Limnology

Lake and River Ecosystems

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the distribution of metal ions but may have marked effects on the phosphate distribution (cf. Golachowska, 1971). Metal ions such as those of ferric iron, manganous manganese, zinc, copper, et cetera, are present in concentrations comparable to or lower than those of phosphates. For these ions, complex formation can significantly affect the distribution of the metal ion, the phosphates, or both. For example, the solubility of aluminum phosphate ($AlPO_4$) is minimal at pH 6 and increases at both higher and lower pH values. Ferric phosphate ($FePO_4$) behaves similarly, although it is more soluble than $AlPO_4$. Calcium concentration influences the formation of hydroxylapatite, [$Ca_5(OH)(PO_4)_3$]. In an aqueous solution lacking other compounds, a calcium concentration of 40 mg liter^{-1} at a pH of 7 limits the solubility of phosphate to approximately 10 μg liter^{-1}. A calcium level of 100 mg liter^{-1} lowers the maximum equilibrium of phosphate to 1 μg liter^{-1}. Elevation of the pH of waters containing typical concentrations of calcium leads to apatite formation (Kümmel, 1981). Moreover, increasing pH leads to formation of calcium carbonate, which coprecipitates phosphate with carbonates (Otsuki and Wetzel, 1972). Sorption of phosphates and polyphosphates on surfaces is well known, particularly onto clay minerals (cf. Stumm and Morgan, 1996), by chemical bonding of the anions to positively charged edges of the clays and by substitution of phosphates for silicate in the clay structure. In general, high phosphate adsorption by clays is favored by low pH levels (approximately 5–6).

Following from these interactions and the distribution of phosphorus in inorganic and organic fractions, the general tendency is for unproductive lakes with orthograde oxygen curves to show little variation in phosphorus content with depth (Fig. 13-1). Similarly, during periods of fall and spring circulation, the vertical distribution of phosphorus is more or less uniform. Oxidized metals, such as iron, and major cations, particularly calcium, can react with and precipitate phosphorus.

Lakes exhibiting clinograde oxygen curves during the periods of stratification, however, possess much more variable vertical distributions of phosphorus. Commonly, there is a marked increase in phosphorus content in the lower hypolimnion, particularly during the later phases of thermal stratification (Fig. 13-1). Much of the hypolimnetic increase is in soluble phosphorus near the sediments. The sestonic phosphorus fraction is highly variable with depth. Sestonic phosphorus in the epilimnion fluctuates widely with oscillations in plankton populations and loadings from littoral areas. Sestonic phosphorus in the metalimnion and hypolimnion varies with sedimentation of plankton, depth-dependent rates of decomposition, and the development of deep-living populations of bacterial and other plankton (e.g., euglenophyceans).

III. PHOSPHORUS CYCLING IN RUNNING WATERS

A. Dissolved and Particulate Phosphorus in Rivers

Dissolved inorganic phosphorus, commonly referred to as orthophosphate or more correctly as soluble reactive phosphorus (SRP) based upon methods used in chemical analyses, averages about 10 μg liter^{-1} worldwide among unpolluted rivers (Meybeck, 1982, 1993b). Total dissolved phosphorus in these waters averages about 25 μg liter^{-1}.

Total dissolved inorganic phosphorus (DIP) of river water often increases by a factor of two- to four-fold

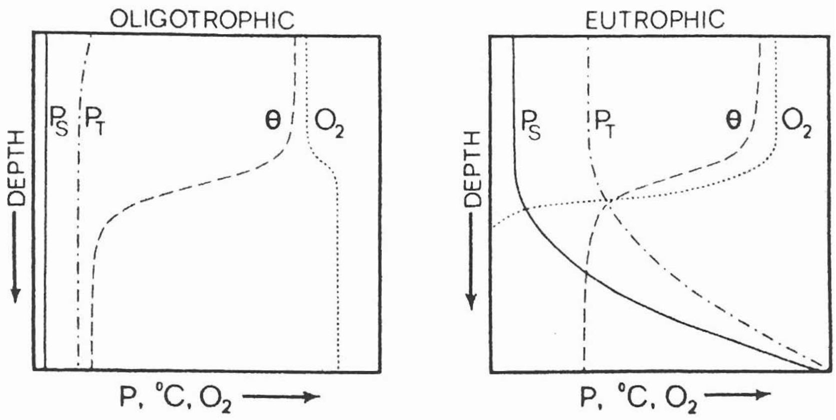

FIGURE 13-1 Generalized vertical distribution of soluble (P_S) and total (P_T) phosphorus in stratified lakes of very low (oligotrophic) and of high (eutrophic) productivity.

during and following increases in discharge from heavy rainfall events or in the early stages of snowmelt. DIP from pollutional sources often increases to levels of 50–100 μg P liter^{-1} from agricultural runoff and to over 1000 μg P liter^{-1} from municipal sewage sources (Meybeck, 1982, 1993b). Where DIP enters streams or rivers at point sources, concentrations decline downstream with net uptake rates in the range of 10–100 mg m^{-2} day^{-1}. As discussed next, uptake occurs both by physical adsorption to benthic substrata and to particulate seston, as well as by assimilation by attached biota. Although uptake of DIP by planktonic seston may be small (ca. 1% of total uptake) in small streams (Newbold *et al.,* 1983a; Mulholland *et al.,* 1990), sestonic uptake increases markedly in larger streams, particularly when dominated by phytoplankton (Newbold, 1992). Some of the seston and adsorbed phosphorus may settle out during base flows and then later be transported downstream during storm-induced high discharge. Exchange from these particles to the water may then occur in these displaced locations.

B. Biological Utilization

Biological uptake of phosphorus by algae, cyanobacteria, bacteria, and larger aquatic plants generally follows Michaelis–Menten kinetics (Chap. 17). Many algae and bacteria assimilate phosphorus at rates more rapid than used for growth. As a result, cells accumulate phosphorus and steady-state growth is saturated by concentrations much lower than the half-saturation constant (where uptake is half its maximum rate). Uptake rates of phosphorus by coarse particulate organic matter and microbiota associated with it commonly reach a maximum in 15–20 days and then decline precipitously (e.g., Mulholland *et al.,* 1984).

The rates of phosphorus uptake correlate with the metabolism of dominant organisms. In highly shaded streams with minimal in-stream photosynthesis, much (60 and 35%, respectively) of the uptake was associated with large (>1 mm) and fine (<1 mm) particles and only 5% with attached algae (Newbold *et al.,* 1983a; Mulholland *et al.,* 1985). In streams where decomposition of leaf detritus was dominant, phosphorus uptake was associated with the attached fungi and bacteria. Much of the phosphorus uptake associated with particulate organic matter is heterotrophic uptake by microbes associated with large and small particles of the benthic detritus (Gregory, 1978; Meyer, 1980; Webster *et al.,* 1991; Suberkropp, 1995). Phosphorus uptake was primarily associated with attached and planktonic algae in streams that were less shaded (e.g., Ball and Hooper, 1963; Petersen *et al.,* 1985). If other growth conditions are adequate, enrichments with phosphorus in the water often result in immediate enhancements of rates of algal photosynthesis and growth (e.g., Hart and Robinson, 1990; Burton *et al.,* 1991; Kjeldsen, 1994). Uptake by macrophytes, particularly by rooted vascular plants that rely largely upon rooting tissues for nutrient uptake, was much less than by attached algae and other microbes.

