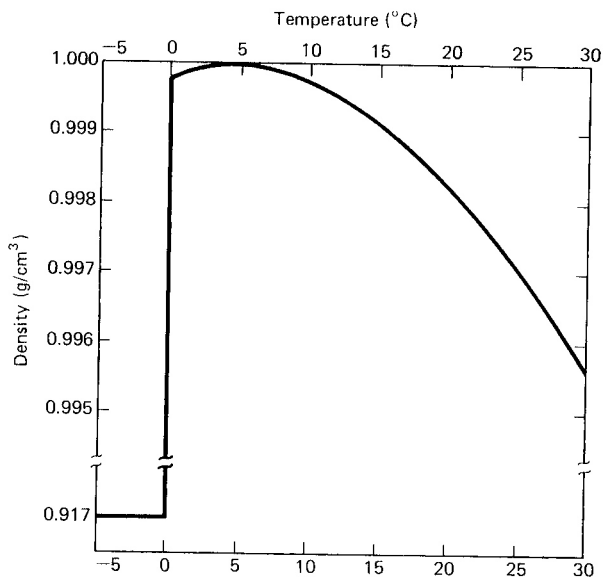
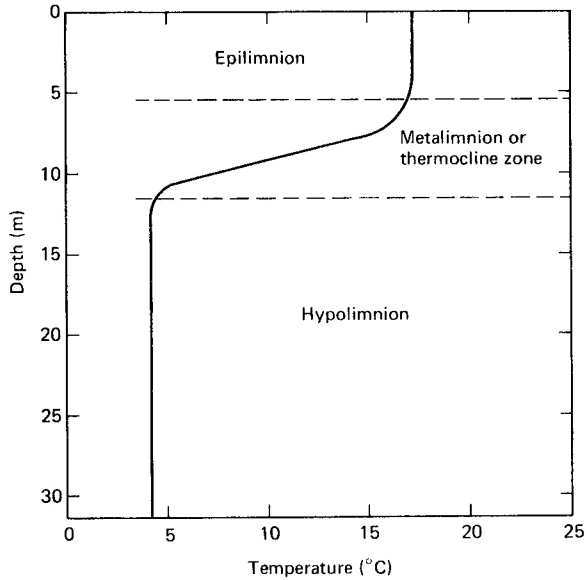


FIGURE 8-7 Typical summer temperature distribution for a lake in a temperate climate.



At times of turnover, the dissolved oxygen content of the entire lake is essentially determined by equilibrium with oxygen in the atmosphere (Table 8-1). When the lake becomes stratified, the oxygen content of the hypolimnion steadily decreases as a consequence of aerobic decomposition of organic matter falling from the epilimnion. Whether or not the hypolimnion

TABLE 8-1 Concentration of Dissolved Oxygen in Water in Equilibrium with Air at a Total Pressure of 1 atm (from data of Truesdale et al., 1955)

Temperature (°C)	Oxygen (mg/l)	Oxygen (mM)	Temperature (°C)	Oxygen (mg/l)	Oxygen (mM)
0	14.16	0.443	18	9.18	0.287
1	13.77	0.430	19	9.01	0.282
2	13.40	0.419	20	8.84	0.276
3	13.05	0.408	21	8.68	0.271
4	12.70	0.397	22	8.53	0.267
5	12.37	0.387	23	8.38	0.262
6	12.06	0.377	24	8.25	0.258
7	11.76	0.368	25	8.11	0.253
8	11.47	0.358	26	7.99	0.250
9	11.19	0.350	27	7.86	0.246
10	10.92	0.341	28	7.75	0.242
11	10.67	0.333	29	7.64	0.239
12	10.43	0.326	30	7.53	0.235
13	10.20	0.319	31	7.42	0.232
14	9.98	0.312	32	7.32	0.229
15	9.76	0.305	33	7.22	0.226
16	9.56	0.299	34	7.13	0.223
17	9.37	0.293	35	7.04	0.220

becomes anaerobic depends on the total amount of organic matter falling into it during a period of stratification. The amount of organic matter produced in the epilimnion is largely controlled by the availability of inorganic nutrients, particularly phosphate. An *oligotrophic* lake is one in which the supply of nutrients is low, so there is little photosynthetic production and the water is oxygenated at all depths. A *eutrophic* lake is one in which the supply of nutrients is high, photosynthetic production is high, and the hypolimnion is anaerobic (Fig. 8-8). In an oligotrophic lake, the p_e of the hypolimnion remains high at all depths; in a eutrophic lake it will decrease with depth and with time since the onset of stratification. When turnover occurs in a eutrophic lake, hydrogen sulfide and other toxic compounds may be mixed into the epilimnion, which may cause widespread mortality among fish that were living in the epilimnion.

