

FACTORS AFFECTING THE TRANSFER OF MATERIALS BETWEEN WATER AND SEDIMENTS

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A review of the factors that may affect sediment-water exchange reactions shows that insufficient information is available at the present time to predict the extent and, in many cases, the net direction of exchange for many compounds in most natural waters. The effect of this buffer system could be to keep the concentrations in the overlying waters relatively constant even though the concentrations of the element in the inflowing waters vary widely.

One of the most important reactions of this type today is the exchange of phosphorus between a lake's sediments and the overlying water as related to the eutrophication of the waters. Lake sediments typically contain one to two thousand milligrams of phosphorus per kilogram of dry sediment. It appears technologically and economically feasible to remove 80 percent of the phosphorus present in domestic wastewaters. The Federal Water Quality Administration and the states bordering on Lakes Erie, Michigan and Superior have agreed to provide 80 percent removal of the phosphorus from wastewaters entering these lakes in a few years hence. It is reasonable to ask what this level of removal will accomplish in reduced algal and aquatic weed growth. The current state of knowledge of algal ecology is such that it is impossible to relate the frequency or severity of algal blooms to specific phosphate levels that will be present in a water for a given phosphate flux to the water. Present available technical information does not appear to be sufficient to predict water quality that will result from 80 percent phosphorus removal.

Knowledge is particularly lacking on the role of sediments of the lake in maintaining phosphate levels in water. It is not known whether the sediments of a lake act as a sink in which the majority of the phosphorus present is refractory, i.e., not available for exchange, or whether the sediments act as a buffer in which phosphate concentrations in the overlying water are controlled by sediment-water exchange reactions.

Harter (1968), working with eutrophic lake sediments, and Pomeroy *et al.* (1965), using estuarine sediments, found that these sediments act as a phosphate buffer to keep the concentrations of phosphate in water constant. Hayes *et al.* (1952) reported that a reduction in phosphate in the inflowing waters to a lake will result in a rapid decrease in concentration of phosphate in the water, i.e., the phosphate present in the sediments will not be released to the overlying water. Frink (1967) suggests that the center of a lake acts as a reservoir for both total

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and available nitrogen and phosphorus. He concludes that nutrients which accumulate in the bottom of a lake as eutrophication proceeds, constitute a vast reservoir apparently capable of supporting plant growths in the event nutrient input is reduced. Ruttner (1963) regards the sediments of a lake as a significant source of nutrients due to interchange of materials between water and sediments. Although the emphasis of current research on exchange reactions is being placed on phosphorus, research is also needed on exchange reactions of many other compounds such as pesticides, toxic metals and nonmetals, other nutrients, etc.

In order to predict the exchange of an element or compound between the sediments and water, each of the physical, chemical and biological factors that may influence exchange must be quantified. A general summary of the current state of knowledge of each of these types of controlling factors is presented in this paper. No attempt will be made to provide a comprehensive review of all previous papers on sediment-water exchange reactions. Rather, the emphasis will be placed on examining the controlling factors with examples of the current state of knowledge for each of these factors.

## PHYSICAL FACTORS AFFECTING EXCHANGE REACTIONS

A simple model for the transfer of materials from the sediments to the overlying water is one in which the rate of exchange is controlled by either physical or chemical (biochemical) processes. For physical control, the rate of exchange is determined by the hydrodynamics of the system. In this case, the rate of release from the particle is faster than the rate of mixing of the water adjacent to the particles with the bulk of the water. For chemical control, the rate-controlling step is one in which the rate of exchange is controlled by the rate of release from the sediment particle. Although few detailed studies have been conducted on the hydrodynamics of natural waters and sediments as they might affect exchange reactions, it appears that the hydrodynamics of the system is often the rate-controlling step in exchange reactions. Currents in the overlying waters tend to transport leached materials away from the sediments and thereby allow concentration-dependent exchange reactions to proceed. Mixing in the waters also tends to promote suspension of particles which enhances exchange reactions. In sediments, mixing tends to carry unleached particles to the sediment-water interface where exchange generally takes place more rapidly. Finally, mixing in the sediments brings the interstitial water to the surface where it may mix with the overlying water. This section of the paper will qualitatively explore the evidence available on the hydrodynamics of sediment-water exchange.

## HYDRODYNAMIC EFFECTS

In lakes, mixing in the water and sediments arises primarily from wind induced currents and physical and metabolic activity of larger organisms. In rivers and streams, the mixing arises from the flow of the water due to difference in elevation of the land through which the rivers and streams flow. In estuaries, the tide is one of the primary driving forces for mixing. In harbors, rivers and other shallow water areas, commercial shipping and, to some extent, pleasure boating can cause mixing of the water and sediments. For example, the author noted that passage of tow boats (barges) on the upper Ohio River resulted in a marked increase in water turbidity, which was the result of boat propellers stirring up bottom sediments. This type of phenomenon resulted in a "sawtooth" pattern of sediment transport. As the tow boat passed, more sediments became suspended. The suspended sediments slowly settled to the bottom while being transported downstream by the current. This pattern was repeated with the passage of the next tow boat.

It is important to point out that the presence of currents does not necessarily mean mixing will occur. Velocity gradients are required before mixing will take place. This is especially important in open water. However, large currents next to the sediment-water interface are a good index for mixing since the velocity at the interface is zero and, therefore, the velocity gradient is high. Although considerable effort has been devoted to current measurement in large bodies of water, such as the Great Lakes, these studies are generally directed toward obtaining information on general circulation patterns, and provide little data on the hydrodynamics of the sediment-water interface.

Bryson and Kuhn (1955) have conducted a study on bottom currents and have calculated wind-induced, hypolimnetic currents as high as 10cm/sec in the nearbottom waters in Lake Mendota. Likens and Hasler (1962) reported horizontal currents of several centimeters per second in a small ice-covered lake in northern Wisconsin. Mortimer (1941,1942) discussed mixing in lakes by eddy diffusion and attempted to estimate mixing coefficients. These studies have shown that appreciable currents do exist in lakes even under conditions of thermal stratification. However, examination of the composition of the water for dissolved chemical species shows that the degree of vertical mixing in lakes may be rather limited. Concentration depth profiles in the limnological literature (see Hutchinson, 1957) provide many examples of rather poor mixing near the sediment-water interface with overlying water. Almost all eutrophic lakes will show large changes in the chemical concentrations of compounds influenced by the sediments except during periods of isothermal conditions. It is frequently found that the greatest concentration gradient exists between the waters immediately adjacent to the sediment-water interface and the overlying waters. For example, Delfino (1968) found that during both summer and winter periods, the greatest concentration gradient for manganese existed between the sediment-water interface and the waters one meter above this interface in Lake Mendota Madison, Wisconsin. Thermal stratification significantly retards mixing in lakes. However, even under isothermal conditions such as during fall overturn, sediments can influence the concentrations of certain chemical species in the overlying waters above this interface in Lake Mendota, Wisconsin. There can be little doubt that thermal stratification significantly retards mixing in lakes. However, even under isothermal conditions, such as during fall overturn, the sediments can influence the concentrations of certain chemical species in the overlying waters during periods of low wind velocity. On several occasions during the fall overturn, the author has noted Lake Mendota to be isothermal and have an essentially constant composition from the surface to the sediment-water interface. However, a few days of low winds often result in an almost complete depletion of dissolved oxygen in the lower 2-3 meters of the lake. Gardner and Lee (1965) have shown that this depletion of oxygen is the result of reactions between the ferrous iron and sulfide present in the sediments and the oxygen in the water. Under these conditions there is sufficient mixing to bring the oxygen-containing waters in contact with the sediments, yet there is insufficient mixing in the water to disperse the low dissolved-oxygen water throughout the water column. Although less frequently studied, there is also good evidence that poor mixing occurs in the horizontal layers at the same depth in some lakes. Delfino (1968) found, during periods of thermal stratification, differences as large as  $\pm 0.5$  mg/l manganese (II) between samples taken one mile apart in the "deep hole" of Lake Mendota at 22 meters below the surface. All samples were taken at 1 meter from the mud-water interface. This suggests that there are large water masses in the near-bottom waters of Lake Mendota that mix slowly.

Other evidence of poor mixing was found by Hawley (1967) in a study on  $\text{CaCO}_3$  saturation in Lake Mendota. Hawley found that Lake Mendota was at or near  $\text{CaCO}_3$  saturation at ice-out in the spring. During the summer thermal stratification period, the hypolimnetic waters were grossly undersaturated with respect to  $\text{CaCO}_3$  even though this water was in contact with sediments that contained 30 percent  $\text{CaCO}_3$ . When samples of the water and sediments were taken into the laboratory and mixed, saturation was obtained in a few hours. Therefore, Hawley concluded that undersaturation in the lake was due to poor mixing of the water adjacent to the sediments with the overlying waters.

