The release rate of nutrients from river and lake sediments

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Many lakes and rivers have reached levels of eutrophication that make them unacceptable for recreational activities and as municipal and industrial water supply sources. The eutrophic state of these inlet waters is a direct result of an increase in the availability of both organic and inorganic nutrients. This increase in nutrient concentration may be caused by wastewater discharges and urban or agricultural stormwater runoff. Such nutrient sources (referred to as external sources) may be largely eliminated through modern methods of wastewater treatment or through diversion techniques. In some inlet waters, there may also be appreciable internal nutrient sources in the form of benthal deposits.

Benthal deposits are the accumulated sludge bottoms found in many eutrophic lakes and rivers. The natural purification of these benthal deposits affects the quality of the overlying water in two basic ways. First, dissolved oxygen (DO) is removed from the overlying water to fulfill the respiration requirements of the aerobic bacteria within the aerobic layer and to satisfy the immediate oxygen demand of the reduced substances emanating from the deeper anaerobic layer; second, organic substances and a variety of nutrients, which include phosphate and ammonia, are concurrently released into the overlying water.[1-3] These releases may be sufficient to maintain the eutrophic state of an inlet water long after external sources have been eliminated.

In view of the important role that benthal deposits play in the nutrient budget of inlet waters, long-term experiments were initiated to study the release rates of nutrients to the overlying water and to measure the oxygen uptake rate of benthal deposits. The benthal deposits were collected from the Muddy River in Boston, Mass., and from Lake Warner, a eutrophic lake near Amherst, Mass.

Experimental Model

The effects of benthal deposits on the overlying water have been studied by many previous investigators, using both batch and continuous laboratory systems. In view of the disadvantages inherent in batch systems,[3] a continuous flow model was adopted in this investigation. The model chosen had several airtight reactors that contained a layer of benthal deposits, the remaining reactor volume being completely filled with water. The overlying water was mixed continuously so that it had properties identical to those of the effluent water. The model may best be described as being continuous with respect to the overlying water and as being batch with respect to the benthal deposits.

This model enabled the investigators to study the effects of different environmental conditions on the release rates of nutrients and the oxygen uptake rates of benthal deposits. To calculate the nutrient release rates and the oxygen uptake rates, a material balance was devised for each reactor.[3] Thus the oxygen uptake rate, D_B in milligrams per hour per square meter, was calculated by applying the DO data from the experiment to the following form:

$$D_B = \left(\frac{C_0 - \dfrac{C_{n+1} + C_n}{2}}{T} - \frac{C_{n+1} - C_n}{t} \right) \frac{V}{A}$$

in which

C_0 = DO in influent, mg/l;
C_n = DO in effluent at time n, mg/l;
C_{n+1} = DO in effluent at time $n + 1$, mg/l;
V = volume of overlying water, l;
A = surface area of sludge bottoms, sq m;
t = time interval n to $n + 1$, hr; and
T = detention time, hr.

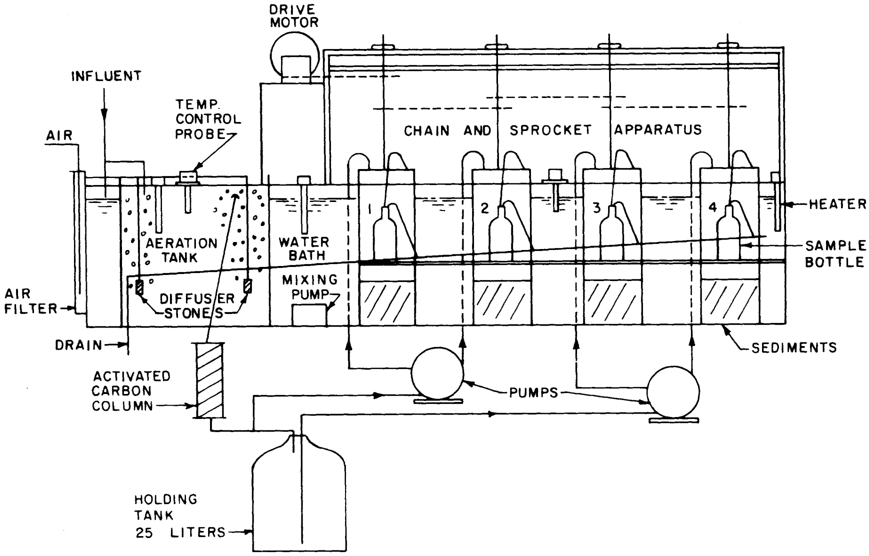

FIGURE 1.—Experimental apparatus.