Pollution may affect the oxygen balance in lakes by introducing reactive organic matter, by introducing nutrients (phosphate and/or nitrate), or by introducing chemicals (e.g., heavy metals or persistent organic compounds) that interfere with biological systems in the lake. The common ways in which organic matter in wastewater is measured are as biochemical oxygen demand (BOD) and chemical oxygen demand (COD). BOD is measured by diluting the sample with oxygenated water, incubating it in the dark at 20°C for five days, and measuring the amount of oxygen that has been consumed. BOD is a predictor of how much direct oxygen

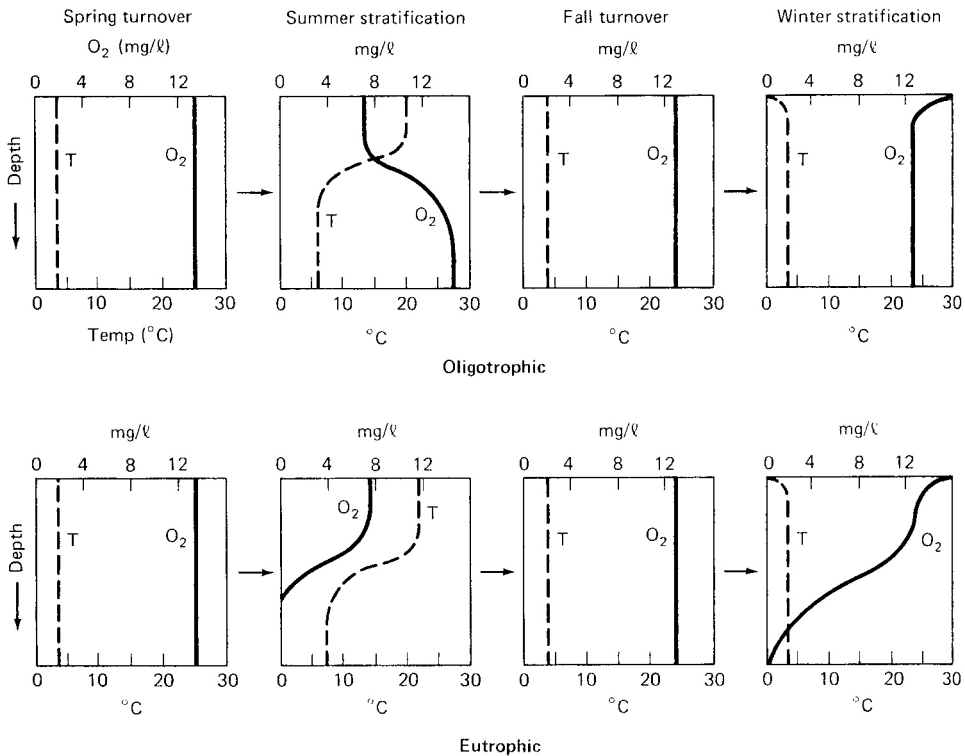


FIGURE 8-8 Idealized distributions of temperature and dissolved oxygen in oligotrophic and eutrophic lakes. The increase in dissolved O_2 with depth in the oligotrophic case in summer is due to the greater solubility of O_2 at lower temperatures (after Wetzel, 1983).

consumption will be caused by a particular pollution source. COD is measured by the amount of a strong chemical oxidizer (potassium dichromate) consumed in oxidizing the organic matter in the water. It is (approximately) a measure of the total concentration of organic matter, both reactive and nonbiodegradable, in the water. COD can be measured more reproducibly and more conveniently than BOD, but BOD is probably a better predictor of oxygen consumption in the environment.