Delfino's (1968) study clearly demonstrated that the waters near the bottom of Lake Mendota are rather poorly mixed even at essentially the same locations and depths. Fairly large water masses in the hypolimnion have significantly different concentrations of elements released from the sediments. This difference in concentrations is particularly important where the rate of exchange of a compound between the sediments in the overlying water is dependent on the water concentration, i.e., equilibrium controlled release. With manganese, for example, the surface sediments would be exposed to markedly different concentrations in the immediate overlying water masses which would pass over the sediments at various times during the day. Findings of this type illustrate the difficulties of interpreting environmental data relating to the release of materials from the sediments to the overlying waters and clearly demonstrate the need for rather detailed sampling programs which would consider both the spatial and temporal distribution of materials in the area under investigation

#### MIXING IN SEDIMENTS

The amount of mixing that occurs in sediments is probably one of the most important, yet least studied, aspects of exchange reactions. The interstitial waters in the sediments often contain much larger concentrations of exchangeable species than the overlying waters. For example, Rittenberg *et al.* (1955) reported that interstitial waters contain about 50 times more apparently soluble orthophosphate than the overlying waters. These results point to the role of hydrodynamics as compared to chemical kinetics in controlling exchange reactions.

In addition to determining the rate of exchange, mixing in sediments also determines the depth of sediment that may ultimately become involved in exchange reactions. The depth over which exchange takes place becomes extremely important when attempts are made to estimate the rate of recovery of a eutrophic lake upon reduction of nutrient input.

The morphology of a body of water is thought to be important in determining its productivity. Rawson (1955) in a study of many different lakes has reported that there is an inverse relationship between depth of water and production. Hopher (1958) proposed that various factors, such as thermal stratification, depth of lake and ratio of volume of water to area of sediment surface, have a significant effect on phosphate exchange from the sediments. Hayes *et al.* (1952) reported that the turnover times of phosphorus were reduced in small shallow lakes.

Some investigators report that only a very thin layer of surface sediment may be involved in the exchange reactions. Hayes *et al.* (1952) reported that only a superficial layer 1 mm thick was involved in the interchange of phosphorus between sediments and water. Similar results were reported by Zicker *et al.* (1956). Mortimer (1942, 1943) states that exchange reactions are

dependent on molecular diffusion in the sediments, and, therefore, there must be very little mixing in the sediments. He states that the oxidized microzone on the surface of the sediments is caused by the diffusion of oxygen into the sediments with the resultant oxidation of iron in the surface sediments to  $\text{Fe}(\text{OH})_3$ . Gorham (1958) reports that the oxidized microzone is probably due to turbulent mixing of the surface sediment into the overlying water, oxidation of iron (II) to iron (III) and sedimentation of the  $\text{Fe}(\text{OH})_3$  on the surface of the sediments. It is possible that in any short period of time only a thin layer of sediment is involved in exchange reactions. However, there is considerable evidence that appreciable mixing of the sediments does take place. Naumann (1930) was the first to propose that natural water sediments should be separated into two zones, an upper zone and a lower "historical" layer where essentially no mixing takes place and no exchange occurs. The upper layer or active deposition zone is that part of the sediments in contact with the overlying waters, and therefore, the layer from which exchange occurs. Naumann estimated that the depth of the upper layer was about 10 cm for lakes in Europe and 5 to 10 cm for the continental shelf. Hayes (1964) states that there is considerable evidence to support Naumann's concept of sediment zones.

Berger and Heath (1968) have outlined a mixing model for particulate matter entering marine sediments. In their model, the sediments consist of the historical (unmixed) layer, a homogeneous layer several centimeters thick which is constantly reworked by benthic organisms, and the water-sediment interface. As particles fall onto the homogeneous layer, they are mixed with the older deposits. The particles are then deposited in historical layers at a rate which is dependent only upon the rate of sedimentation and the thickness of the homogeneous layer.

Environmental data on chemical diffusion in sediments are lacking. Nichols *et al.* (1946) reported that copper had penetrated Lake Monona sediments to a depth of 8 feet in 20 years since the lake was first treated with copper sulfate for algae control. These authors concluded that the action of burrowing fauna was responsible for the transport of copper. Recently, Sanchez (1970) has taken a new set of cores from Lake Monona in order to reexamine the mixing of copper in the sediments of this lake. He was unable to find the copper at the depths reported by Nichols *et al.* Sanchez used a 3.5-inch diameter piston corer that takes relatively undisturbed sediment samples while Nichols *et al.* used a small diameter gravity corer. Sanchez feels that the data reported by Nichols *et al.* are in error due to the corer used.

The data from a study by Veith (1968) on the transport of toxaphene in Fox, Ottman and Silver Lakes, Wisconsin, indicate that this compound was rapidly transported to the 5 to 10 cm and 10 to 15 cm depths of sediments. Estimates of vertical transport rates for toxaphene in these three lakes were 0.63 to 1.1 cm/day in Fox Lake, and 0.4 cm/day in Ottman and Silver Lakes. He proposed that mixing of the sediment rather than chemical diffusion was primarily responsible for the distribution of toxaphene in sediments since it is unlikely that chemical diffusion rates could account for the rapid migration observed. Skoch (1968), in a study of cores from a station in western Lake Erie, reported that 5 to 7 cm of surface sediment were mixed by wave action and currents. The water depth at the sampling station was 11 meters.

Recent studies in the University of Wisconsin Water Chemistry Laboratory tend to support this concept of a mixing zone's extending down to some 5 to 10 cm below the sediment-water interface for many lakes in which the sediment-water interface is well-defined.

Studies by Peterson (1970) on lead, Kobayashi (1970) on arsenic, Veith (1968) on toxaphene, Sanchez (1970) on copper, and Bortleson (1970) and Sridharan (1970) on phosphorus content and distribution in lake sediments have all shown that, in general, the mixing depth for these materials is in the order of 5 to 15 cm. Peterson (1970) has found that the lead content of lake sediments is very high in the surface few centimeters with concentrations approaching 500 parts per million. However, below a depth of 50 cm in the sediments, the concentrations are at the background levels and are essentially constant for the rest of the core. These data show that there has been a marked increase in the flux of lead to many lakes. This increase can reasonably be attributed to the use of lead in gasoline.

Since the large-scale use of leaded gasoline has only occurred in the past 20 to 40 years, it is possible to use this increased concentration of lead in the upper parts of a lake sediment core to estimate the amount of mixing in the sediment. This procedure is possible only if the rate of sedimentation in the lake is slow compared to the time period over which the chemical was introduced into the lake. This criterion is met by all of the various studies that will be reported in this section of the paper since, in general, these studies are being conducted on lakes which have been found to fill at a rate of a few millimeters per year. Many of the lakes have sedimentation rates considerably less than this.

Kobayashi (1970) has studied the distribution of arsenic applied to Wisconsin lakes for aquatic weed control. In general, the sodium arsenite applied to these lakes has been used for only the last few years. Therefore, the distribution of arsenic in a sediment core could give a clue as to the amount of mixing that is occurring within the lake sediments. In general, Kobayashi has found, on the basis of the distribution of arsenic, the depth of mixing is in the order of 5 to 20 cm. The previously reported studies by Veith on the distribution of toxaphene used in lakes for rough fish control have shown that toxaphene was mixed to a depth of 5 to 15 cm in the sediments of three different lakes in the period of a few months. Sanchez (1970) found that the copper used to control algae in Lake Monona has a distribution pattern very similar to that found by Peterson for lead. This indicates that the copper basic carbonate which precipitates in this lake accumulates and is mixed in the sediments.

Similar evidence of this type is provided by Bortleson (1970) and Sridharan (1970), both of whom are studying the distribution of phosphorus in lake sediments. Bortleson worked with approximately half a dozen different lakes in central and northern Wisconsin, while Sridharan worked with lower Green Bay, Wisconsin sediments. In both cases these investigators have found that under conditions where the flux of phosphorus has markedly increased within the past few years, this phosphorus is mixed in the sediments to a depth of 5 to 10 cm. The current University of Wisconsin Water Chemistry studies, coupled with the previous studies of other investigators, clearly show that the upper layer of sediments over which exchange reactions and mixing may take place is in the order of a few centimeters in thickness.

Further evidence for mixing of sediments with the overlying water is provided by Davis (1968) who found that about 80 percent of the pollen caught in pollen traps located in Frains Lake in Michigan was actually suspended pollen that had been previously deposited in the sediment one or more times. She also found that this resuspension caused a difference in the total amount of pollen deposited in various parts of the lake sediments. The nearshore environment accumulated less pollen than the deep water.

Delfino, Bortleson, and Lee (1969) found the concentrations of various chemical species present in Lake Mendota sediments were proportional to the depth of the water overlying the sediments. Phosphorus, iron and manganese increased in concentration with increased depth of water. Frink (1969a) observed similar results; he found that the ratio of clay content to organic matter and nitrogen and phosphorus increased in concentration in the sediments with increasing depth of water.