Average sestonic algal abundance has been positively correlated with total phosphorus and average phosphorus concentrations of many streams at moderate levels of nutrient loadings (Jones *et al.,* 1984; Soballe and Kimmel, 1987; Nieuwenhuyse and Jones, 1996) but becomes increasingly less responsive, as in lakes, to nutrient loadings at higher phosphorus concentrations. Summer mean chlorophyll concentration of seston among temperate streams exhibits a curvilinear relationship with summer mean total phosphorus concentrations (Fig. 13-2). The amount of nutrient loading to a river increases with greater catchment area. The analyses indicated that the phosphorus–sestonic chlorophyll relationship increased some 2.3-fold as the area increased from 100 to 100,000 km^2 (Fig. 13-2). It is important to note that the primary productivity of rivers is generally much less responsive to increased nutrient loadings than is the productivity of lakes. As will be discussed later in the sections on algal productivity, nutrient availability is generally higher in rivers than lakes. Nutrient losses in lakes are greater and large quantities are stored in parts of the ecosystem that are not readily available to the producers.

C. Adsorption and Release

The kinetics of abiotic adsorption and desorption of phosphorus onto and from organic and inorganic particles, such as natural sediment and suspensoid particles, generally comply with Langmuir isotherms. Fine particles (<0.1 mm) account for nearly all of the sorption capacity for phosphorus (0.1–1.0 μg P g^{-1} sediment per μg P liter^{-1} water; Meyer, 1979; Logan, 1982; Stabel and Geiger, 1985). The adsorption capacities of particles saturate and reach quasi-steady state in which uptake and release are about balanced.

The abundance of phosphate is also regulated by solubility reactions, particularly in relation to solid–solution associations with colloids or particles. Phosphorus concentrations in turbid rivers with low calcium concentrations are influenced by a solid ferric hydroxide-phosphate present in colloidal suspensions or on suspended particulates (Fox, 1993). In hardwater streams, the solubility of inorganic phosphorus can decrease as pH increases above 8.5, as is common in areas of intensive photosynthesis (Diaz *et al.,* 1994). Precipitation of inorganic phosphorus as calcium are exported downstream for subsequent utilization (Mulholland *et al.*, 1988).

The spiralling of phosphorus has been measured in only a few streams. In a first-order woodland stream in Tennessee, the spiralling length was 190 m, most of it (165 m) associated with the water movement, and the remainder (25 m) in the particulate components, mostly coarse and fine particulate matter (Newbold *et al.*, 1983a). Less than 3% of the total passed through the invertebrate and vertebrate consumers. Phosphorus uptake lengths ranged from 21 to 165 m and varied inversely with the quantity of detritus on the stream sediments (Mulholland *et al.*, 1985). In a larger river in Michigan, phosphorus uptake lengths varied between 1100 and 1700 m (Ball and Hooper, 1963). Most streams, however, have considerable uptake capacity for phosphorus, with uptake lengths in the range of 5–200 m (e.g., Hart *et al.*, 1991).

In unshaded streams where autotrophic production constitutes an appreciable component of organic matter subsidy of streams, heavy grazing by macroinvertebrate consumers of attached algae and other microbes can reduce the uptake of phosphorus from the water (Mulholland *et al.*, 1983, 1985b). This reduction can result both from decreases in the microbiota as well as increased reduction in sizes of particles. The fine particles of organic matter and phosphorus are then scoured relatively easily and are the predominant form exported downstream (Meyer and Likens, 1979).

Long-term evaluations of phosphorus dynamics in streams are rare. Examination of an average annual phosphorus budget for a forested second-order stream ecosystem of New Hampshire illustrates some of the potential transport and transformation processes (Table 13-3). Phosphorus inputs were dominated by dissolved and fine particulate phosphorus (63%) and falling and windblown litter (23%). Subsurface inflows (10%) and precipitation (5%) were relatively small sources of phosphorus in this ecosystem. The geologic export of phosphorus in the stream water was the only removal vector of consequence. On an annual basis, no annual net retention of phosphorus occurred in the stream. However, over short periods of time, inputs exceeded exports, with phosphorus accumulation. The accumulated phosphorus was exported in large pulses during precipitation-mediated episodes of high-stream discharge. Similar exports have been observed in many other stream ecosystems (e.g., Long and Cooke, 1979; Verhoff *et al.*, 1982; Munn and Prepas, 1986; Wetzel, 1989). For example, in a detailed analysis of daily phosphorus dynamics in a small second-order stream in Michigan passing through a wetland to a lake, between 60 and 80% of the annual PO_4—P from this stream to the receiving lake occurred during three major precipitation events (Wetzel, 1989). Dissolved inorganic and organic nitrogen loadings from the stream, however, were not as strongly coupled to discharge and were controlled to a greater extent by biological retention processes.

TABLE 13-3 Phosphorus Budget for a Forested Second-Order Stream, Bear Brook, New Hampshire[a]

	mg P m^{-2} yr^{-1}		*% of Total*	
Inputs				
Dissolved		346		28
Precipitation	63		5	
Tributaries	152		12	
Subsurface	131		10	
Particulate		900		72
Fine: tributaries	459		37	
Coarse:	441		35	
Litter	283		23	
Tributaries	158		13	
Total Inputs		1246		100
Exports (fluvial):				
Dissolved		242		19
Particulate		1059		81
Fine	807		62	
Coarse	252		19	
Total exports		1301		100

[a] Rounded to whole numbers; modified from Meyer and Likens (1979) and several papers cited therein.

IV. PHOSPHORUS AND THE SEDIMENTS: INTERNAL LOADING

The exchange of phosphorus between sediments and the overlying water is a major component of the phosphorus cycle in natural waters. There is an apparent net movement of phosphorus into the sediments in most lakes. The effectiveness of the net phosphorus sink to the sediments and the rapidity of processes regenerating the phosphorus back to the water depend upon an array of physical, chemical, and biological factors. The correlation between the amount of phosphorus in the sediments and the productivity of the overlying water is modest to weak, and the phosphorus content of the sediments can be several orders of magnitude greater than that of the water. The important factors are (1) the ability of the sediments to retain phosphorus, (2) the conditions of the overlying water, and (3) the biota within the sediments that alter exchange equilibria and effect phosphorus transport back to the water.