Normal sewage treatment processes reduce BOD and COD to low levels but are relatively ineffective in removing phosphate and nitrogen. Agricultural fertilizers also contribute these nutrients to surface waters. The most important way in which pollution affects lakes is thus by increasing the supply of nutrients, particularly phosphate, to the epilimnion. The phosphate content of sewage was significantly decreased when the phosphate content of commercial detergents was reduced in the late 1960s. Advanced waste treatment methods to remove phosphate from sewage are now becoming more common.

When an oligotrophic lake becomes eutrophic as a result of pollution, it is difficult to reverse the process. One might think that in a eutrophic lake undecomposed organic matter would be deposited in sediments, and this would remove phosphorus from lake waters. Although this does occur, the effect is usually overwhelmed by the consequences of reduction of ferric compounds. Ferric oxides adsorb phosphate strongly, and when the oxides are reduced (to Fe^{2+} , FeS_2 , or FeCO_3), a large amount of phosphate is released to solution (Williams et al., 1976). Bacteria in the surface sediments of anaerobic lakes may also store significant quantities of phosphate, which is released to the water column when the water becomes aerobic (Gächter and Meyer, 1993). Thus, when a lake first becomes eutrophic, phosphate is transferred from the sediment to the hypolimnion, and when turnover occurs, this additional phosphate will be mixed into the epilimnion. The extra supply of phosphate will further aggravate the problem of eutrophication.

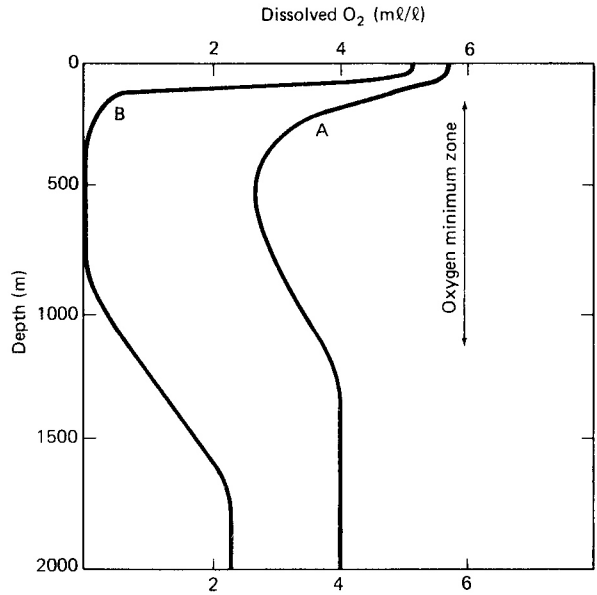
The circulation in tropical lakes is less straightforward than that of lakes in which circulation is controlled by seasonal temperature changes. In many tropical lakes, temperature differences between night and day are sufficient to cause frequent mixing, and hence prevent stratification. Thermal stratification may occur when a mass of cold water is formed during an unusually cold period, and a permanent epilimnion forms above it. Chemical stratification is also common. This occurs where water of higher salinity, formed in an arid period or by dissolution of salts in the lake bed, underlies more dilute surface water. Such chemical stratification may persist for many years. Lakes that do not turn over annually, usually because the deep water is more saline than the surface water, are called *meromictic*.

THE OCEAN

The ocean differs from lakes in many respects other than scale. "Turnover" in the oceans is continuous, as cold surface water sinks at the poles, circulates at depth, and returns to the surface. The distribution of nutrients (and hence photosynthesis) in the oceans is controlled almost entirely by regeneration of nutrients in the water column and redistribution by circulation, whereas in lakes the distribution of nutrients is controlled more by the concentration of nutrients in the inflow waters than by processes in the lake itself (although there are exceptions to this generalization).

Typical profiles of dissolved oxygen in the ocean are shown in Fig. 8-9. The surface zone is well oxygenated as a result of both photosynthesis and exchange with the atmosphere.