The sediments of a lake can be qualitatively divided into three broad types according to their fluidity, i.e., ease of penetration by a sounding weight. In some lakes the sediment-water interface is very diffuse and extends over several meters in depth. For example, in two Wisconsin lakes, Lake Rose in Vilas County and Comstock in Marquette County, a thermistor probe of an underwater thermometer (a brass probe 3/4" in diameter, 5" long, weighing about 400 grams) will penetrate about 2 meters into the sediments before sufficient resistance is encountered to stop it. In contrast, a 2.5 ft. diameter steel plate weighing approximately 6 pounds will stop approximately 2 meters above the position of the thermistor probe. The difference in the depths measured by using a sounding line with a thermistor probe and those determined by using a steel disk can give a qualitative scale on the fluid nature of lake sediments. Where large differences are observed, such as in Lakes Rose and Comstock, the sediments are extremely fluid and, in this case, can best be approximated as a slurry. The second type of lake that is sometimes encountered, such as Lake Superior or nearshore sediments of many lakes, is one in which the depths obtained by thermistor probe and the disk are identical, i.e., there is essentially no penetration of the sediments. Both of these types of lakes are rare.

The majority of lakes that the author and the University of Wisconsin Water Chemistry students have examined in the past few years (about 50 lakes) fall into the type where there will be a few centimeters difference in the depth of penetration of a disk and the thermistor probe. The author would suggest that some type of standard measurement be established by which the fluidity of the sediments is determined since this is likely to be an extremely important parameter in determining the hydrodynamics of exchange of materials between the water and the sediments. There can be little doubt that highly fluid sediments such as those found in Lakes Comstock and Rose show a much greater exchange and mixing in the sediments as compared to the more dense sediments like those in Lake Superior.

Organisms are thought by many to be the primary means by which sediments are mixed. Emery (1963) and Emiliani and Flint (1963) have concluded that mixing by benthic organisms in the sea extends only a few centimeters into the sediment, is vertical and not lateral, and is accomplished primarily by worms. Hughes (1968), in a study of the persistence of toxaphene in lakes treated for rough fish removal, noted indirect evidence that fish may provide significant mixing of sediments. When fish were present, the lake under study was very turbid and Secchi disk

visibility was limited to a depth of a foot or so. After treatment when all fish were killed, Secchi depths of several meters were found. Fish eradication was not the only change imposed by the toxaphene treatment, but in this situation it appears that the elimination of fish was the dominant factor.

Arrhenius (1963) observed clouds of resuspended sediment just above water-sediment interface in the sea. These clouds could have been due to both organisms and bottom currents.

Mixing in the sediments is also promoted by anaerobic fermentation reactions of bacteria in which carbon dioxide and methane gases are produced in large quantities. The interstitial waters become sufficiently supersaturated with these gases so that bubbles are formed. As these bubbles rise through the sediments and water, they may cause extensive mixing. The release of gases from some sediments is sometimes sporadic when the bubbles are trapped near the sediment surface until the sediments are disturbed by major currents such as caused by boats, outboard motors, etc. Reeburgh (1969), from a study of the distribution of dissolved gases in Chesapeake Bay sediments, concluded that the sediments were mixed to a depth of 25 cm below sediment-water interface, and gas formation played a significant role.

Another means by which sediments are mixed with the water is benthic algae. In some lakes, large mats of benthic algae are present in shallow water. Oxygen produced by photosynthesis can be trapped in the mat and give it sufficient buoyancy so it will float to the surface, carrying with it large quantities of attached sediments. In a short period of time, the attached sediments become dislodged and drop back to the bottom. The "raining down" of sediments provides an excellent opportunity for exchange reactions.

Insect larva and other organisms that inhabit the sediments at some stage during their life cycles may play an important role in a transport of chemicals from sediments to water. Neess (1961) as reported by Lee (1962) found that insects which hatch in Lake Mendota sediments transport 1.9 metric tons per year of iron from the lake to the surrounding watershed. More iron is transported out of the lake by the emergence of insects than leaves the lake by the outlet which has an average discharge of 100 cubic feet per second. The cycle of insect transport is a fairly closed one since the insects acquire high concentrations of elements within their body tissues from the sediments, emerge from the lake, fly short distances and die. The next rainfall brings large numbers of these insects back to the lake via storm water runoff. Therefore, most of what is removed by the insects' emergence is cycled back to the sediments in the form of dead insect bodies. The insects do, however, bring about a significant change in the form of the elements present in the sediments.

Studies of oxygen demand of sediments can provide some additional clues to the extent of mixing in the sediments. Stein and Denison (1966) used L-shaped plexiglass containers outfitted with a dissolved oxygen electrode to examine the oxygen uptake by an estuary sediment. They found much higher rates of oxygen uptake in undisturbed sediments than in sediments which had been taken by a dredge and brought into a laboratory for measurement. The reason for the difference between these two samples was that the organism burrows were destroyed when sediments were taken into the laboratory, thereby greatly decreasing the area over which oxygen transport and reaction could take place. Edwards and Rolley (1965) have, on the other hand,

taken a series of cores of river sediments to investigate oxygen consumption and found that the rate of oxygen utilization was independent of the depth of the core, provided that the depth exceeded two centimeters. These results indicate that the mixing within these sediments was minimal on a short-term basis.

Carey (1967) determined the oxygen consumption of Long Island Sound sediment by measuring oxygen uptake of cores. He found that the rate of oxygen utilization was a function of rate of stirring in the overlying water. Pamatmat and Banse (1969) measured *in situ* oxygen consumption of Puget Sound sediments using bell jars. They obtained results which were similar to those reported by Carey (1967).

Although organisms are an important cause of mixing in sediments, wind-induced motions and other currents also contribute to mixing of the sediments. The previously mentioned studies on hypolimnetic currents reported by Bryson and Kuhn (1955) for Lake Mendota have been used by Hanson (1952) to show that these currents are of sufficient magnitude to suspend and transport the surface sediments. Kanishige (1952) found evidence for large-scale movement and mixing of the surface sediments of Lake Mendota. Using repetitive sampling at precisely positioned locations, he noted large differences in the concentrations of some chemical species such as iron and sulfide between summer and winter at the same location. He concluded that the observed changes were due to movement of the sediments rather than some chemical process.

It should be emphasized that the depth of mixing in lake sediments can be markedly different than the 5 to 15 cm reported here depending on the characteristics of the lake sediments. In extremely flocculant, slurry-like sediments encountered in some lakes, such as Lake Comstock, mixing extends to a depth of a few meters. Andrews (1969) reported that commingtonite, a principal component of taconite tailings, is found in the upper 2 mm of cores obtained in the Wisconsin part of Lake Superior. He uses this observation to infer that taconite tailings discharged to Lake Superior from Reserve Mining Company of Silver Bay, Minnesota, are transported across the lake to the Wisconsin side. If this is indeed the case, then mixing in Lake Superior sediment is in the order of a few mm/10 years since Reserve Mining Company has discharged taconite tailings to this lake for the past 14 years.

The relationship between the velocity of water and the suspension of sediment particles from typical lake sediments is poorly understood. Some data are available from studies of the relationships between stream discharge and sediment transport for rivers and streams. However, these studies do not provide the needed information for typical lake sediments, which are, in general, markedly different in character from river sediments. Lake sediments are generally finer, more cohesive and are frequently flocculant. Heezen and Hollister (1964) have presented a review of transport of oceanic sediments. This review, however, does not provide adequate information on the very fine materials that are present in many lake sediments.

This discussion of the mixing that takes place in sediments should not be interpreted to mean that complete mixing takes place in the active deposition zone of the sediments. Bortleson (1970) has examined the chemical composition of cores of lake sediments and found that for several different lakes, the magnitude of the change in the chemical composition versus depth of core

observed is a direct function of the depth interval in which the core is segmented prior to analysis.

In Lake Mendota cores, the same general concentration profiles were observed whether 2, 5 or 8-cm intervals of core were used. However, the greatest changes with depth were noted in the smallest (2-cm) depth interval. If complete mixing occurred over 5 to 10 cm within the upper sediments of Lake Mendota, the same chemical composition should have been observed whether 2 or 5-cm intervals were used. This was not the case. Therefore, it must be concluded that the mixing that occurs in the range of 5 to 15 cm for many different lakes is only a partial mixing and should not in any way be considered a complete mixing in any finite time interval.