The release rates of the nutrients were calculated in a similar manner.

Experimental Apparatus

The experimental apparatus, built specially for this study, consisted of eight airtight reactors in two separate water baths. The first water bath contained four Plexiglas cylinders, which are hereafter referred to as Reactors 1, 2, 3, and 4 and are shown in Figure 1. The second bath contained four 10-l Pyrex, wide-mouth bottles, hereafter designated as Reactors 5, 6, 7, and 8. In both water baths, the temperature was controlled by submersible electric heaters coupled to thermoswitches. The tank water was continuously mixed by a circulation pump to prevent thermal gradients from forming within the tank.

Reactors 1 through 4 were 6-in. (15.2-cm) inside diam Plexiglas cylinders, were 13-in. (33-cm) long, and were sealed with a top and bottom plate 0.5-in. (1.27-cm) thick to maintain airtight conditions. Figure 2 shows a cross section of the reactors used in this investigation. Mechanical mixing was continuous at 12.4 rpm, which proved to be sufficient in maintaining completely mixed conditions in the overlying water without disturbing the benthal deposits. Reactors 5 through 8 had no provision for mechanical mixing. The influent to these reactors was discharged just over the mud surface, and the effluent was collected from the top of the reactor, as is shown in Figure 2. The effluent from all the reactors flowed through biochemical oxygen demand (BOD) bottles, which provided the samples for the different analyses required in the experiment.

The most important objective of this experiment was to study the effect of DO concentration of the overlying water on the release rates of nutrients from the benthal deposits. In order to control the oxygen concentration in the influent to each reactor, Boston City tap water was first aerated in a tank submerged in the water bath, as is shown in Figure 1. The detention time in this tank was sufficient to bring the water to saturation level with respect to DO for the temperature under consideration. From this tank, the water passed through an activated carbon adsorption column and into a 25-l glass jug. In this jug, the oxygen concentration could be lowered to any level down to zero by purging with high-purity nitrogen gas. From the jug, the water was pumped to the reactors at predetermined flow rates. The system proved reliable in controlling

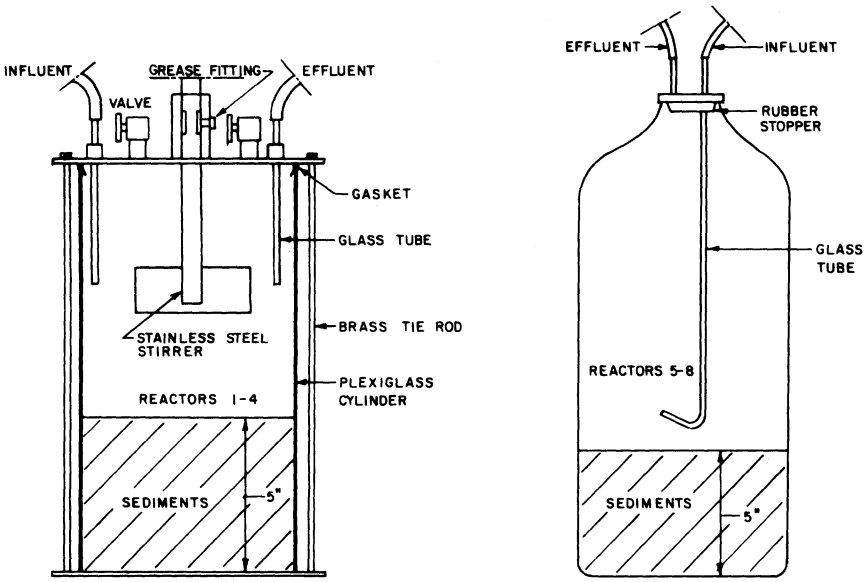

FIGURE 2.—Representative reactors.

the oxygen concentration in each reactor without the need for any chemical addition.

PROCEDURE

The benthal deposits for this investigation were obtained from the Muddy River in Boston and from Lake Warner, near Amherst. The Muddy River is a small, sluggish stream that has been receiving untreated combined sewer overflows for many years. The river water is often dark and turbid, and sludge bottom accumulations of up to 12 ft (3.66 m) have been reported.[4] During the summer months, obnoxious odors are evident along the course of the river. These factors all indicate that the river is highly eutrophic. The sludge samples for the experiment were extracted with a Petersen dredge from a shallow area of about 2 ft (0.61 m).