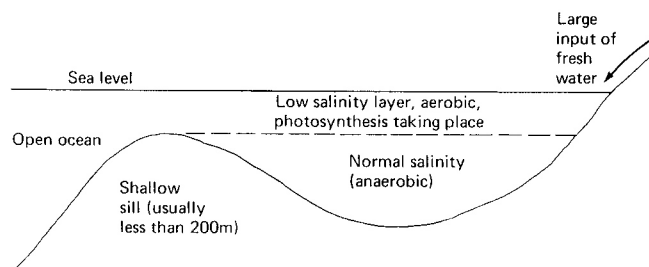
FIGURE 8-9 Schematic illustration of the distribution of O_2 with depth in the ocean. Curve A is a region of average surface productivity. Curve B is a region of very high surface productivity.



Below the surface zone is the oxygen minimum zone. This is the depth interval where most of the organic matter falling from the surface zone undergoes decomposition. Over most of the ocean, decomposition of organic matter is not sufficient to use up all the oxygen in the oxygen minimum zone, so the entire water column is aerobic. Under areas of exceptionally high surface productivity, areas of upwelling where nutrients are returned to the surface, water in the oxygen minimum zone may be anaerobic. The deep water below the oxygen minimum is generally well aerated. Most readily decomposable organic matter from the surface has already been decomposed before it reaches the deep zone, and oxygen in the deep zone is constantly replenished by the sinking of oxygenated water at the poles.

Anaerobic basins occur in the oceans where the circulation of deep water is obstructed and surface productivity is high (e.g., the Cariaco Basin off Venezuela). Such basins always have a sill depth near the oxygen minimum zone (Fig. 8-10). At greater depths, the supply of readily decomposable organic matter is so slow that even closed basins with little apparent circulation remain aerobic. Anaerobic conditions also occur in coastal basins such as the Black Sea and the fjords of northern Europe and North America, where a layer of relatively fresh

FIGURE 8-10 Schematic illustration of anaerobic conditions in a fjord.



(low salinity) water traps a body of normal salinity water out of contact with the atmosphere or the open ocean.

The sediments of anaerobic basins are commonly black and rich in organic matter and iron sulfide. They also commonly show annual layering, caused by seasonal variations in the supply of sediment from land or in the production of calcite skeletons by planktonic organisms. The fine layering of the sediments is preserved because burrowing organisms which normally disrupt sea-floor sediments cannot live where the overlying water is anaerobic.

Although anaerobic conditions are rare in open ocean water, they are common in the interstitial waters of near-shore marine sediments. After a sediment is deposited, organic matter in it decays, consuming oxygen and then sulfate from the interstitial water. The detailed mechanisms controlling redox conditions in interstitial waters are complex (e.g., Berner, 1974, 1980), depending primarily on the amount of organic matter supplied to the sediment and the overall sedimentation rate. Sedimentation rate is particularly important because it controls the amount of time during which organic matter can undergo decomposition in oxygenated water at or near the sediment-water interface. In general, the interstitial waters of sediments around the margins of the continents are anaerobic, because sedimentation rates are high, and because, in shallower water, organic matter has not had as much time to decompose as it falls through the water column. Continental-margin sediments below wave base are generally black, green, or gray in color, and contain pyrite. At greater distances from the continents (deeper water and slower sedimentation rates), the sediments near the sediment-water interface are oxidizing, but the sediments at greater depths below the interface are reducing. Toward the centers of the ocean basins, far from the continents, the interstitial water of the entire sediment column is likely to be oxidizing.

GROUNDWATER

Redox levels in groundwater are determined essentially by the relative rates of introduction of oxygen by circulation and the consumption of oxygen by bacterially mediated decomposition of organic matter (or occasionally sulfides or ferrous silicates or carbonates). The most important variables in natural systems appear to be:

1. *Oxygen content of recharge water.* Recharge water may enter an aquifer through fractures in bare rock, or it may percolate through a soil rich in organic matter. In the first case the recharge water will be oxidizing and will have significant redox buffer capacity at high p_e values. In the second case it may be anaerobic when it enters the aquifer, and it is unlikely to have much redox buffer capacity at high p_e values.