A. Exchanges across the Sediment–Water Interface: Overview

The deposition of phosphorus into lake sediments occurs by five mechanisms (Williams and Mayer, 1972;

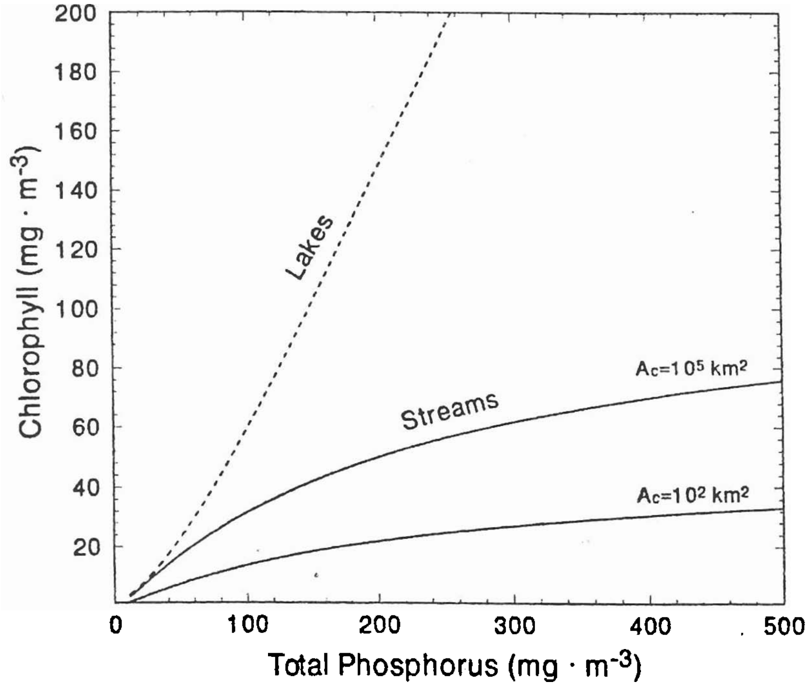

FIGURE 13-2 Phosphorus–sestonic chlorophyll relationships in temperate streams and lakes. Solid curves indicate predicted chlorophyll concentrations in rivers of differing catchment areas (A_C) of 100 and 100,000 km^2. The dashed curve depicts the trajectory of chlorophyll concentration in *P*-limited lakes in which total N:P > 25 (Forsberg and Ryding, 1980). (After Nieuwenhuyse and Jones, 1996.)

phosphate, highly stable as hydroxyapatite, increased to >60% at Ca concentrations approaching 100 mg liter^{-1} and pH values of 9.0 or greater. If calcium carbonate crystallizes under these conditions, phosphorus can be coprecipitated into the crystals and also adsorbed to the surfaces of the carbonates (Otsuki and Wetzel, 1972; cf. Chap. 11). These carbonate deposits are common in travertine encrustations in rivers that receive ground waters supersaturated with calcium and bicarbonates.

Thus, the major divalent metal ions in water, calcium and magnesium, tend to destabilize particles and enhance aggregation and sedimentation rates. In contrast, dissolved organic matter tends to stabilize colloidal particles in stream and lake water, slowing aggregation rates and thereby lowering sedimentation rates (Tipping and Higgins, 1982; Ali *et al.,* 1985). Separation distances and efficacy of van der Waals forces for attraction and aggregation, however, vary greatly with different types and concentrations of natural dissolved organic compounds and with the ionic strengths of charged colloids or particles (O'Melia, 1998).

As particulate organic matter increases, as is common from leaf-fall in late fall and winter in temperate woodland streams, phosphorus uptake can increase as the particulate organic matter increases (Mulholland *et al.,* 1985; Klotz, 1986). It is during this time as well that fungal activity is maximal on particulate organic matter (e.g., Suberkropp, 1995) and bacterial activities are maximal on dissolved organic matter leaching from the particulate organic matter (Wetzel and Manny, 1972b). Phosphorus uptake length, and hence total spiralling length, decreases in winter. These rates are counteracted at other times when detrital particulate organic matter is reduced by high discharge associated with storms.

D. Recycling of Phosphorus in Streams

As discussed earlier in terms of the biota of lakes, phosphorus can be released from biota by excretion in inorganic and organic forms from living microbiota or as the organisms senesce, die, and lyse. Phosphorus can also be released, as discussed earlier, during egestion of consuming animals. As in lakes, the dissolved organic phosphorus compounds in streams are utilized enzymatically appreciably more slowly than is dissolved inorganic phosphorus (reviewed by Newbold, 1992). Because of their slower rates of utilization, an accumulation of phosphorus compounds of high molecular weight (>5000 Daltons) occurs, and these compounds

Boström *et al.*, 1988; Wetzel, 1990a): (1) Sedimentation of phosphorus minerals imported from the drainage basin. Most of this material settles rapidly and is deposited largely in nearshore areas. (2) Adsorption or precipitation of phosphorus with inorganic compounds by three mechanisms: (a) Phosphorus coprecipitation with iron and manganese; (b) adsorption to clays, amorphous oxyhydroxides, and similar materials; and (c) phosphorus associated with carbonates. It is difficult to distinguish direct adsorption of dissolved phosphorus of lake water onto particles in the sediments from diagenetic and transfer processes within surface sediments. (3) Sedimentation of phosphorus with allochthonous organic matter. (4) Sedimentation of phosphorus with autochthonous organic matter. (5) Uptake of phosphorus from the water column by attached algal and other attached microbial communities and to a lesser extent by submersed macrophytes, with eventual transport back to the sediments by translocation and deposition with detritus.

Once the phosphorus is within the sediment in various forms, exchanges across the sediment–water interface are regulated by mechanisms associated with mineral–water equilibria; sorption processes, particularly ion exchange, oxygen and other electron acceptor-dependent redox interactions; and the physiological and behavioral activities of many biota (bacteria, algae, fungi, macrophytes, invertebrates, and fish) associated with the sediments. The sediment–water interface separates into two distinct domains. In all but the upper few millimeters of sediment, exchange is controlled by motions on molecular scales with correspondingly low diffusion rates (Duursma, 1967). In the water, exchange is regulated by much higher and more variable rates of turbulent diffusion (Mortimer, 1971). The exchange rates between various deposits of phosphorus and the interstitial water of the sediments depend on local adsorption and diffusion coefficients and their alteration by enzyme-mediated reactions of the microbiota.

Numerous processes operate, often simultaneously, to mobilize phosphorus from particulate stores to dissolved interstitial phosphorus and then to transport that dissolved phosphorus across the sediment–water interface into the overlying water (Fig. 13-3). Orthophosphate is bound to particles by physical adsorption as well as chemical binding of different strengths (complex, covalent, and ionic bonds). Physical and chemical mobilization includes desorption, dissolution of phosphorus-containing compounds, particularly assisted by microbially mediated acidity, and ligand exchange mechanisms between phosphate and hydroxide ions or organic chelating agents (Boström *et al.*, 1982; Stumm and Morgan, 1996). Microbial biochemical mobilization processes include mineralization by hydrolysis of phosphate–ester bonds, release of phosphorus from living cells as a result of changing environmental conditions, particularly redox, and autolysis of cells.

The internal phosphorus loading to a lake from the sediments depends on hydrodynamic and biotic mechanisms that transport dissolved phosphorus from the sediments to the lake water. Because of the steep concentration gradients of phosphorus between interstitial water and the overlying water, molecular diffusion is a primary transport into the overyling anaerobic water (Fig. 13-3). Currents from wind-induced water turbulence can disrupt gradients and resuspend sediment particles. Disturbance of sediments by benthic invertebrates living on or in the sediments and by bottom-feeding fishes can, when occurring in large densities, cause appreciable bioturbation of sediments. Microbial generation of gases, particularly CO_2, CH_4, and N_2, can accumulate, form bubbles, and rise to the surface. Such ebullition can disrupt gradients and accelerate diffusion of phosphorus upward. The metabolism and growth of plants living on and within the sediments can both suppress and enhance the transport of phosphorus across the sediment–water interface. Because of the major importance of the movement of phosphorus from large accumulations in the sediment to the overlying water, each of these processes is discussed in greater detail in subsequent sections.