TABLE I.—Benthal Deposit Characteristics

	Muddy River Sediments	Lake Warner Sediments
Dry solids (%)	42.5	22.6
Volatile solids (%)	11.8	13.4
Total P (mg P/g of dry solids)	1.3	1.1
Total P (mg P/g of dry solids after ashing at 600°C)	1.4	2.5

Lake Warner is also eutrophic, but is surrounded by farm country. The major tributary to the lake is a clean trout stream, the Mill River. The samples were extracted from the lake bottom with an Ekman dredge at a water depth of 3 ft (0.91 m).

All samples were thoroughly mixed before placement in the reactors. The depth of mud in each reactor was kept at approximately 5 in. (12.7 cm); this depth gives results indicative of a natural system.[3] Table I is an analysis of the deposits used in this study.

Once the mud was transferred into the reactors, tap water was gently pumped over the deposits until the reactors were filled. Continuous flow was then maintained through each reactor at predetermined rates.

Throughout each experimental run, the necessary precautions were taken to eliminate any factors other than the benthal deposits that could influence the quality of the overlying water. The units were closed and airtight in order to avoid any interchange with the atmosphere. Direct sunlight was excluded to minimize algae activity. All-flexible tygon tubing was regularly changed as the tubes eventually became coated with biological growth. One of the reactors did not contain any deposits and thus served as a blank in all experimental runs. The effluent from this reactor was used as a basis for calculating the oxygen uptake rates and the nutrient release rates from the benthal deposits. All analyses were performed according to "Standard Methods."[5]

RESULTS

The emphasis of this investigation was on measuring the release rates of orthophosphate phosphorus from natural sediments under different environmental conditions. Concurrently, the release rates of ammonia, iron, and the oxygen uptake rate from the sediments were measured.

In the first experimental run, the effect of oxygen concentration in the overlying water on the release of phosphates from the Muddy River sediments was monitored. Reactors 2 through 4 contained 5 in. (12.7 cm) of sediments; Reactor 1 contained no sediments and thus served as a blank. The temperature was maintained at 20°C throughout the run. The experiment was initiated on a continuous flow basis to a final fill-and-draw sample phase. During the fill-and-draw phase, a daily water sample was taken from each reactor for analysis, and an equal volume of tap water was added to the reactor. Thus this phase may be described as being batch with respect to both the overlying water and the benthal deposits. Reactors 2 and 3 were maintained under anaerobic conditions, beginning with the fill-and-draw phase. Nine days later, both units reached the apparent steady-state level of 1.9 to 2.1 mg PO_4-P/l in the overlying water, as is shown in Figure 3. Concurrently, aerobic conditions were maintained in Reactor 4 during the fill-and-draw phase. During this aerobic cycle, the steady-state concentration was 0.055 mg PO_4-P/l in the overlying water. After 7 days, Reactor 4 was allowed to become anaerobic. The phosphate concentration then increased in Reactor 4 as it had in Reactors 2 and 3 (see Figure 3). Because of technical problems, the experiment was terminated early. The experimental run indicated that the maximum phosphate concentration in water in contact with the Muddy River sediments will be 2 mg/l when the oxygen concen-

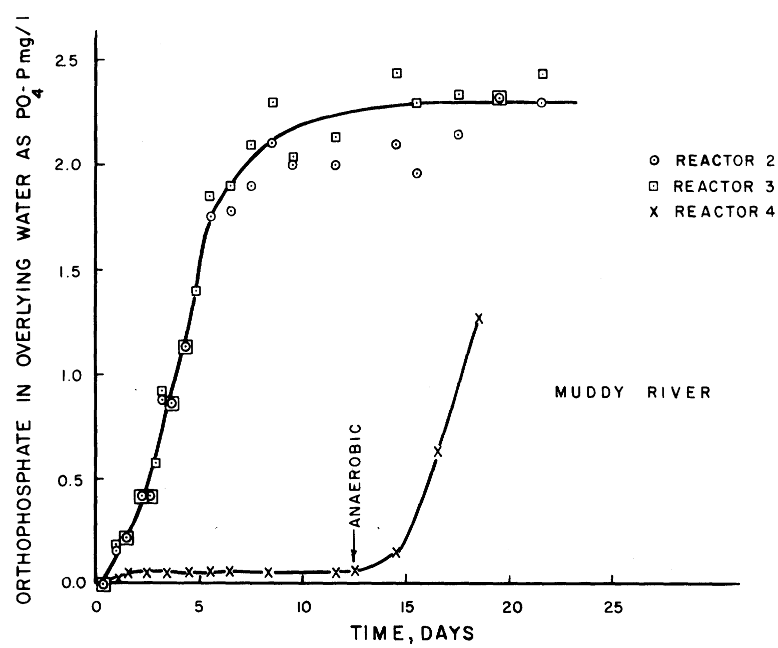

FIGURE 3.—Phosphate concentration in overlying water in contact with river sediments.

tration of the overlying water is zero. Concurrently, it was demonstrated that the maximum ammonia nitrogen concentration would be between 3 and 6 mg NH_3-N/l.