The above discussion of the factors influencing exchange of materials between water and sediments clearly points to the importance of mixing processes both within the water and in the sediments. Many previous investigators have attempted to examine these exchange reactions by bringing samples of sediment into the laboratory and allowing them to stand quiescently in a jug or column. The concentrations of the materials in the overlying waters were measured versus time. It was hoped by these investigators that laboratory systems would give some estimate of the magnitude of the exchange reactions. These investigators failed to take into account the importance of the hydrodynamics of the lake. Laboratory systems not only failed to duplicate lake currents, but they also did not account for the mixing action brought about by organisms. Therefore, it is reasonable to suggest that, in general, the laboratory studies of the quiescent conditions represent somewhat less than the actual amounts of exchange that will take place in the environment.

Another approach which is being widely used today in the University of Wisconsin Water Chemistry Laboratory involves working with completely mixed systems or systems that are sufficiently mixed such that the rate of mixing does not control the rate of exchange. For example, it has been found that with some lake sediments, mixing once or twice a day is sufficient to enable the exchange process to proceed at a rate which is independent of mixing. If the completely mixed system is used, it is possible to get a well defined maximum rate of release that might occur in the environment. The actual environmental rate will be somewhat less than this amount since the same degree of mixing in the environment and in a completely mixed laboratory system is rarely achieved. It is hoped that by using the completely mixed laboratory system, these results may eventually be equated to the environment with some greater degree of certainty. This may be possible at some later date when additional information is available on the degrees of mixing that actually occur in natural waters and in sediments. In this way the maximum rates of release could be adjusted downward according to the estimates of the hydrodynamics of the system. This discussion should not be taken to infer that the author feels it is possible to completely reproduce the environmental situation in the laboratory. However, by proper choice of conditions it is possible, in the opinion of the author, to gain some insight into environmental situations such that laboratory studies can be used to guide detailed field studies in which the actual rates of exchange are evaluated.

An estimate of the order of magnitude of the difference between static and mixed systems is available from the work of Austin (1970) and Sawyer *et al.* (1945). Using "deep hole" Lake Mendota sediments, Sawyer reported that 0.6 percent of the total nitrogen present in a sample

was released to the overlying water in 100 days under static conditions. With mixed and aerated Lake Mendota sediments from the same general locations, Austin obtained a 31 percent release of the nitrogen present to the overlying water. Therefore, it appears that mixing the sediments resulted in an approximate 50-fold increase in the rate of release of nitrogen.

One, and possibly the only, way to estimate the role of lake sediments in influencing the concentration of aquatic plant nutrients in the water is to measure the rate at which nitrogen and phosphorus concentrations change upon changing the input to the lake. In the near future, phosphorus removal will be initiated at many sewage treatment plants throughout the United States. At selected lakes where wastewaters are the main source of phosphorus for the lake, studies should be initiated immediately to determine phosphate input from the various sources and the concentrations in the water. After the initiation of phosphate removal from the wastewaters, studies should be made to determine the phosphate concentration in the water. By knowing the amount of phosphate present in the water, the reduction of phosphate input from wastewater, the input from other sources and the hydrologic characteristics of the lake, it would be possible to estimate the amounts of phosphate released from the sediments.

Care must be used in this study to allow for the flushing of the lake. From the rate of decrease in the concentration in the water as compared to the theoretical exponential flushing rate of the lake, it will be possible to estimate rate of phosphorus release from the sediments. Current efforts to develop systems models for the aqueous environmental chemistry of phosphorus in the University of Wisconsin Water Chemistry Program and at other institutions will likely lead to estimates of the significance of recycling from lake sediments.

## BIOLOGICAL FACTORS IN EXCHANGE REACTIONS

In addition to mixing the sediments, organisms can greatly alter the thermodynamics and kinetics of exchange reactions by both direct and indirect mechanisms.

The direct effects are associated with metabolic activity which results in the uptake of an element and possible transformations of an element from one form to another. For example, the release of nitrogen from lake sediments to overlying waters is controlled by microorganisms which transform the organic nitrogen present into more soluble forms such as  $\text{NH}_4^+$  and  $\text{NO}_3^-$ . Austin (1970) working with Lake Mendota sediments has found that 10 to 20 mg/l of ammonia nitrogen are released to the water under laboratory conditions in a period of several months. Under anoxic conditions, the nitrogen was released as ammonia, while with oxygen present, the ammonia was nitrified to nitrate. These reactions were controlled by microorganism activity.

Generally, it is believed that bacteria play dominant roles in biological transformation. However, higher organisms, such as zooplankton and fish, may bring about certain kinds of exchange reactions in their intestinal tracts that may not be possible by bacteria. For example, the characteristics of a fish's gut may be markedly different from the water so that release of an element from a particle may be obtained inside the fish which would not take place in the environment. Pomeroy *et al.* (1963) have shown that phosphate is released from the detritus particles as they pass through a zooplankton and other organisms.

The indirect effects of microorganisms on exchange reactions involve those biochemical reactions which result in a change in chemical characteristics of the water which thereby alter exchange reactions. These biochemical reactions include primarily photosynthesis and respiration reactions although normal metabolic uptake can be important for certain elements. Both photosynthesis and respiration reactions tend to alter the pH of the solution and influence the amount of organic matter present in the water. The pH of the water often plays a dominant role in exchange reactions. As is discussed under chemical factors, sorption-desorption, precipitation-solubilization, redox and complexation reactions often depend on solution pH.

In addition to those reactions involving pH changes, another important reaction caused by microorganisms is the reduction of sulfate to sulfide. Since many metal sulfides are highly insoluble, this reaction can control the exchange of many transition metals. Also, this reaction may be important in phosphate exchange since Hasler and Einsele (1948) and Sugawara *et al.* (1957) have proposed that sulfide displaces phosphate from a ferrous precipitate thereby releasing the phosphate to the water.

The general trophic level of a body of water plays an important role in exchange reactions. The growth and death of photosynthetic organisms control the redox system (aerobic or anaerobic) present in the water and sediments. For example, it is well known that reducing conditions often tend to promote release of many compounds to the overlying water, such as phosphorus, iron and manganese.

For any given lake the chemical inputs of oxygen and aquatic plant nutrients plus sunlight provide the driving forces for all exchange reactions which are dependent on oxidation-reduction reactions and others, such as acid-base, precipitation, complexation and sorption reactions since many of these reactions are dependent indirectly on various biochemical processes. Lee and Hoadley (1967) have reviewed the ways in which biochemical reactions can affect chemical composition and other chemical reactions that may take place in natural waters. This review should be consulted for greater detail on this topic.

Atmospheric oxygen is a driving force in many chemical reactions that occur in lake waters since it is available in essentially inexhaustible supply and, except for periods of stratification, its rate of supply is sufficiently great to maintain oxidizing conditions. However, reducing conditions do occur whenever the rate of input of oxygen-demanding materials, such as biochemical oxygen demand in wastewaters, exceeds the rate of oxygen supply from the atmosphere and from photosynthetic reactions of aquatic plants.

The other driving force of various chemical reactions that occur in natural waters is the loadings of aquatic plant nutrients to the water. Aquatic plant nutrients increase algal growths which later decompose and exert an oxygen demand in stratified waters and in the sediments. Oligotrophic waters, i.e., those with low aquatic plant nutrient loadings, show little or no oxygen depletion in hypolimnetic waters or in the sediments. However, eutrophic waters generally show marked and, in many cases, complete oxygen depletion in the hypolimnion during the periods of thermal stratification. This oxygen depletion is directly related to the primary productivity of the euphotic zone (that zone or volume of water in which light penetration is sufficient to allow photosynthesis) since the death of organisms produced in the euphotic zone results in a

biochemical oxygen demand in the hypolimnetic waters when dead organisms settle into these waters. From this discussion it becomes quite clear that many exchange reactions are directly or indirectly dependent on the photosynthetic and respiratory activity of microorganisms. Examples of various kinds of exchange reactions that are influenced by direct and indirect effects of microorganisms are presented along with chemical factors that affect these reactions.

Biological circulation is the transport of chemicals as the result of the movement of the organisms present in water. A good example of biological circulation is the previously cited emergence of insects as a means by which phosphorus, iron and manganese and other elements are transported from lake sediments. Biological circulation could play an important role in the exchange reactions of some elements. For example, Beers and Kelly (1965) have found that diurnal variation in the ammonia content of the ocean surface waters is attributed to the diurnal migration of zooplankton within these waters. Evidently the zooplankton come to or near the surface at night, release ammonia in large quantities and, then during daylight hours, descend to greater depths. In lakes, this diurnal variation can extend from the sediments up to the surface. Although no evidence has been provided for these organisms' having an effect on exchange reactions, it is reasonable to propose that some zooplankton organisms could absorb certain compounds from the sediments, carry them through diurnal migration up to the surface waters during the night time period and release some part of these compounds to these waters. This area will require additional study before the significance of such reactions can be fully evaluated.