B. Oxygen Content of the Microzone

The most conspicuous regulatory features of the sediment boundary are the mud–water interface and the oxygen content. The oxygen content at this microzone is influenced primarily by the metabolism of bacteria, algae, fungi, planktonic invertebrates that migrate to and live within the interface, and sessile benthic invertebrates. Microbial degradation of dead particulate organic matter that settles into the hypolimnion and onto the sediments is the primary consumptive process of oxygen in deepwater areas of lakes. The rate of oxygen depletion is governed by the rates of organic loading to the hypolimnion and by lake or reservoir morphology (cf. Chap. 9). For example, it has been estimated that 88% of the hypolimnetic oxygen consumption in the central basin of Lake Erie resulted from bacterial degradation of algae sedimenting from the trophogenic zone (Burns and Ross, 1971). Decomposition of more labile organic fractions, largely of plant origin, occurs while it is settling to the sediments, and, depending on rates of input and sedimentation, the sediments often receive organic residues that are relatively resistant to rapid decomposition.

Sediment demand for oxygen is high and is governed by the intensity of microbial and respiratory metabolism, slow rates of diffusion, and by the fact

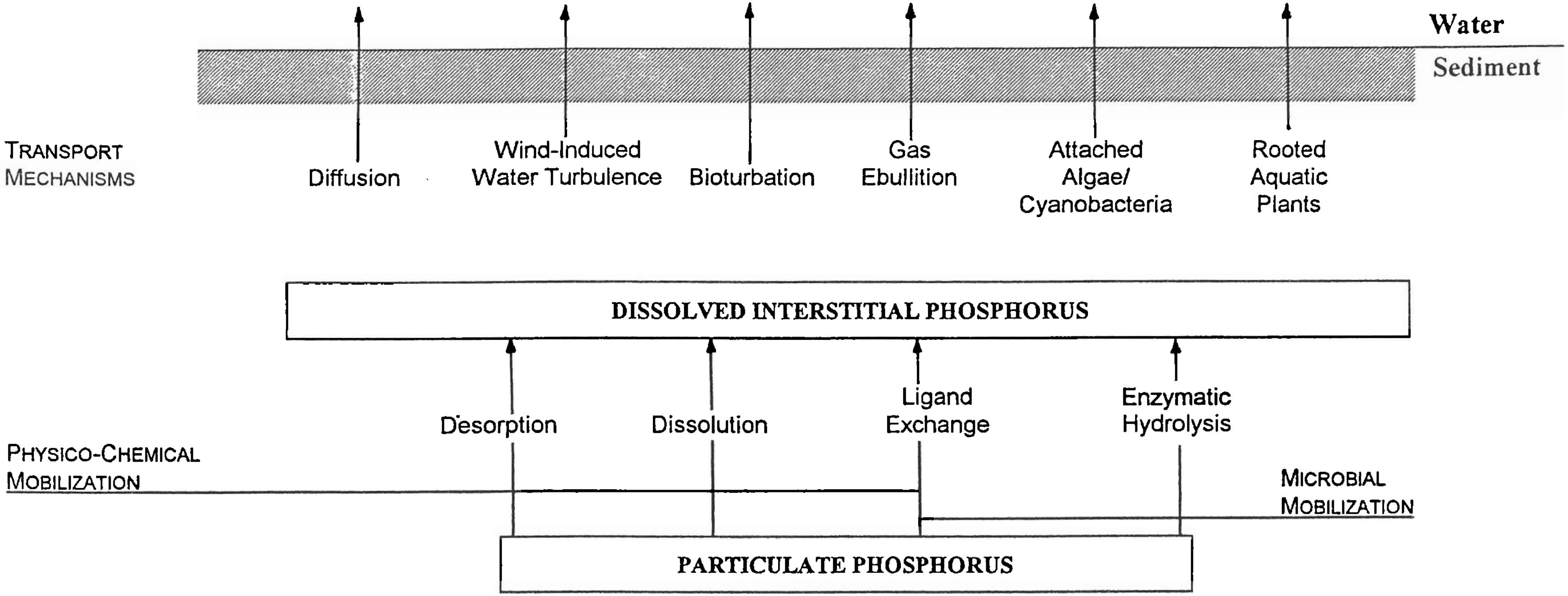

FIGURE 13-3 Processes involved in the mobilization of phosphorus from particulate stores into dissolved states of interstitial water of the sediments and transport across the sediment–water interface into the overlying water. (Modified extensively from Boström *et al.*, 1982, 1988, and Wetzel, 1999c.)

that inorganic elements, such as Fe^{++}, accumulate in reduced form when released into the sediment from decomposing biota. Diffusion regulates transport and is essentially molecular in the sediments, unless the superficial sediments are disturbed by overlying water turbulence. Oxygen from well-aerated overlying water, as in oligotrophic lakes or in more productive lakes at periods of complete circulation, will penetrate only a few centimeters into the sediments by diffusion. Oxygen penetration into the sediments is governed by the rate of oxygen supply to the sediments, turbulent mixing of superficial sediments, if any, and by the oxygen demand per unit volume of the sediment. The superb experimental and observational work of Mortimer (1941, 1942, 1971) has demonstrated the importance of an oxidized microzone to chemical exchanges, especially of phosphorus, from the sediments. At the sediment surface, a difference of a few millimeters in oxygen penetration is the critical factor regulating exchange between sediment and water. These relationships are exemplified by two lakes with organic sediments: The first lake maintained oxygen concentrations at the sediment interface >8 mg liter^{-1} throughout summer stratification, while in the second lake, oxygen levels at the interface decreased to <1 mg liter^{-1}.

In the first situation, illustrated by Mortimer's studies of Lake Windermere, England, oxygen concentration at the sediment surface did not fall below 1 or 2 mg liter^{-1}. Electrode potentials, which approximate composite redox potentials (cf. Chap. 14), of the oxygenated overlying water and surficial sediments to a depth of approximately 5 mm were uniformly high (+200 to 300 mV). Below 40–50 mm in the sediments, the potentials were uniformly low (approximately −200 mV), indicative of extreme reducing conditions and total anoxia (Fig. 13-4). The sediment remained oxidized to a depth of about 5 mm throughout the period of summer stratification. Seasonal differences were observed in the sediment depth at which the transition from high to low potential occurred, but the region of low potential never extended into the water. After five months of stratification, the point of zero mV moved toward the surface of the sediments, to −5 mm from approximately −12 mm at the time of spring turnover and moved downward to −10 mm during fall circulation. The integrity of the oxidized microzone was maintained in a thin but operationally very significant layer during stratification periods. The oxidized microzone was further maintained by diffusion and by turbulent displacement of the uppermost sediments to the overlying water during turnover periods (cf. Gorham, 1958). The effectiveness of the oxidized microzone in preventing a significant release of soluble components from the interstitial waters of the sediments to the overlying water was demonstrated in experimental chambers for over five months (Fig. 13-5, *left*). Phosphorus, in particular, was prevented from migrating upward.