Once this maximum phosphate concentration was determined, a second experimental run was initiated to measure the phosphate release rate from sediments under aerobic and anaerobic conditions. The water bath temperature for Reactors 1 through 4 was maintained at 24°C and for Reactors 5 through 8 at 30°C. The release rate for Reactor 2 is shown in Figure 4. The initial high values are caused by the disturbance of the benthal deposits when the reactors are first filled with water. The phosphate release rate decreased to 0.3 mg PO_4-P/hr/sq m after 10 days under aerobic conditions. At this time, the overlying water was made anaerobic. Immediately, the release rate jumped to a maximum of 3.3 mg PO_4-P/hr/sq m and remained at that level for approximately 3 days. Under continuing anaerobic conditions, the release rate dropped in a stepwise fashion to 2.0 and then to 1.1 mg PO_4-P/hr/sq m. When conditions were made aerobic, the release rate was stabilized at a value of about 0.3 mg PO_4-P/hr/sq m. Figure 4 also shows that the release of iron is closely related to the release of phosphates from sediments. A similar run was made with Reactor 5, and the results are shown in Figure 5. The release pattern is similar to that of Reactor 2, but the magnitude of the release rate is greater. This may be partly the result of the temperature difference or the nature of Reactor 5, in which there was no mechanical mixing.

In the release of nutrients from sediments, biological activity in the sediments may have a pronounced effect. In addition to intermixing the sediments, organisms may alter the thermodynamics and kinetics of exchange reactions by both direct and indirect mechanisms. In general, bacteria play a dominant role in biological transformations.[6] To assess the effect of biological activity on the phosphate release rates, a new experiment was initiated by using sediments from Lake Warner.

The benthal deposits from Lake Warner were placed in Reactors 3 and 4. The deposits in Reactor 4 were thoroughly mixed with 5 g of dihydrostreptomycin sulfate, whereas the influent water to this reactor contained approximately 125 mg/l of this antibiotic. This concentration proved to be adequate in limiting bacterial

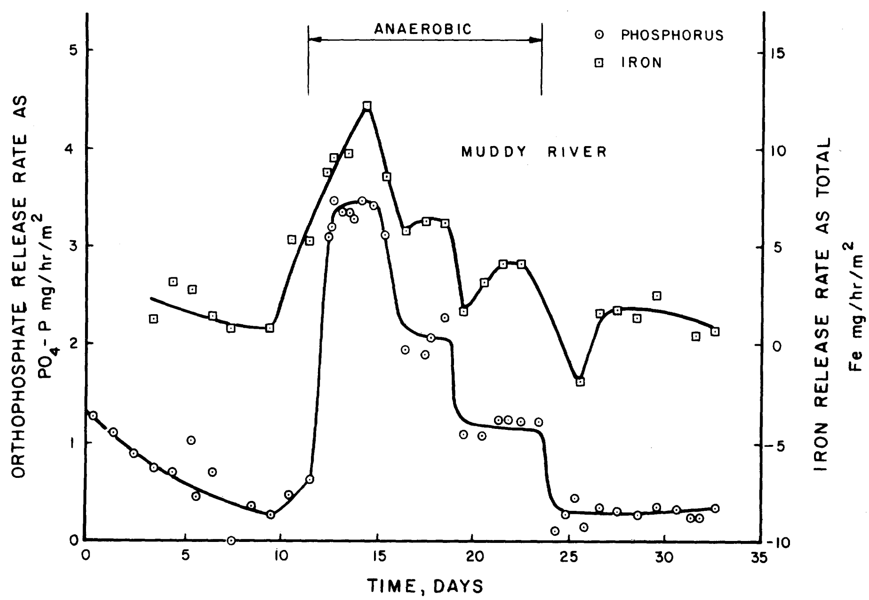

FIGURE 4.—Release rates of phosphates and iron from river sediments.