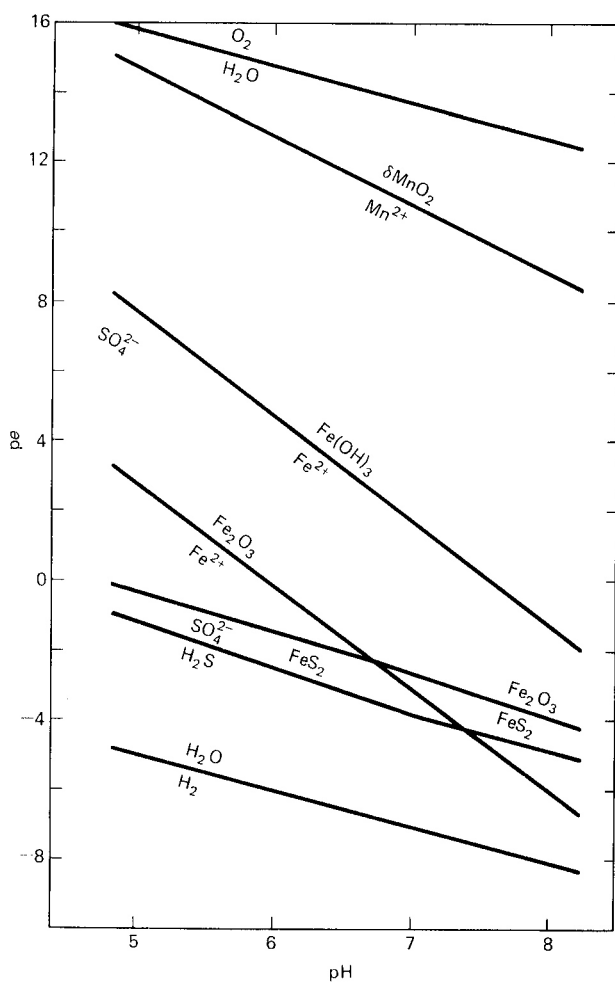
2. *Distribution and reactivity of organic matter and other potential reductants in the aquifer.* Aquifers vary greatly in the amount of organic matter present and, more important, in the reactivity of that organic matter. The organic matter of sedimentary rocks is generally refractory; that is, it is not easily utilized by bacteria. It is refractory both because the more easily metabolized components have already been utilized, and because the effects of elevated temperature and pressure are to convert the original organic compounds into compounds that are less readily utilized by bacteria. Most sedimentary rocks (and hence most aquifers) have been buried under a thickness of younger rocks at some time in their history, and hence have been exposed, to some degree or another, to elevated temperatures and pressures. As an example, coal (organic matter) should reduce any sulfate in groundwater

in a coal seam. However, groundwaters in coal seams often have high sulfate contents, and sometimes show no evidence of dissolved sulfide. Sulfate-reducing bacteria are incapable of utilizing directly the organic compounds that are common in coal, so sulfate reduction in groundwaters in coal is generally a slow process. The sulfides present in many coals were formed in the environment of deposition (an anaerobic sediment) rather than from later groundwater.

3. Distribution of potential redox buffers in the aquifer. In a groundwater system, the mass of potential redox buffers (for example, MnO_2 , Fe(OH)_3 , and Fe_2O_3) per unit volume of groundwater is often large, and the reactions tending to lower pe are generally slow. The redox levels in groundwaters thus often correspond to buffering by the Mn^{2+} - MnO_2 , the Fe^{2+} - Fe(OH)_3 , or the Fe^{2+} - Fe_2O_3 pair (Fig. 8-11).

4. Circulation rate of the groundwater. Since bacterial reactions that tend to lower pe are usually slow, the pe of a particular water depends very much on the residence time of water in the aquifer. The residence time depends on both the velocity of the water and the "length"