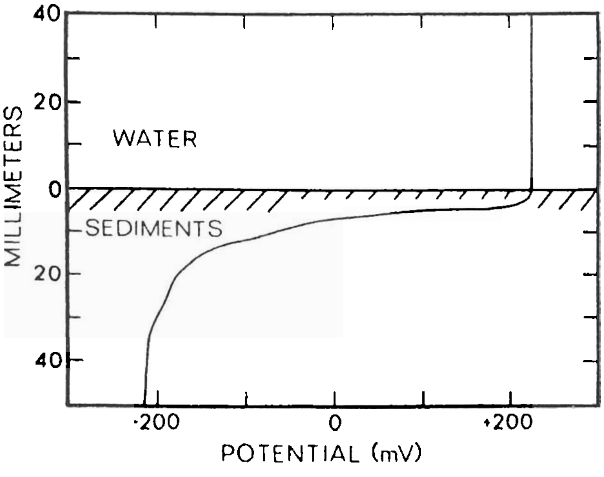

FIGURE 13-4 Diagrammatic profile of composite electrode potentials, not corrected for pH variations, across the sediment–water interface in undisturbed cores from the deepest portion of Lake Windermere before, during, and after stratification. (Based on data of Mortimer, 1971.)

The ability of sediments to retain phosphorus beneath an oxidized microzone at the interface is related to several interacting factors. Much of the organic phosphorus reaching the sediments by sedimentation is decomposed and hydrolyzed (Sommers *et al.,* 1970). Most of the sediment phosphorus is inorganic, for example, apatite, derived from the watershed, and phosphate adsorbed onto clays and aluminum and ferric hydroxides (Frevert, 1979a, b; Detenbeck and Brezonik, 1991; Andersen and Jensen, 1992; Danen-Louwerse *et al.,* 1993). Additionally, phosphate coprecipitates with iron, manganese, and carbonates (Mackereth, 1966; Harter, 1968; Wentz and Lee, 1969; Otsuki and Wetzel, 1972; Boström *et al.,* 1988). Work on Wisconsin lake sediments and the Great Lakes indicated that phosphorus was present in the sediments predominantly as apatites, organic phosphorus, and orthophosphate ions covalently bonded to hydrated iron oxides (Shukla, 1971; Williams *et al.,* 1970, 1971a–c; Williams and Mayer, 1972; Golterman, 1982, 1995). In calcareous sediments of hardwater lakes containing 30–60% $CaCO_3$ by weight, $CaCO_3$ levels were not directly related to inorganic and total phosphorus. These sediments had a lower capacity to adsorb inorganic phosphorus than noncalcareous sediments (cf. Stauffer, 1985; Olila and Reddy, 1993). The observations imply that $CaCO_3$ sorption is less important than iron–phosphate complexes in controlling the

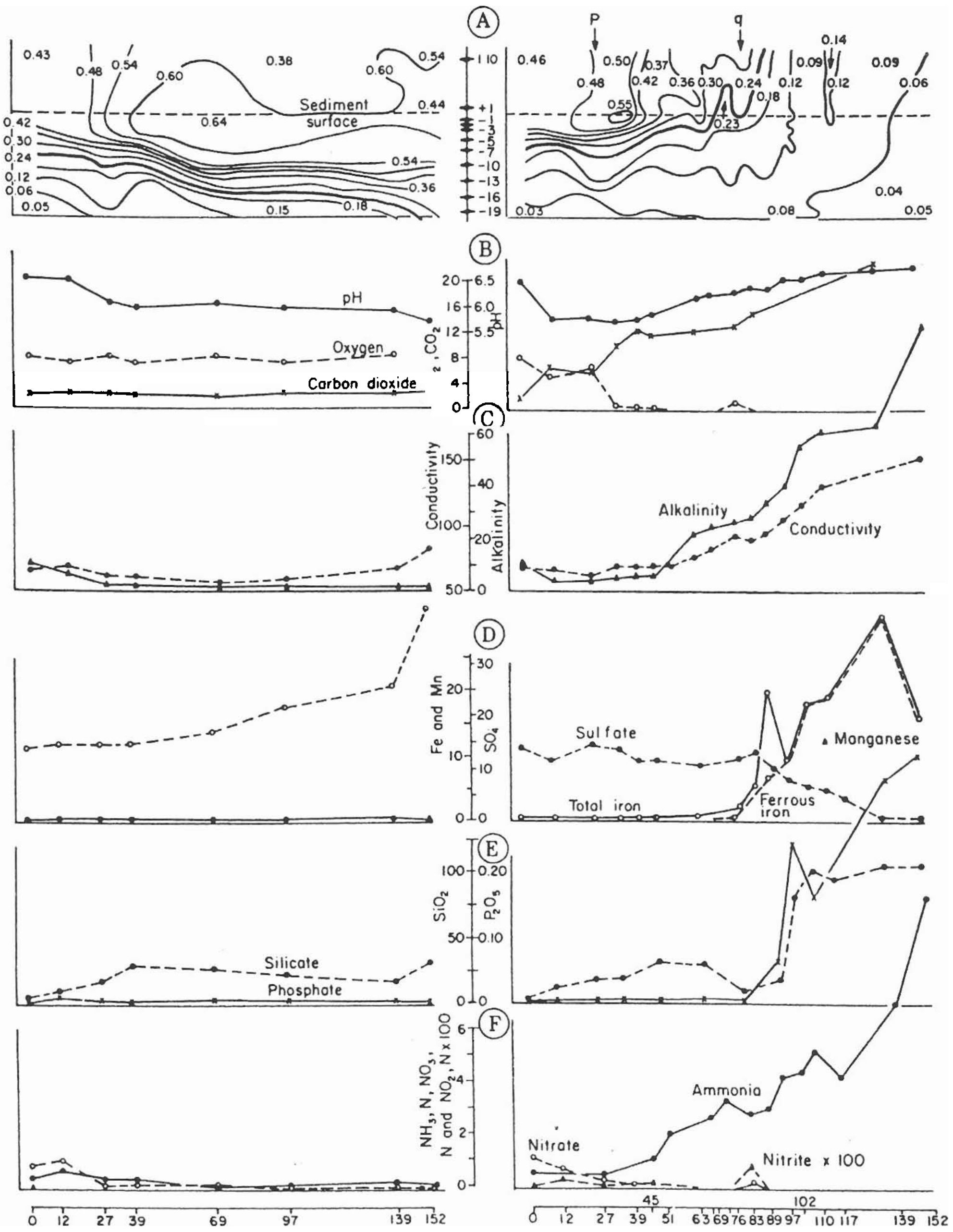

FIGURE 13-5 Variation in chemical composition of water overlying deepwater Lake Windermere sediments over 152 days in experimental sediment–water tanks. *Lefthand series:* aerated chamber; *righthand series:* anoxic chamber. (a) Distribution of redox potential (E_7; Eh adjusted to pH 7) across the sediment–water interface in mm; (b) pH, concentrations of O_2, and CO_2 in mg liter^{-1}; (c) alkalinity expressed as mg $CaCO_3$ liter^{-1} and conductivity, in μS cm^{-1} at 18°C; (d) iron (total and ferrous as Fe) and SO_4 in mg liter^{-1}; (e) phosphate as P_2O_5 and SiO_2 in mg liter^{-1}; (f) nitrate, nitrite ×100, and ammonia, all as N, in mg liter^{-1}. (Mortimer, C. H.: *Limnol. Oceanogr. 16*:396, 1971, and *J. Ecol. 29*:280, 1941.)

concentrations of phosphorus in sediments (Andersen, 1975; Frevert, 1980). Although phosphorus exchange by adsorption and desorption within the sediments between sediment particles and interstitial water can be as rapid as a few minutes (Hayes and Phillips, 1958; Li *et al.,* 1972), the rate of transfer across the sediment–water interface depends on the state of the microzone. The oxidized layer forms an efficient trap for iron and manganese (see Chap. 14) as well as for phosphate, thereby greatly reducing the transport of materials into the water and scavenging materials such as phosphate from the water.