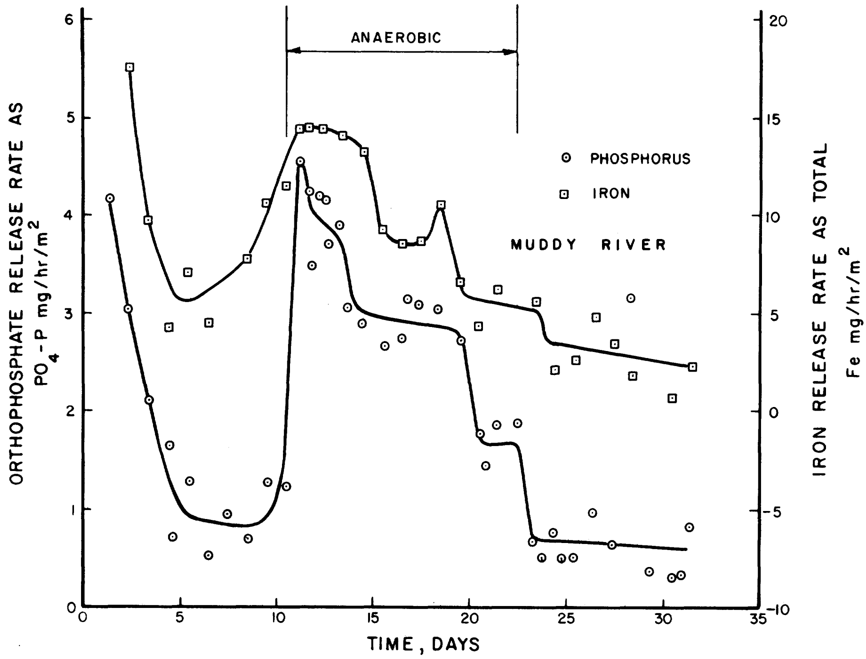

FIGURE 5.—Release rates of phosphates and iron from river sediments.

activity. As a result, the sediments in this reactor compacted to a greater degree than the sediments in the other reactors. There was neither gas production nor sludge worms in the upper layer of the altered deposit. In the other reactors, sludge worms and their tracks were clearly visible in the upper 0.5 to 2 in. (1.27 to 5.08 cm) of mud; there was also evidence of occasional deeper burrowing.

Figures 6 and 7 show the phosphate and total iron release in milligrams per hour per square meter for Reactors 3 and 4, respectively. In Figure 6, there is an immediate increase in the phosphate release rate from almost zero to 0.8 mg PO_4-P/hr/sq m when conditions are first made anaerobic. As conditions remain anaerobic, the release rate increases to a maximum of 1.15 mg PO_4-P/hr/sq m and then drops to about 0.1 mg PO_4-P/hr/sq m when conditions are made aerobic again. Figure 7 shows that, when biological activity was arrested, there was a delay of about 7 days after anaerobic conditions began before an appreciable increase in phosphate release was noted. As conditions remained anaerobic, the release rate increased to a maximum of 1.2 mg PO_4-P/hr/sq m. When conditions were made aerobic, the release rate immediately dropped, as is shown in Figure 6. In both Figures 6 and 7, the relationship between the release rate of phosphates and that of iron is apparent.

The release rate of ammonia nitrogen was measured concurrently with the release of phosphates from both the lake and the river sediments. Figure 8 shows the release rate to be about 5 mg NH_3-N/hr/sq m for Lake Warner and about 15 mg NH_3-N/hr/sq m for the Muddy River sediments. The variations in DO concentrations on the overlying water had no effect on the release rate of ammonia from both sediments. The ammonia release rate did show a slight decrease with time. This decrease is probably a result of the nature of the experimental model, which was batch with respect to the sediments.

The oxygen uptake rate of benthal deposits was measured in all experimental runs. The oxygen demand of the Muddy River deposits averaged 0.078 g/hr/sq m for the first experimental run and 0.113 g/hr/sq m for the second run. This dif-