The organisms themselves can provide a driving force for exchange reactions which, in turn, bring about a much greater flux of materials than would otherwise be possible. For example, if the exchange of an aquatic plant nutrient is dependent on the concentration in the water and if the organisms present in the water remove the nutrient as fast as it is released from the sediments, then much greater quantities of this nutrient can be removed from the sediments in the presence of aquatic plants than in their absence. This is possible since in the absence of aquatic plants, the water would come to an equilibrium value which would inhibit further exchange. Gerhold and Thompson (1969) have reported this type of phenomenon for the growth of various kinds of algae in laboratory cultures using calcium hydroxyapatite as the phosphate source. In these studies, the algae act as an infinite sink for phosphorus, driving the reactions in the direction of transferring materials from the insoluble apatite to the organisms.

Golterman *et al.* (1969) reported that the phosphate present in a number of Dutch lake sediments was available for growth of algae. Using *Scenedesmus* sp., they found that the algae could grow with lake sediments as the only source of phosphorus in the culture media. Recently, Walton (1970) has found that approximately 30 percent of the soluble orthophosphate present in Lake Wingra water is not readily available for algal growth. It is likely that the discrepancy between molybdate orthophosphorus and bioassay orthophosphorus is possibly due to the presence of either colloidal phosphorus that passes through a  $0.45\mu$  filter and/or organic phosphorus which is hydrolyzed in the molybdate test. Similar results have been previously reported by Rigler (1968). Hayes (1955) and Hayes and Phillips (1958) have discussed the role of bacteria in the exchange of phosphorus between lake sediments and organisms present in water. Phillips (1964) has presented a review on the ecological role of phosphorus in water with respect to various microorganisms. This review should be consulted for additional information in this area.

## CHEMICAL FACTORS INFLUENCING EXCHANGE REACTIONS

The chemical factors that may influence exchange reactions include the chemical characteristics of the water and sediments and the chemical transformations that lead to exchange. Although many studies have examined the chemical characteristics of the overlying waters, few studies have examined the chemical characteristics of the sediments. Because of the complexity of the system, studies on the characterization of sediments usually have been restricted to gross characterization of the total content of carbonate, organics, iron, clays, etc. Many early workers proposed well-defined mineralogical species as being present in lake sediments, such as ferric phosphate, ferrous phosphate, ferrous sulfide, hydroxyapatite, etc. Yet attempts to isolate and identify materials that yield well-defined x-ray diffraction patterns from lake sediments usually fail to find any, or the amounts found are usually so small compared to the total as to be insignificant.

Based on the current state of knowledge, it must be concluded that natural sediments consist of essentially amorphous materials that remain to be characterized. It is doubtful that any appreciable concentration of any well-defined mineralogical species will be found in sediments. Some investigators have attempted to "show" the presence of a well-defined precipitate by the fact that a certain solubility product is exceeded. Thermodynamically, ferric phosphate, hydroxyapatite, etc., should be present under equilibrium conditions. However, many natural waters have concentrations of some species that greatly exceed a solubility product. It appears that the kinetics of these reactions control the forms present, and a lake sediment should not be considered as a system that is at thermodynamic equilibrium.

Based on the studies of Bortleson (1968, 1970), it has been found that there is very little relationship between sediment concentration of an element and its concentration in the overlying water. Some of the lakes in northern Wisconsin which are good examples of highly oligotrophic waters contain the highest concentration of nitrogen and phosphorus in the sediments, while southern Wisconsin lakes which are highly eutrophic contain considerably lower concentrations of nitrogen and phosphorus. There must be very little exchange of nitrogen and phosphorus present in the sediment in the northern Wisconsin oligotrophic lakes. The apparent contradiction between sediment composition and degree of eutrophication is because the composition of lake sediments is dependent not only on the rate at which the chemical species of interest is being deposited in the sediments, but also on the rate at which all other species are deposited. Lakes that deposit large amounts of clastics (inorganic materials derived from the watershed) and/or  $\text{CaCO}_3$  will show lower phosphate concentrations for the same degree of eutrophication and other characteristics. All southern Wisconsin lakes, for example, are calcareous lakes and the sediments consist of large percentages of  $\text{CaCO}_3$ . Rather than using concentrations of chemical species in sediments to characterize the rate of its exchange reactions, Bortleson (1968) has proposed that sedimentation intensity (mg of element deposited per unit area/yr) be used. When units of this type are used, the oligotrophic lakes show much lower phosphorus sedimentation intensities than the eutrophic lakes.

Unfortunately, this approach requires the dating of the core in order to estimate rates of sedimentation for the lake. Ogden (1967) found that a series of replicate C-14 dates is needed in a core to establish sedimentation rates. Bortleson (1970) has used ragweed pollen in cores as a useful guide in establishing a date in a core since the first clearing of the land in the northern

Midwest resulted in a significant increase in ragweed. Nriagu and Bowser (1969) suggest that the magnetic spherules may be used to help date a core since they found that their presence in Lake Mendota cores was related to the combustion of coal in the watershed.

Each of the major types of chemical reactions, such as acid-base, precipitation, complexation, redox, biochemical and sorption reactions, may play an important role in exchange reactions. A review of the various types of reactions that may control exchange reactions is presented below.

## ACID-BASE

Acid-base or protolysis reactions could affect exchange reactions in many different ways since many chemical reactions are pH-dependent. Normally natural water sediments do not show large pH changes as they are usually fairly well buffered in most lakes by large amounts of clay minerals, particulate organic matter and, in calcareous lakes, precipitated calcium carbonate. In eutrophic lakes, the hypolimnetic waters may show a decrease of several pH units during summer stratification due to (a) biochemical respiration of organics present in the sediments, (b) raining down of plankton from the overlying waters, and (c) oxidation reactions of reduced iron, sulfur, and manganese species present in the sediments. For example, in Lake Mendota just before fall overturn, the hypolimnetic waters have a pH of approximately 6.5, while the epilimnetic waters have a pH ranging from 8.5 to 9. The high surface water pH is due to photosynthesis which causes a removal of CO<sub>2</sub>. Both the epilimnion and hypolimnion have a pH near 8 at spring overturn.

The 2-unit pH change noted for the hypolimnetic waters of Lake Mendota could have a significant effect on exchange reactions, particularly if the pK of one of the exchanging species is at or near the pH of the water. For example, in the case of phosphates the pK for the  $\text{HPO}_4^{2-}$ - $\text{H}_2\text{PO}_4^-$  is near 7. Since this pK is near the pH of the hypolimnetic waters, it is reasonable to propose that if the sorption tendencies of these two species is markedly different, a change in pH could change distribution of the phosphorus between the sediments and the overlying waters.

In addition to changes in the species present on the sediment surface or in the water, a change in pH can also affect the nature of the sorption sites. For example, Morgan and Stumm (1964) have shown that sorption of manganese (II) by manganese dioxide is highly pH-dependent in the pH range of 7 to 8. The proposed mechanism for the pH dependence is a change in the degree of protolysis of the sorption sites. Delfino (1968), working with Lake Mendota sediments under laboratory conditions, bubbled various N<sub>2</sub>-CO<sub>2</sub> gas mixtures through these sediments and was able to show that the manganese concentration present in solution in equilibrium with these sediments was a direct function of the pH of the solution. Increasing amounts of manganese (II) were released as lower pH's in the pH range 6-8 were used. This phenomenon was reversible; if the partial pressure of carbon dioxide in the gas decreased, a high pH in solution would result with a decrease in the amount of manganese (II) present in the solution. It is not possible from Delfino's work to determine whether this is an effect on a sorption reaction or a solubilization-precipitation reaction which controls the concentration of manganese (II) in these sediments. It does, though, clearly demonstrate how minor changes in pH could have a significant effect on the release of materials from lake sediments. A similar set of studies conducted by Spear (1970) on the release of phosphorus from sediments showed that in the pH range 6-8, Lake Mendota sediments did not show marked changes in the amount of phosphorus released in short periods of

time under anoxic conditions. In other words, pH did not appear to play a significant role in controlling the immediate release of phosphorus from these sediments.

Acid-base reactions can also affect exchange reactions which are dependent on precipitation or complexation reactions. For example, many complexing agents and precipitating species in natural waters are conjugate bases of weak acids, such as organic acid, carbonate, etc. It will be shown later that a change in pH could affect the amount of materials released by these reactions. Changes in pH could not only affect the position of equilibrium for many of these reactions, but also could affect the kinetics of exchange reactions. For example, Stumm and Lee (1961) and Morgan and Stumm (1965) have shown that the oxidation of ferrous iron and manganese (II) by dissolved oxygen is dependent on the square of the hydroxyl ion concentration in solution. Thus, a one-unit pH change will cause a hundredfold increase in the rate of these reactions. It should be pointed out that pH changes have significant effects on exchange reactions not only in the bulk of the solution but also at the surface of particulate materials such as calcium carbonate crystals or of microorganisms (bacteria and algae). For example, the pH immediately adjacent to a photosynthesizing algal cell should be higher than the pH in the bulk solution. If the exchange reaction is markedly dependent on pH, it may be found that the exchange takes place at or near the surface of the organisms rather than in the bulk of the solution so that bulk measurements of pH may give an incorrect indication of the actual pH in which exchange takes place. Further research is needed in this area to define the role of the microenvironmental pH and other chemical characteristics to fully understand their importance in influencing the exchange of materials between water and sediments.