Iron interacts with dissolved humic substances (cf. Chap. 23) to bind phosphorus at acidic to near-neutral pH values, irrespective of redox conditions, in the surficial sediments of certain softwater lakes (Jackson and Schindler, 1975; Francko, 1986). This process should enhance sediment retention of phosphorus in lakes with high loading of iron and humic substances.

C. Phosphorus Release from the Sediments

Because of the obvious importance of phosphorus as a nutrient that often accelerates the productivity of fresh waters, much interest has been devoted to the phosphorus content of sediments and its movement into the overlying water. Lake sediments contain much higher concentrations of phosphorus than the water (Olsen, 1958, 1964; Holden, 1961; Hepher, 1966; Holdren *et al.*, 1977; Boström *et al.*, 1982; and many others). Under aerobic conditions, the exchange equilibria are largely unidirectional toward the sediments. Under anaerobic conditions, however, inorganic exchange at the sediment–water interface is strongly influenced by redox conditions (Frevert, 1979b). The depth of the sediment involved in active migration of phosphorus to the water is considerable (e.g., Carignan and Flett, 1981). In undisturbed anoxic sediments, given sufficient time (2–3 months), phosphorus moved upward readily from a depth of at least −10 cm to the overlying water, regardless of whether the sediments were calcareous eutrophic muds or acidic and peaty in nature (Hynes and Greib, 1970). Comparison of movement in sterile sediments and sediments with anaerobic bacteria showed no significant difference; thus, diffusion predominated.

Phosphorus-mobilizing bacteria, especially of the genera *Pseudomonas, Bacterium,* and *Chromobacterium,* were abundant to at least 15 cm in reservoir sediments (Gak, 1959, 1963). Their abundance and vertical distribution varied with the type of sediments. Low numbers occurred in sandy sediments with small amounts of silt, and the bacteria were concentrated near the interface. Their numbers increased more uniformly with depth in sandy sediments with moderate amounts of organic matter and silts. The greatest numbers of bacteria were found in silts high in organic matter. Hayes and Anthony (1958, 1959) and Anthony and Hayes (1964) examined the relationship of bacterial densities and organic content of sediments in detail and found only a weak correlation in a large number of lakes. Bacterial numbers in the sediments increased proportionally, especially at the interface, with several indices of increasing lake productivity in lakes of neutral or alkaline pH and with low concentrations of humic compounds. In general, however, bacterial production rates are correlated with phosphorus and carbon in the sediments (Eckerrot and Pettersson, 1993). Bacterial biomass in sediments of organically stained acidic bog lakes was also high.

Although bacteria are of major importance in the dynamics of phosphorus cycling in the water, as will be discussed in the following section, their role in expediting phosphorus exchange across the sediment interface is relatively minor in comparison to chemical equilibria processes (Hayes, 1964). Bacterial decomposition is proportional to bacterial densities at the interface and directly related to the general productivity of the lake (Hayes and MacAuley, 1959; Hargrave, 1972). The sediment microflora is important in increasing the concentrations of phosphorus dissolved in the interstitial water of the sediments (Fleischer, 1978). Bacterial metabolism at the interface, however, has relatively little effect on biogenic fixation and removal of phosphate from the overlying water. Using sterilized and natural sediments, it was found that microbial fixation and transport of phosphorus from the water to the sediments amounted to <5% of the total movement under anaerobic reducing conditions (Hayes, 1955; Macpherson *et al.*, 1958; Olsen, 1958; Pomeroy *et al.*, 1965). Under aerobic conditions, bacteria of the interface did significantly increase the microbial transport of phosphorus to the sediments (Hayes, 1955; Hayes and Phillips, 1958), and this loss was related to the amount of microbial phosphorus sedimenting to the interface (cf. also Frevert, 1979a).

Mobilization of sediment-associated P to the overlying water has therefore been ascribed largely to PO_4^{3-} release from Fe(III) oxide as these compounds are reduced by anoxic conditions in surface sediments and the overlying water (Mortimer, 1941; Boström *et al.*, 1982). When release of PO_4^{3-} is compared on a molar ratio to PO_4^{3-} liberated per unit of organic carbon mineralized by bacterial metabolism, the availability of alternate electron-acceptor compounds, such as sulfate (SO_4^{2-}), becomes as important within the interstitial waters of the sediments as the oxidative conditions of the overlying water (Hasler and Einsele, 1948; Sugawara *et al.*, 1957; Caraco *et al.*, 1989, 1990; Roden and Edmonds, 1997). The relative PO_4^{3-} release from sediments can be significantly higher as sulfate concentrations increase from natural or anthropogenic sources, particularly in oligotrophic, softwater lakes.

Iron sulfide formation coupled to sulfate reduction can reduce the abundance of Fe compounds that can complex PO_4^{3-} and thereby promote release of PO_4^{3-} into sediment porewater. When sulfate content is low or absent in anaerobic sediments, microbial reduction generates Fe(II) compounds from microbial reduction of Fe(III) oxide. PO_4^{3-} can be retained effectively with

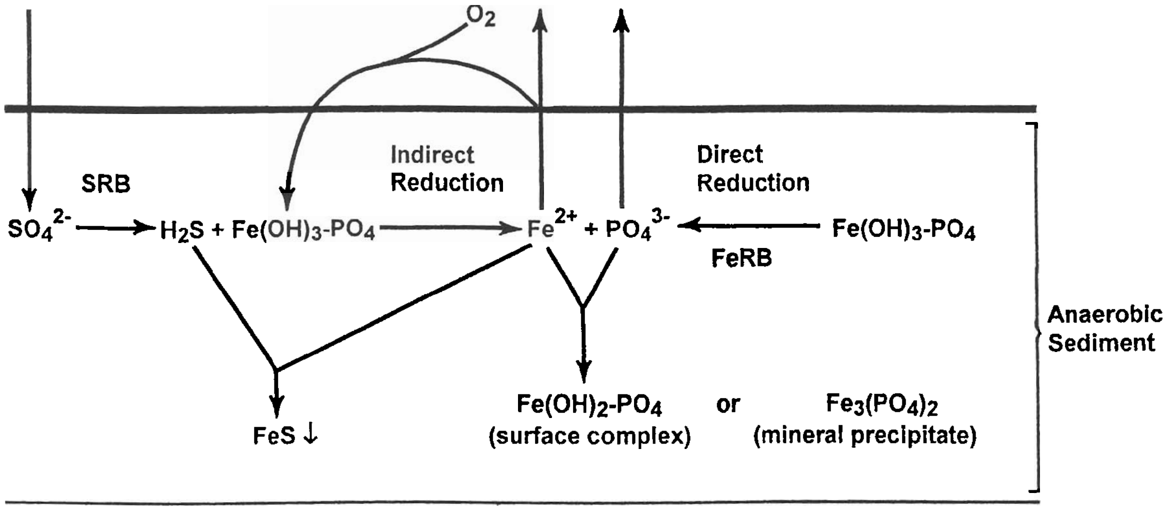

FIGURE 13-7 Interactions of sulfate on the reduction of Fe(III) and release of Fe(II) and phosphate. SRB = sulfate-reducing bacteria; FeRB = iron-reducing bacteria. (Modified from Roden and Edmonds, 1997.)