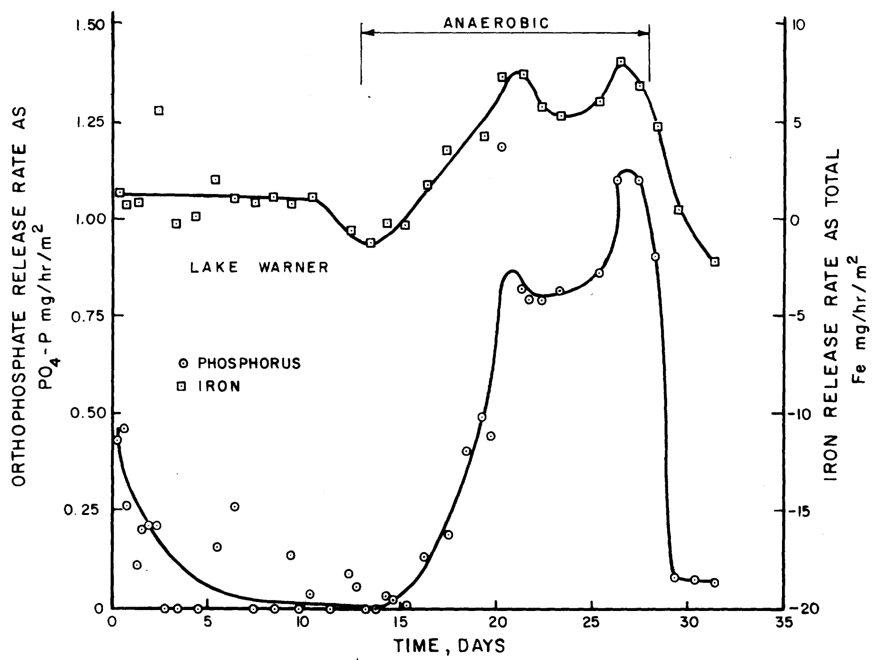

FIGURE 6.—Release rates of phosphates and iron from lake sediments.

ference may be caused by the difference in temperature between the first and the second run. The oxygen uptake rate, as measured in this study, is a result of the oxygen demand of the aerobic bacteria in the mud surface and of the immediate chemical demand of anaerobic decomposition end products emanating from the deeper sludge layers. Both of these mechanisms will be affected by temperature

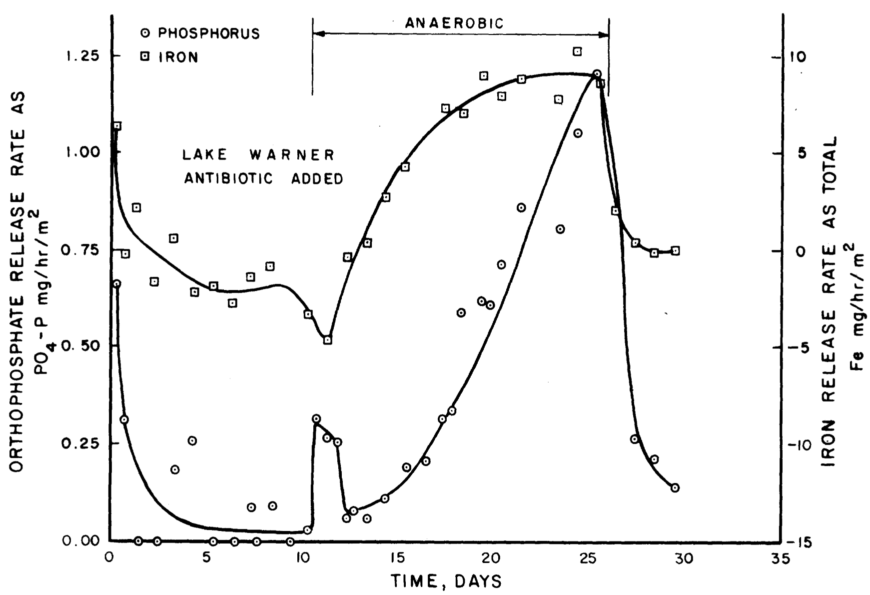

FIGURE 7.—Release rates of phosphates and iron from lake sediments.