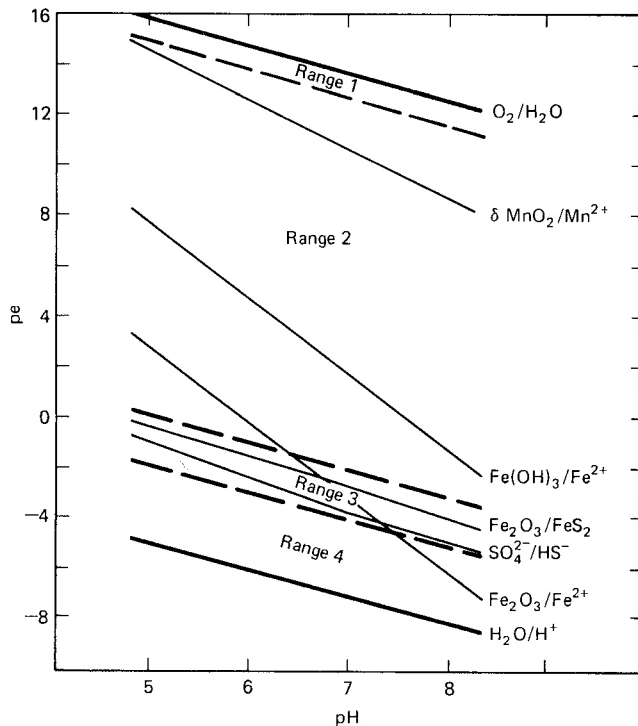
FIGURE 8-11 Some possible redox buffers in a groundwater system. Solid-solution boundaries are drawn for activity of solute = 10^{-6} .



of the aquifer system from recharge to discharge. In general, the longer the residence time, the lower the resulting pe .

It is difficult to generalize about redox conditions in groundwater, as all four factors vary from place to place. If a groundwater contains free oxygen (range 1 on Fig. 8-12), either its residence time underground is short, or the aquifer contains essentially no metabolizable organic matter. The absence of organic matter may be inherited from the time the aquifer rock was deposited, or it may be that organic matter originally present has been removed by prolonged passage of oxygenated groundwater. Aerobic bacteria can utilize a greater variety of organic compounds than can sulfate-reducing bacteria. Most shallow groundwaters probably plot in Range 1. Many groundwaters also plot in range 2 of Fig. 8-12. The water contains no free oxygen, but no significant sulfate reduction has taken place. This redox level does not cause the water to be unsuitable for domestic supply purposes, although high (1 ppm or greater) concentrations of dissolved iron or manganese are sometimes a problem. Groundwaters in range 3 (buffered by sulfate reduction) are common where residence times are long or where much reactive organic matter is present. A high concentration of sulfide makes a water unsuitable for domestic supply purposes. Although waters in range 4 (well below the sulfate-sulfide boundary) are common in modern muds, they are relatively uncommon in aquifers, which are normally ancient rocks. The organic matter (with notable exceptions such as petroleum) in most ancient rocks is utilized so slowly by bacteria that many thousands of years are required for all the sulfate to be reduced and for the pe to reach the very low values.

FIGURE 8-12 Positions of redox ranges discussed in text.



SUMMARY

1. Redox conditions in natural waters are usually determined by the balance between the supply of oxygen from the atmosphere and the consumption of oxygen by microbial decomposition of organic matter.

2. After all free oxygen has been consumed, pe decreases progressively as a sequence of biological reactions occurs. The most important of these reactions are ferric iron reduction, sulfate reduction, and fermentation.

3. In lakes and the ocean, production of organic matter (and hence subsequent consumption of oxygen) is largely controlled by the availability of the inorganic nutrients phosphate and nitrate.

4. Changes in pe have a large effect on the solubility and hence mobility of many metals.

REVIEW QUESTIONS

A lake in a cold-winter climate has a mean depth of 20 m, a surface area of 10 km², an epilimnion thickness of 3 m, and an inflow and outflow of 5×10^8 m³/y.

1. What is the residence time (Chapter 1) of water in the lake?
2. If organic water can be approximated by the formula CH₂O, how many moles of organic matter per m² of lake surface would it take to consume all of the oxygen introduced to the metalimnion and hypolimnion during spring turnover? (Assume 4°C and the solubility of oxygen in Table 8-1.)
3. If summer stratification lasted six months, and all the phosphate in the inflow were used to produce organic matter [Eq. (8-2)] which fell into the metalimnion and hypolimnion, what concentration of phosphate in the inflow would result in depletion of all the oxygen in the metalimnion and hypolimnion?

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