Fe(II) compounds but Fe-associated PO_4^{3-} is quantitatively released when amorphous Fe(III) oxide of the sediment is converted to iron sulfides (Roden and Edmonds, 1997). Conversion of reactive sediment Fe compounds to iron sulfides by sulfate-reducing bacteria leads to more efficient release of Fe-associated PO_4^{3-} than does direct microbial Fe(III) oxide reduction (Fig. 13-7).

Other processes can contribute to the composite release of Fe-associated PO_4^{3-} from sediments. For example, the uptake of excessive amounts of P by aerobic bacteria (e.g., Fleischer, 1986) and storage as polyphosphates could be rapidly degraded and released with the onset of anaerobic conditions (DeMontigny and Prairie, 1993; Gachter and Meyer, 1993). Because organic sediments are aerobic for only one or a few millimeters, this contribution is likely small in comparison to other mechanisms.

The sorption capacities of Fe(III) oxide decrease as pH levels increase above 6.5 (Stumm and Morgan, 1996). Large increases in pH values can occur within the sediments for several millimeters as a result of diurnal fluctuations in photosynthesis by epipelic algae (Fig. 13-8) and by submersed aquatic macrophytes and associated epiphytic algae. Simultaneous increases in oxygen concentrations (Fig. 13-8) and adsorption to or with photosynthetically induced precipitation of $CaCO_3$ (e.g., Mickle and Wetzel, 1978a) can counteract the availability of desorbed PO_4^{3-}.

The rate of phosphorus release from lake sediments increases (about doubles) markedly if the sediments are disturbed by agitation from turbulence (Zicker *et al.*, 1965). Covering anaerobic sediments with sand or polyethylene sheeting greatly impedes the loss of oxygen in the overlying water and decreases sediment release of phosphorus, iron, and ammonium (Hynes and Greib, 1970).

Algae growing on sediments are able to effectively utilize phosphorus from the sediments (Golterman *et al.*, 1969; Björk-Ramberg, 1986). Moreover, algae suspended in water with various particulate inorganic compounds of extremely low solubility were capable of extracting sufficient phosphorus for growth; without sediment phosphorus sources, the phosphorus content of the water limited algal growth under experimental conditions. The presence or absence of bacteria had little effect on algal utilization of phosphorus. These results stress the importance of extractable phosphates in the sediments if they are agitated into the water column, as in shallow lakes, even though their solubilities may be extremely low.

Some phosphorus release occurs under aerobic conditions from littoral sediments, particularly as temperatures warm above 10–15°C, as concentrations in the overlying water decline below equilibrium levels and as pH increases from intense photosynthetic activity of submersed macrophytes and attached algae (Twinch and Peters, 1984; Drake and Heaney, 1987; Boers and van Hese, 1988; Carlton and Wetzel, 1988; Boers, 1991; James and Barko, 1991). Because the volume of the littoral water is often small in comparison to that of the total lake, the littoral water often cools more rapidly at night than the pelagic zone. Convective flows from the littoral as interflow to the base of the epilimnion can move appreciable quantities of phosphorus from the littoral areas to the pelagic zone.

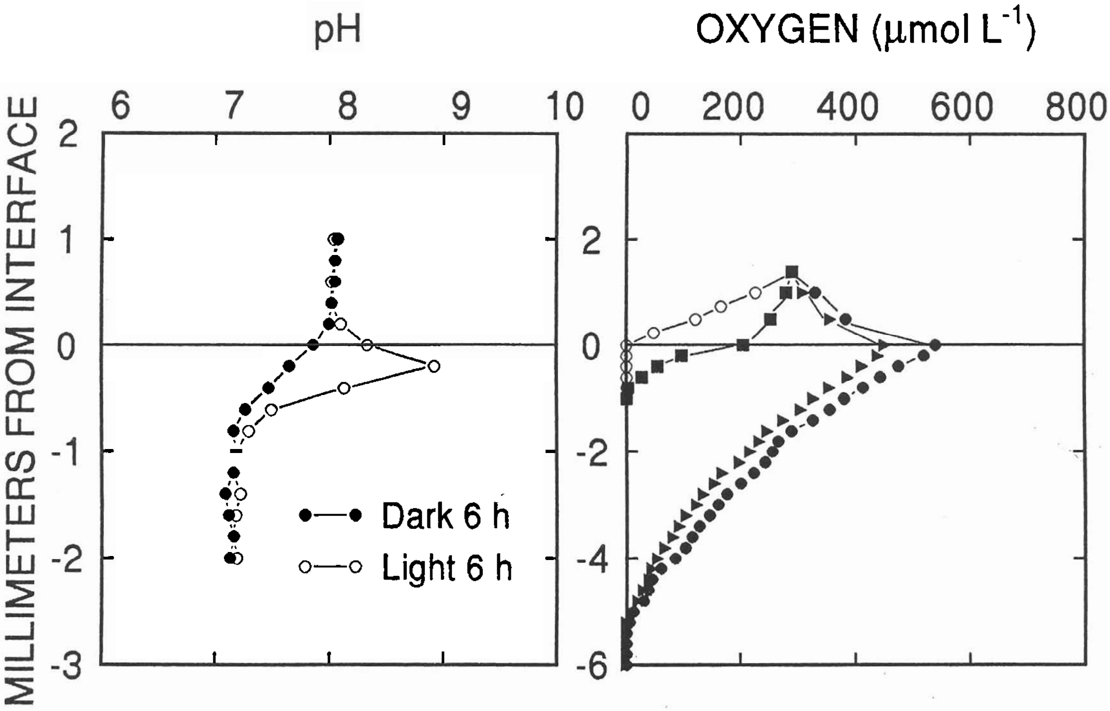

FIGURE 13-8 Distribution of pH (*left*; illumination 30 μmol quanta m^{-2} s^{-1}) and dissolved oxygen (*right*) immediately above and within sediments colonized by epipelic microalgae and bacterial communities. Oxygen microprofiles (*right*) during darkness (○—○), and after 1 h (■—■), 8 h (△—△), and 10 h (●—●) illumination with 10 μmol quanta m^{-2} s^{-1}. (Extracted from data of Carlton and Wetzel, 1987, 1988.)

D. Benthic Algae and Phosphorus Release from Sediments

Thus, oxygen is a primary factor influencing the release of phosphorus from sediments. If the sediments receive light, even at very low intensities (<50 μmol quanta m^{-2} s^{-1}), photosynthesis of epipelic algal communities growing on the sediments can quickly (minutes) produce high, often markedly supersaturated, concentrations of oxygen within the community usually <2 mm in thickness (Fig. 13-8) (Revsbech *et al.*, 1983; Carlton and Wetzel, 1987). This oxygen can diffuse several millimeters into the interstitial water of the supporting sediments at rates greater than it is consumed by bacterial respiration and chemical oxidations. By this mechanism, diurnal changes occur in the oxidized microzone of the sediments from fully oxidized in the daylight hours to fully reducing at nighttime. It was shown experimentally that the rate of phosphorus efflux from sediments is inversely related to the extent of sediment oxygenation and the magnitude of epipelic algal photosynthesis (Carlton and Wetzel, 1988). Although much of the reduced phosphorus efflux is caused by direct chemical redox changes, the microbial community also assimilates and complexes nutrients in organic compounds (cf. Kelderman *et al.*, 1988; Hansson, 1989).