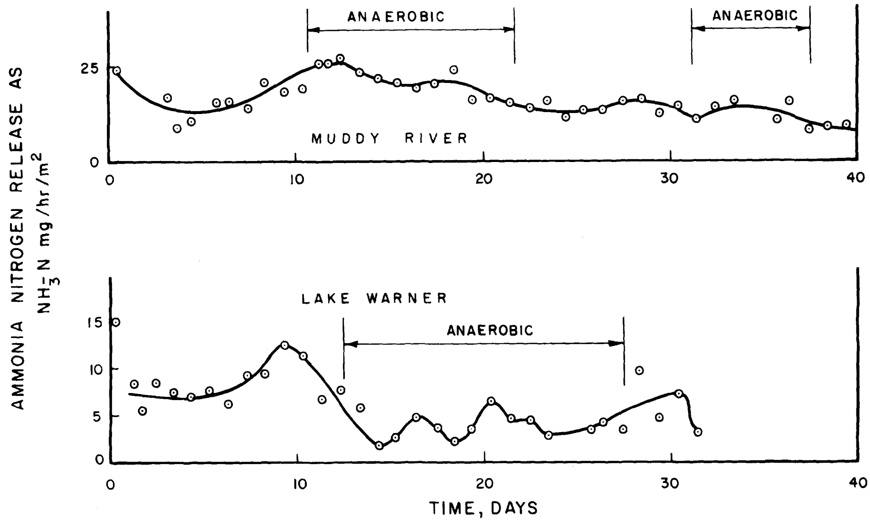

FIGURE 8.—Release rates of ammonia nitrogen from sediments.

variations. The Lake Warner sediments had an oxygen demand of 0.072 g/hr/sq m. In addition to exerting an oxygen demand, sediments release organic material that contributes to the flowing BOD load. The release rate of organics as measured by chemical oxygen demand (COD) averaged 0.02 g/hr/sq m. This shows that the effect of benthal deposits on the DO profile of rivers will be mainly through the oxygen uptake rate rather than through the contribution to the flowing BOD load.

When the release rates of metals were measured, it became evident that only the release rate of iron was of any significance. Figures 4, 5, 6, and 7 clearly show how the release rate of iron varies with the oxygen concentration in the overlying water. Under anaerobic conditions, the maximum release rate for iron was 14 mg/hr/sq m for the Muddy River sediments and 8 mg/hr/sq m for the Lake Warner sediments. In addition to iron, the release rates of calcium and aluminum were measured. The variation in the concentration of both calcium and aluminum was so small that no trend could be derived from the data.

DISCUSSION

In sediments, phosphorus may exist as calcium phosphate, organic phosphorus, orthophosphate dissolved in the interstitial water, aluminum and iron phosphate compounds, and as phosphates adsorbed on silicates.[7] In the natural purification of these sediments, phosphate release from organic forms may occur through dephosphorylation by the phosphatase enzymes of the various microorganisms involved. In the degradation of organic matter, organic and inorganic acids are also formed, which may effectively dissolve inorganic phosphate compounds. A number of organic acids may also act as chelating agents, complexing calcium, iron, manganese, and aluminum. Such reactions result in additional solubilization of phosphorus.[8] The resulting mineralized phosphorus may be released to the overlying water or retained by the sediments. Though the exact retention mechanism of phosphorus by the sediments is not known, it is believed that the aerobic layer of sediment plays a major role. When such an aerobic layer exists, it possesses a certain capacity for adsorption, by which many of the nutrients including phosphorus are retained by the sediments.

The existence of the aerobic layer in sediments depends on the oxygen concentration in the overlying water. By using the vertical distribution of the electrode potential in benthal deposits, many investigators have shown that the aerobic layer may not be more than a few millimeters deep.[2, 3, 9] Below this depth, conditions are anaerobic. Figure 9 shows that the electrode potentials in the anaerobic layer are not affected by the level of oxygen concentration in the overlying water. This suggests that changes in the oxygen concentration of the overlying water will only affect conditions within the top few millimeters of sediments. Therefore, a decrease of oxygen concentration in the overlying water down to zero will eliminate the aerobic layer, destroy the adsorption capacity of the sediments, and result in an immediate nutrient release.[2] Such a series of events seems to have occurred in this experiment.

The orthophosphate release rate from the Muddy River sediments averaged 9.6 mg PO_4-P/day/sq m under aerobic conditions while the release rate increased to a maximum of 96 mg PO_4-P/day/sq m under anaerobic conditions. The Lake Warner sediments showed a release of 1.2 mg PO_4-P/day/sq m under aerobic conditions and a maximum of 26 mg PO_4-P/day/sq m under anaerobic conditions. These values compare favorably with values of past investigators (see Table II).