## PRECIPITATION

Precipitation-solubilization reactions may have a direct effect on the transfer of materials to and from the sediments of lakes. One of the means by which materials are transferred is through the formation of insoluble compounds. There are numerous references in the limnological and oceanographic literature concerning the precipitation of some chemical species in natural waters, yet a review of this literature usually shows that, in general, few chemical precipitates have been isolated from natural water sediments. The problem here appears to be twofold. First, it is extremely difficult to isolate a precipitate from natural water sediments because of the large amounts of other materials that are normally present in the sediments. Many of these other materials are amorphous, are of mixed crystalline structure, or are organic remains of organisms, etc. Second, one of the most important precipitating species, the basic carbonates, seems to have variable composition depending on the water from which they have precipitated. For example, copper precipitates in natural waters as a basic carbonate if the water has sufficient bicarbonate alkalinity. The exact form that precipitates may be either azurite or malachite. Sanchez (1970) has attempted to study the precipitation of copper basic carbonate in simulated lake water systems and found it extremely difficult to reproduce the composition of the precipitate from one day to the next. In addition, there is also a significant aging effect on the precipitate in which the composition changes with time, especially if left in contact with the mother liquor.

As mentioned above, some investigators have reasoned that since the solubility product of a particular chemical species is exceeded, this species should be found in the sediments. For example, Ohle (1937) and Einsele (1938) have both discussed the reactions between ferric iron and phosphate and have concluded that ferric phosphate must be one of the precipitating species

that controls phosphorus concentrations in natural waters. However, examination of their work shows that this conclusion is primarily based on a solubility product consideration and that they did not distinguish between sorbed phosphorus on the surface of the hydrous ferric oxide and the ferric phosphate species. To the knowledge of the author, ferric phosphate has never been isolated from natural water sediments. In fact, there is considerable evidence that ferric phosphate does not exist in natural waters. This statement does not mean that iron does not play a dominant role in phosphate exchange reactions. On the contrary, ferric iron is probably the key element that controls phosphorus concentrations in many natural waters.

In recent years there has been an attempt to use operationally defined extraction procedures developed for soils to characterize lake sediments. The procedures, like those proposed by Chang and Jackson (1958) and Williams *et al.* (1967), can yield useful information on the characterization of an element in lake sediments provided that these empirical procedures are correlated with exchange reactions and the characteristics of a waterbody. However, insufficient information is available at the present time to describe with any degree of certainty the actual forms of these elements measured by the selective extraction procedures used in the soils field.

Frink (1969b) found that the Chang and Jackson procedure may be used to characterize aluminum and iron phosphate. Some modifications were necessary in order to evaluate all forms of phosphate present. Armstrong (1969) found that these procedures do not work well in calcareous sediments because such sediments will resorb any phosphorus that is released. The results obtained from the use of these procedures must be viewed with caution because specific forms of elements are not measured; in fact, the various types of compounds measured depend to a major degree on how the test is performed. Slight deviations in procedure could cause significantly different results.

The results of operationally defined tests can be divided into two broad categories which are probably related to exchange reactions. In the case of phosphorus, the categories are occluded phosphorus and non-occluded phosphorus. The occluded forms are, in general, nonacid leachable and are probably not subject to any degree of leaching. The occluded forms include calcium, iron and aluminum phosphates which can, under certain conditions, be exchanged. Wentz and Lee (1969) have shown that for Lake Mendota sediments, the acid leachable part of the phosphorus is empirically correlated with the degree of eutrophication of the lake, i.e., more acid leachable as the lake becomes more eutrophic as shown in a core of the lake sediments. It is quite possible that these operationally defined tests will provide some valuable insight into the mechanisms by which the various elements are retained within the sediments. One of the more important aspects of this area is that there is an urgent need today for detailed studies of the actual forms of various elements measured by these tests.

One of the primary problems in studying exchange and precipitation reactions is the problem of defining exchange. An investigator in this area must somewhat arbitrarily decide what is in true solution and what is present in very finely divided particles that may be colloidal in nature. The generally accepted operational definition of soluble is based on passage through a 0.45 micron pore-size membrane filter and may lead to serious errors for certain substances in some waters. Hood and Slowey (1964) have found that significant amounts of some trace metals present in the Gulf of Mexico water will pass through 0.45 micron filters, yet will not pass through 0.001

micron filters. It should be remembered that 0.45 microns is on the upper end of the colloidal size range which is normally given as 1 millimicron to 1 micron. It is possible that a considerable part of the operationally defined soluble species present in natural waters is particulate and that some of the apparent exchange reactions are not actually exchange reactions. Investigators in this area should use a variety of filters to check some of their samples to be certain that they are not dealing with very small particles. Also highspeed centrifugation is an important tool that should be used to examine the actual character of species apparently in solution.

Often the hydrous oxide precipitates of iron, manganese and aluminum are reported to play important roles in the exchange reactions of other species in solution. For example, Jenne (1968) has proposed that the hydrous oxides of iron and manganese control exchange reactions for manganese, iron, cobalt, nickel, copper, and zinc in soils and water. Mackereth (1965, 1966) studied the distribution of phosphorus in three English lakes. He feels that in the noncalcareous sediments of these lakes, the means by which phosphorus is deposited is either coprecipitation with iron and manganese or incorporation into biological matter, largely phytoplankton. Bortleson (1968) found a good correlation between iron, manganese and phosphate in cores of lake sediments. Schofield (1968) concluded that phosphate was held in oxidizing sediments as an iron phosphate and occluded forms, while under reducing conditions, aluminum phosphates were prevalent. Smith (1965) presented a review of the accumulation of iron and aluminum phosphates in soils. That review should be consulted for additional information in this area. Wentz (1967) recently reviewed various methods by which phosphorus is held in sediments.

In Europe, Muller (1966, 1967), Muller and Tietz (1966) and Wagner (1966, 1967, 1968) have studied the characteristics of lake sediments with emphasis on the forms of phosphorus present. In general, their results are in accord with the findings of studies on English and American lakes.

Stumm (1964) states that the phosphate concentration in natural waters seldom exceeds 0.3 mg/l. He concludes that hydroxyapatite may be limiting phosphate concentrations in natural waters since he computes that the equilibrium concentration of phosphate in contact with hydroxyapatite is 0.03 mg/l at a pH of 7. He goes on to state that if the hydroxyapatite equilibrium applies in natural waters, then the addition of phosphate from a source rich in phosphorus, i.e., sewage effluent, would tend to cause the phosphate to be precipitated in the sediments. From a thermodynamic point of view, Stumm is correct. Yet, based on both laboratory and field observations, it is unlikely that hydroxyapatite plays an important role in the environmental chemistry of phosphate in natural waters. There are many eutrophic lakes in which the concentration of phosphate in solution greatly exceeds 0.03 mg/l. For example, the Madison lakes typically have 10 to 50 times this amount of phosphate. It appears that the kinetics of nucleation of hydroxyapatite in natural waters may control the formation of the precipitate.

Gerhold and Thompson (1969) reported that calcium hydroxyapatite,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , was identified as the principal phosphate mineral present in samples of bottom sediments from western Lake Erie. That statement should not be interpreted to mean that hydroxyapatite is a dominant form of phosphate in sediments. The majority of the phosphate in the samples studied by Gerhold and Thompson was amorphous and, thus, could not be characterized as mineral

phosphate. They studied the availability of calcium hydroxyapatite as a phosphate source for algae and found that under optimum conditions, the phosphate released from hydroxyapatite was sufficient to keep the algae at maximum growth rate. However, they found that less total growth was obtained when hydroxyapatite was the main phosphorus source as compared to orthophosphate. Clesceri and Lee (1965) found similar results. They observed that less total growth was obtained when condensed phosphates, pyrophosphate or tripolyphosphate were used as a phosphate source, and better growth was obtained when orthophosphate was the phosphorus source. The reason that the source of phosphate influences the ultimate growth of algae are not apparent based on the work done to date.