E. Phosphorus Translocation by Migrating Phytoplankton

Several algae and cyanobacteria of lakes exhibit vertical migrations from nutrient-rich sediments or lower water strata to the euphotic trophogenic zone on a seasonal or daily basis. For example, a motile cryptomonad alga and a dinoflagellate migrate vertically from phosphorus-rich strata below the metalimnion at night to surface waters in early morning in sufficient quantities to enrich the epilimnion (Salonen *et al.*, 1984; Taylor *et al.*, 1988). Migrations of a large part of certain benthic-inhabiting cyanobacteria to the epilimnion have been implicated in translocation of benthic phosphorus sufficient to increase phytoplanktonic productivity (Barbiero and Welch, 1992).

F. Phosphorus Cycling Mediated by Aquatic Plants and Epiphytic Microflora

Lakes, reservoirs, and rivers are coupled with their drainage basins by intervening wetlands and littoral zones, the ***land–water interface zones,*** through which much runoff and seepage water flows before entering the main water bodies. The aquatic plants of the interface zones are major biotic components in many, if not most, lakes and in the flood plains of river ecosystems.

As the oxygen content of water near the sediment interface declines, the oxidized microzone barrier weakens. As seen from Mortimer's experiments (Fig. 13-5, right-hand series), the release of phosphorus, iron, and manganese increased markedly as the redox potential decreased. With the reduction of ferric hydroxides and complexes, ferrous iron and adsorbed phosphate were mobilized and diffused into the water. The same general reactions were observed in the hypolimnetic water just overlying the sediments in eutrophic Esthwaite Water (Fig. 13-6), a pattern that has been observed repeatedly in productive dimictic lakes since its initial detailed description by Einsele (1936). A sudden release of ferrous iron and phosphate into the water occurs at the time when the +0.20 isovolt (E_7 = +200 mV) emerged above the interface surface. This event is preceded by nitrate reduction and the slow release of bases (alkalinity), CO_2, and ammonia. As long as an abundance of nitrate remains and nitrate reduction continues in the overlying water (ca. >0.1–1 mg NO_3—N liter^{-1}), no release of iron-bound phosphate occurred from the sediments to the anoxic hypolimnion (Andersen, 1982; Tirén and Pettersson, 1985; Foy, 1986). Manganese is reduced and mobilized at a higher redox potential than iron.

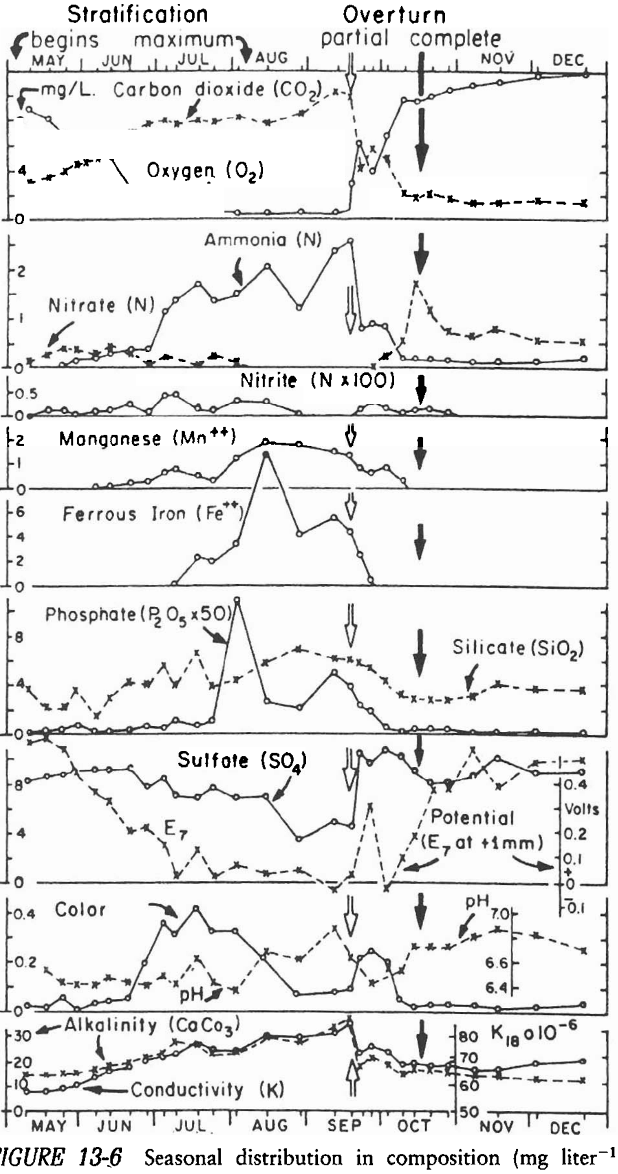

FIGURE 13-6 Seasonal distribution in composition (mg liter^{-1}) and properties of water within 30 cm of the sediments at 14 m in Esthwaite Water, England. Components as in Figure 13-5; color in arbitrary units. (From Mortimer, C. H.: *Limnol. Oceanogr.* *16*:387, 1971.)

The introduction of oxygen during autumnal circulation[1] causes ferrous iron to be oxidized and produces a simultaneous reduction of phosphate, part as ferric phosphate, which is less soluble than ferric hydroxide, and part by adsorption onto ferric hydroxide and $CaCO_3$. Although manganese is oxidized more slowly than iron, it nonetheless is effectively precipitated at the time of overturn. Ferrous iron released from the sediments is always in excess of phosphate, and when oxidized, it precipitates much of the phosphate. Some of the ferric phosphate in particulate form may slowly hydrolyze and restore some phosphate to the upper waters and littoral areas (Hutchinson, 1957). Although most phosphate is returned eventually to the sediments, much (>50%) of the hypolimnetic phosphorus upwelled during autumnal circulation is available biologically (Nürnberg, 1985). Often, however, other growth conditions (temperature, light) are not optimal at that time of year.

In very productive lakes where hypolimnetic decomposition of sedimenting organic matter produces anoxic conditions and hydrogen sulfide, some ferrous sulfide (FeS) is precipitated. Ferrous sulfide, like many other metal sulfides, is exceedingly insoluble and forms at a redox potential of about + 100 mV. If large quantities of FeS precipitate, sufficient iron can be removed to permit some of the phosphate accumulated in the hypolimnion to remain in solution during autumnal circulation. The addition of sulfate to a lake in order to increase the bacterial production of hydrogen sulfide (H_2S) and to accelerate the loss of iron has been suggested as a method of fertilizing lakes by regenerating phosphate from the sediments (Hasler and Einsele, 1948).

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[1] The normal seasonal erosion in the autumn of the epilimnion and metalimnion with progressive oxygenation of the upper portion of the hypolimnion can be periodically intensified during storm periods, particularly in reservoirs (e.g., James *et al.*, 1990). Stratification can be reestablished subsequently for short periods until the next intensive wind period occurs.