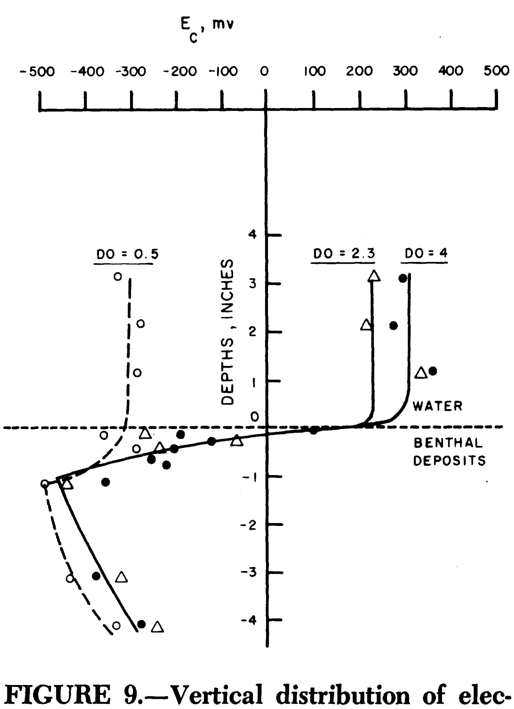

FIGURE 9.—Vertical distribution of electrode potential in deposits.[3] (In. × 2.54 = cm.)

TABLE II.—Phosphate Release Rates from Sediments

Investigator	Sediments	Release Rate (mg PO_4-P/ day/sq m)
Fillos and Molof[3]	Simulated sludge	154 Maximum anaerobic 3 Average aerobic
Capaccio[10]	Muddy River	91 Maximum anaerobic 3 Average aerobic
Vollenweider[11]	Lake Baldeggersee (*in situ*)	9–10 Average anaerobic
Pomeroy *et al.*[12]	Doboy Sound	0.031 Estimated
This study	Muddy River	96 Maximum anaerobic 9.6 Average aerobic
This study	Lake Warner	26 Maximum anaerobic 1.2 Average aerobic

The effects of oxygen concentration on the release rates of phosphates are shown in Figures 4 to 7. Phosphate release increased to a maximum once conditions were made anaerobic; in the case of the Muddy River deposits, it decreased step-by-step, although anaerobic conditions were maintained. In all experimental runs, the phosphate and the iron release rates were closely related. Such data suggest that, although the release mechanics of phosphorus may involve complex reactions, iron plays a dominant role. Comparison of the release rates from Reactors 3 and 4 (bacterial activity was greatly reduced in Reactor 4 by the use of dihydrostreptomycin sulfate) further suggests that the release of phosphates may be controlled by physical-chemical reactions.

All these observations indicate that, during aerobic conditions in the overlying water, phosphates emanate from the deeper anaerobic layers of the benthal deposits toward the surface. When they reach the surface, the phosphates are retained in the aerobic layer in which they are adsorbed predominantly by ferric complexes. When the conditions become anaerobic, the ferric complexes break down and the phosphates are thus released into the overlying water. A high release rate is then observed for a period of time. The stepping down effect is probably a result of the fact that the aerobic layer is slowly depleted from all the available phosphates through complex desorption processes, in which iron complexation reactions play a dominant role.[6]

In addition to the phosphate and iron, the release rates of ammonia, aluminum, and calcium from sediments were measured. The data from all the reactors showed no trend in terms of the effect of oxygen concentration in the overlying water on the release rate of ammonia from sediments. The observation suggests that the overall release rate of ammonia from sediments is probably controlled by some factor other than the oxygen concentration in the overlying water. In the case of aluminum and calcium releases, the change in concentration between the influent and the effluent from the reactors was too small to be measured by the procedures used in the experiment.[5] Therefore, no release rates for aluminum and calcium were calculated.

The oxygen uptake rate of benthal deposits as measured in this experiment includes the respiration requirements of biological activities in the sediments and the immediate oxygen demand of reduced substances, such as ferrous and sulfide ions, emanating from the lower anaerobic layers. The oxygen demand of the Muddy River sediments was measured as 0.078 g/hr/sq m while that from Lake Warner was 0.072 g/hr/sq m. These values are within the range of values reported in the literature.[3] The organic releases were measured by using the COD procedure, which gave an average release rate of 0.02 g/hr/sq m under aerobic conditions. This value is about 25 percent of the oxygen uptake rate. The COD release rate thus reaffirms that benthal deposits affect the DO profile of natural waters mainly through the oxygen uptake rate mechanism.[3]

It is clear from this study that short-duration intermittent anaerobic conditions in the immediate overlying water are capable of causing dramatic increases in the release rates of nutrients from sediments. Such anaerobic conditions may be localized and may result from the oxygen demand of the sediments themselves. Therefore, in any lake management procedure, the sediments must be treated as intermittent sources of nutrients and as a continuous sink for oxygen. Care must be taken to prevent intermittent anaerobic conditions along the water-sediment interface.

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