Exchange reactions via precipitation and solubilization mechanisms may be complicated by such phenomena as supersaturation due to slow rates of nucleation and also the armoring of particles by other types of materials. On the one hand, Chave (1965) has reported that calcium carbonate particles present in the sea contain organic coatings which inhibit their solubilization in waters that are undersaturated with calcium carbonate. On the other hand, Hawley (1967), in a study of the calcium carbonate saturation in Lake Mendota, did not find any coatings that would inhibit equilibrium provided that adequate mixing was present. Hawley noted that the epilimnion of Lake Mendota was approximately a hundredfold supersaturated with respect to calcium carbonate. This supersaturation has been observed by many investigators in surface waters of the warmer parts of the ocean. Hawley has proposed that since rapid equilibration takes place upon the addition of pure calcium carbonate to the system, the cause of the supersaturation is a lack of nuclei in the water. Stumm (1969) has found that hydroxyapatite does form on the surface of calcium carbonate crystals under laboratory conditions. If this phenomenon takes place in the environment to any significant degree, it is quite possible that significant amounts of hydroxyapatite are present in lake sediments. If present, however, it would exist as a veneer on calcium carbonate particles. This would pose serious difficulties for separating the hydroxyapatite from the calcium carbonate by the conventional procedures normally used.

## COMPLEXATION

Complexation reactions could be important in sediment-water exchange processes especially in the area of metal ion exchanges which are influenced by various kinds of organic compounds. These reactions could be both homogeneous and heterogeneous. In heterogeneous reactions, metal ions would attach themselves to the surface of solids by means of the complexing functional group on the solid. Both Plumb (1968) and Christman (1967) have presented evidence to show that some of the ferric iron present in natural waters exists in the form of a complex with natural organics. Shapiro (1964) has shown that natural water organics tend to control particle size of ferric hydroxide precipitates in the range of 0.45 to 0.1 microns in diameter. Hood (1967), Williams (1969), and Williams and Stark (1966) have shown that copper and boron exist in sea water as complexes with naturally occurring organic materials. It is likely that the complexation between metal ions in natural organics takes place within the organic carbon matrix between either aromatic alcohol groups or acid groups.

The formation of a complex in solution would greatly enhance the exchange since the complex would tend to drive the reaction toward the solution phase. However, complexation with solids would act in just the opposite direction because soluble species would become associated with the sediments. At the present time, it is impossible to predict what the situation would be for any

given metal species in natural waters. There is insufficient information available now to show the types of organics that are present in natural waters and also their role in complexing various species. There can be little doubt, though, that at least some of the metal ions, such as copper, are strongly complexed in most natural waters and that this could have a significant effect on the behavior of these ions.

The formation of ion pairs in solution (Davies, 1962) could affect exchange reactions since any species involved in an ion pair would tend to be removed from the solid phase. Based on the magnitude of the equilibrium constants presented by Garrels and Thompson (1962), ion pairs would not be present in normal freshwaters, with the possible exception of  $\text{MgCO}_3$ . The equilibrium constant for the  $\text{MgCO}_3$  ion pair given by Carrels and Thompson is such that in many hard waters, the magnesium normally present would tie up a significant part of the free carbonate species. However, a study by Morton (1967) in the University of Wisconsin Water Chemistry Laboratory has shown that the Garrels and Thompson value for the magnesium carbonate ion pair is probably in error by a factor of 10. Because this value is in error, it is felt that this ion pair does not exist in normal fresh waters. An exchange reaction involving such species as sodium, potassium, calcium, magnesium, bicarbonate, carbonate and sulfate could be influenced by ion pairs in estuarine and marine environments.

## OXIDATION-REDUCTION

The overall redox state of the sediments has been shown to play a very important role in controlling the exchange reactions of some species. In some cases, oxidizing conditions tend to promote the release of species such as those discussed previously regarding Austin's (1970) studies on nitrogen release from lake sediments in which nitrate is formed under oxidizing conditions.

Considerable efforts have been made by some investigators to attempt to quantify the overall oxidation-reduction characteristics of lake waters and sediments by measurements of Eh using platinum or other noble metal electrodes. At best, the approach used by these investigators gives only a crude estimate of the overall oxidizing and reducing conditions within the sediments. It should not be used to predict the ratios of oxidized to reduced species. Morris and Stumm (1967) should be consulted for additional information on the problems and significance of Eh measurements.

Redox conditions which exist within sediments may be one of three types: either (1) oxygen is present and conditions are aerobic (oxidizing); (2) both oxygen and sulfide are absent and conditions are thus transitional between oxidizing and reducing; or (3) sulfide is present and conditions are anaerobic (reducing). This system is not applicable when sulfate limits sulfite production in natural waters, although, in general, this type of situation would be encountered rarely.

Whether the redox conditions within the sediments are oxidizing, reducing or transitional depends to a major extent on the morphology of the lake, the thermal structure of the lake and the nutrient flux to the lake. These factors influencing redox conditions must be taken into account because atmospheric oxygen is a driving force for redox conditions within a lake and tends, if given the opportunity, to carry all species to the oxidized state. However, with high

nutrient fluxes, anoxic conditions are created in the hypolimnion of lakes or in the sediments which bring about a reduction of the species present.

In the case of redox reactions, though, the few studies that have been conducted in this area clearly show that, in general, kinetics plays an extremely important role in determining the forms of the elements present. Many of the redox reactions take place at slow rates under environmental conditions. Also, the rates of many of these reactions are sufficiently slow or are controlled by biochemical processes such that it is rare to find a water in complete thermodynamic equilibrium for the various oxidizing and reducing species.

Various investigators have found that ferric iron in lake sediments influences and often controls the exchange of phosphates from the sediments to the overlying waters. As previously discussed in this paper, it appears that the actual species present in the sediments is not ferric phosphate but some complex or hydrous oxide of ferric which tends to sorb the phosphorus from the water. It is generally found that under reducing conditions, the phosphate is released because the ferric is reduced to ferrous iron, and the ferrous phosphates and related compounds are highly soluble. The classical work of Mortimer (1941) in this area is often cited as evidence to support the general belief that phosphate is not released under aerobic conditions.

However, work in the University of Wisconsin Water Chemistry Laboratory by Spear (1970), Sridharan (1970) and Bortleson (1970) has shown that for sediments from Lake Mendota, Trout Lake and Green Bay, appreciable release of orthophosphate occurs under aerobic conditions. In the case of Lake Mendota sediments, Spear found that under anaerobic conditions approximately 1 to 2 mg/l of orthophosphate was released in a jug-type experiment in a period of a few hundred hours. Conditions of the experiment were such that nitrogen gas was bubbled through the mud-water system which consisted of about 500 mls of mud from the deeper part of Lake Mendota mixed into approximately 20 liters of either distilled water or lake water. When oxygen or air was used in place of nitrogen in the same experiment, about 1 mg/l of orthophosphate was released in a period of 1,000-2,000 hours.

Similar results were observed by Bortleson working with the same sediments and also by Sridharan working with Green Bay sediments. Sridharan and Bortleson both found that the amount of aerobic release of phosphorus is highly dependent on sediment characteristics which may vary considerably, depending on the location from which the sample was collected. For example, less phosphorus release was noted in cores of Lake Mendota sediments below the surface as compared to surface samples. Also, much larger quantities of phosphorus were released from samples taken near the mouth of the Fox River in Green Bay as compared to samples of sediment taken in open water parts of the Bay. On the basis of these studies, orthophosphate is apparently released very slowly from these sediments compared to the rate of release under anaerobic conditions.

It should be mentioned that these studies were conducted so that the sediments in the water were completely mixed at all times. In this way the rate of release was controlled by the exchange reaction rather than the hydrodynamics of the system. Many of the previous investigators such as Mortimer (1941) have attempted to work with static systems and have, in general, worked for shorter, periods of time. This may explain why they did not observe the aerobic release.

Gorham and Swain (1965) have reviewed the influence of oxidizing and reducing conditions upon the distribution of some elements in lake sediments. Their review should be consulted for further details.

The FWPCA *Water Quality Criteria* (1968) lists as one of its recommendations that "the addition of sulfates or manganese oxide to a lake should be limited if iron is present in the hypolimnion as they ( $\text{SO}_4^{2-}$  and  $\text{MnO}_x$ ) may increase the quantity of available phosphates." Justification for that statement apparently comes from a paper by Hasler and Einsele (1948) in which two methods for the release of phosphate phosphorus from hypolimnetic waters appear. Those authors suggest that as long as the iron to phosphorus ratio is 2:1 or greater in the oxygen-depleted hypolimnion, the entire dissolved phosphorus will be bound to oxidized iron at the turnover, and  $\text{FePO}_4$  being insoluble will be deposited in the sediments.

The first method for the release of phosphorus from the sediments is based on the anaerobic reduction of sulfate to sulfide, presumably by *Delsulfovibrio desulfuricans* and other sulfate-reducing bacteria. The sulfide produced can react with reduced iron to precipitate iron (II) sulfide. The precipitation of iron sulfide reduces the concentration of iron in the hypolimnion below the level needed to maintain phosphorus bound as insoluble  $\text{FePO}_4$ . At the fall or spring circulation, the dissolved phosphate will be transported throughout the lake and serve as an aquatic plant nutrient.

The second "mobilization" scheme is predicated on the assumption that dissolved iron in the hypolimnion occurs together with relatively large amounts of manganese, and that the addition of manganese oxide to water containing ferrous iron will result in a redox reaction between iron (II) and manganese (IV). The oxidation of iron (II) to iron (III) allows ferric iron to be removed from solution as ferric hydroxide, while reduced manganese goes into solution. This mechanism also reduces the quantity of dissolved iron in the hypolimnion and allows free movement of phosphate within the lake at the overturn.

Hasler's and Einsele's (1948) proposed schemes are generally in accord with the thermodynamics of the aqueous environmental chemistry of iron, manganese, phosphorus and sulfur with the exception that the phosphate present in lake sediments is probably not  $\text{FePO}_4$  but some other form. To date, however, no experimental evidence has been provided to verify whether or not the kinetics of these reactions are such that they will take place at a sufficient rate in natural waters to cause a significant release of phosphorus from lake sediments. Studies are currently underway by Olson (1970) to evaluate the significance of these reactions in natural waters.

## SORPTION

Sorption reactions are probably the most important type of reaction with respect to controlling the exchange of materials between sediments and waters. The sorption of phosphorus on natural water sediments has been one of the most extensively studied sorption reactions. The reader should consult the studies by Olsen (1964, 1966), Carritt and Goodgal (1954), Jitts (1959), MacPherson *et al.* (1958), Harter (1968), Pomeroy *et al.* (1965) and Golterman (1967) for discussions on the exchange of phosphorus between sediments and the overlying waters. All of these studies have shown that phosphate tends to be sorbed readily by lake sediments. Sorption,

in general, is a fairly fast process, is somewhat reversible, and is dependent on pH, with maximum sorption occurring in the slightly acid pH range.

Recently, Murrmann and Peech (1969) studied the sorption release of phosphates from soil-water systems and found maximum uptake in the slightly acid pH range of 4-7. They concluded that the concentration of phosphorus in solution was determined by the amount of labile, isotopically exchangeable phosphate rather than the solubility of some crystalline phosphate.

Livingstone and Boykin (1962) studied the vertical distribution of phosphorus in a sediment core from Linsley Pond. Their results suggest that sedimentary phosphorus is bound by sorption reactions with clastic minerals. They computed the ratio of phosphorus to organic matter, to inorganic matter, and to total dry weight throughout the sedimentary column and concluded that the ratio of phosphorus to inorganic matter was the most nearly constant of the three. From this, they reasoned that regardless of the binding agent, the ratio of phosphorus to binding agent was constant at all depths.

If this is true, the productivity of a lake would then be determined by sorption reactions in the surface sediments. Wentz (1967) calculated the ratio of available phosphorus (acid leachable) to inorganic, organic and clastic matrices for cores from Lake Mendota. He found results similar to Livingstone and Boykin's (1962) in which the ratio of available phosphorus to inorganic matter was most nearly constant. Bortleson (1968) made similar calculations for Trout Lake in northern Wisconsin and found similar results, i.e., the ratio of phosphorus to inorganic content was essentially constant. Bortleson (1968) also found that phosphate content of three different lake sediment cores correlated best with the iron and manganese content. Although all of these results do fit a sorption model, other reactions such as precipitation also fit this model and, therefore, these results do not identify the mechanism of phosphorus binding in sediments.

Olsen (1966) cites three types of reactions by which phosphorus may become fixed in sediments: (1) biologically, by metabolic processes in bacteria, phytoplankton and higher plants; (2) chemically, by reactions with calcium, iron and aluminum; and (3) by sorption whereby the phosphorus is fixed to the surface of solids. In natural waters, probably all three of these reactions occur simultaneously. Additional study is necessary to determine which one(s) predominate in a given lake.

Bailey and White (1964) have presented a comprehensive review of the sorption and desorption of pesticides by soil particles. Such factors as soil type, physico-chemical nature of pesticide soil reactions, nature of the saturating cation at the cation exchange site, moisture content and temperature all play an important role.

Of the various types of solids present in natural waters, clay minerals rank high on the list in terms of sorption capacity. Some clay minerals such as montmorillonite and vermiculite have cation exchange capacities in the order of 100 milliequivalents per hundred grams. Kennedy (1965), in a study of types of clay minerals present in rivers of the United States, found that the typical cation exchange capacities of the particulate matter present in most rivers was in the order of 10-75 milliequivalents per hundred grams. By comparing the concentrations of various alkali and alkaline earth metals in the river water with those present on the surface of clays, he

concluded that significant cation transport occurs in rivers via sorption of these species on the surface of the particulate matter. Also, he was able to show that the particulate matter would tend to act as a buffer for controlling the cation composition of many rivers.

Fruh (1963) has examined the sorption characteristics of Lake Mendota sediments for cesium. He found that these sediments have cation exchange capacities in the order of 100 milliequivalents per hundred grams and that the uptake of cesium by these sediments could be several times the cation exchange capacity. A significant part of the sorbed cesium was leachable in distilled water. He also found that the amount of readily leachable cesium from these sediments was dependent to some degree on the length of time of exposure of the sediments to the cesium-containing solution. Fruh (1965) conducted a study of the sorption of cesium on vermiculite and was able to formulate the sorption-desorption reactions into a mathematical relationship that was analogous to the functions used to describe enzyme catalysis and inhibition. The cesium vermiculite system has the property of lattice collapse that may have a significant role in certain types of exchange reactions. Some cations, such as cesium and potassium, cause the collapse of the clay-mineral lattice for the expandable layer clays. This collapse is time-dependent and depends on cation concentrations. The importance of lattice collapse is that it is essentially an irreversible process whereby certain elements become trapped within the lattice. Although this may reduce the amount of an element potentially available for exchange, there may also be a significant decrease in the sorption characteristics of the clays with the lattice collapse because a significant part of the "surface" has been lost.

Clay minerals also show significant sorption capabilities for some anions such as phosphate while other anions, for example, nitrate, show essentially no sorption tendencies on clay minerals. The relative tendency for sorption of these two species helps explain why nitrate is transported in ground waters and phosphate generally is not. Tranquillo (1970) is currently studying the transport of phosphate from septic tank sewage disposal systems in quartz sand aquifers. He has shown that these sands have very low sorption capacities for phosphate and that septic tank systems could contribute phosphorus to a nearby water course once this low capacity for sorption has been met. However, very small amounts of certain contaminants, such as calcium carbonate, ferric hydroxide, clay minerals, etc., can markedly increase the sorption characteristics of the aquifer.

Boucher (1967), working with some quartz and aquifer materials from the Little Plover region of Wisconsin, found that both lindane and dieldrin were transported in this aquifer. Both of these pesticides showed some tendency for sorption. However, they also were readily leachable from the sands.

The sorption of organics by clay minerals has been reviewed by Bader (1962). He found that various kinds of clay minerals could sorb large amounts of organics and that this sorption was empirically correlated with the cation exchange capacity of the clay. This observation should not be interpreted to mean that the mode of sorption was ion exchange. Rather, it shows that the types of groups that promote cation exchange capacity also promote sorption of organics. The most significant finding of Bader is that clay minerals such as montmorillonite can sorb very large amounts of simple organic compounds. In some cases he computed that some 60 layers of

some organics were sorbed on these clays. He also found that a significant part of this sorption was irreversible, that is, the materials could not be leached from the clay minerals.

Wang (1967) investigated the influence of sorbed organics on the sorption of parathion and DDT on clay minerals. He found that rhodamine B enhanced the sorption of parathion on montmorillonite, while phenol inhibited it. These results point to the possibility that exchange reactions of natural water sediments could be altered by the presence of certain organics in the solution which would be sorbed on the clays.

There is a need for studies that will yield a much better understanding of sorption of species in natural-water sediments. Various studies have shown that natural-water sediments have a very large capacity for the uptake of both organic and inorganic species. Also, previous studies have found that under certain conditions, natural-water sediments can release the sorbed species to the water. Yet, any kind of general relationship to describe these reactions is almost completely lacking. Until this kind of information is available, it will be almost impossible to make any kind of intelligent estimate of the amount of exchange that will take place for a given type of sediment in a body of water.

#### SUMMARY AND CONCLUSIONS

This paper has attempted to show, in a general way, the factors that may be involved in various kinds of exchange reactions between waters and sediments. Basically, the exchange reactions have been broken down into physical control, where hydrodynamics plays the important part in determining the rate of exchange, and biological and chemical control, where the processes bringing the material onto or from the surface of the solid play the important role. Knowledge of exchange reactions and the factors influencing them appears to be extremely meager. In fact, it is almost impossible to make any predictions about the magnitude or rate of exchange for any species in a system that has not been investigated. Hopefully, current research in this area will help to eliminate this deficiency in knowledge within a few years.

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