SIGNIFICANCE OF OXIC VS ANOXIC CONDITIONS FOR LAKE MENDOTA SEDIMENT PHOSPHORUS RELEASE

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Summary

Laboratory leaching tests conducted on Lake Mendota sediments have shown that under oxic and anoxic conditions, phosphorus is released from the sediments to the water. The initial rate of release under anoxic conditions is much more rapid than under oxic conditions; however, over extended periods of time, oxic release approximately equaled that obtained under anoxic conditions. It is believed that oxic release of phosphorus is primarily related to mineralization reactions and that this mode of release plays a much more important role in lake self-fertilization than generally thought.

Another approach used to estimate relative significance of oxic vs anoxic release is one in which an overall mass balance of the total phosphorus within the lake is assessed at intervals of every few weeks over the annual cycle. From this, a total mass of phosphorus present in the water body or parts thereof can be assessed. From estimates of the amounts of phosphorus derived from external sources, it is possible to obtain an estimate of the net flux of phosphorus to and from the sediments. This approach has been utilized in a three-year study of Lake Mendota located near Madison, Wisconsin. This study has shown that there can be substantial phosphorus released from the sediments under oxic conditions which can play a major role in stimulating late spring-early summer blue green algal blooms. Substantial amounts of phosphorus are released from the sediments during the summer under anoxic conditions. Little of this phosphorus reaches the euphotic zone during the summer recreational period except during periods of thermocline migration caused by high winds. The results of both the laboratory and field studies indicate that ferric iron probably plays a relatively minor role in controlling phosphorus release from Lake Mendota sediments.

Introduction

Increasing emphasis is being placed today on controlling excessive fertilization of lakes and impoundments. One of the primary concerns in any control program is that of the role of lake sediments in recycling nutrients. The basic issue is one of whether the sediments of the lake are sinks for phosphorus or do they act as buffers maintaining a certain phosphorus level in the overlying waters.

In order to gain some insight into the potential significance of lake sediments in controlling overlying water phosphorus concentrations, a series of studies has been conducted on Lake Mendota near Madison, Wisconsin. Two experimental approaches have been used. The first involved taking sediment samples into the laboratory and incubating them for a period of time during which phosphorus measurements were made. The other approach involved examining overall phosphorus dynamics in the lake where the total mass of phosphorus present

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in the lake was determined in relation to the annual phosphorus input and removal by the outlet. From the net phosphorus input and the total content of the lake, it is possible to discern the flux of phosphorus to and from the sediments. This paper summarizes the results of a series of studies designed to elucidate the overall role of Lake Mendota sediments in controlling the overlying phosphorus concentrations.

Literature review

The classical limnological model for phosphorus dynamics in lakes and impoundments is one involving the iron cycle where, under oxidizing conditions, ferric iron combines with orthophosphate and is transported to the sediments. Under reducing conditions, ferric iron is reduced to ferrous with liberation of phosphate to the overlying waters. In addition, there is phosphate transport from the water column to the sediments through the sedimentation of planktonic organisms, detrital minerals and precipitates. This model is based primarily on the classical work of Einsele (1936, 1937, 1938a, 1938b, 1941) and Mortimer (1942), conducted in the 1930's and 1940's. A number of other studies conducted since that time (using radioisotopes), principally those of Hayes (1963), have shown that there is very rapid exchange of phosphate among various phosphorus pools in lakes.

Lee (1970) presented a review of the various reactions governing the exchange of materials between water and sediments. He pointed to the importance of mixing processes within sediments, the overlying waters and between the sediments and water in controlling the release of phosphorus and other compounds from natural water sediments. This conclusion was based to a considerable extent on the fact that most lake sediment interstitial water phosphorus concentrations are considerably higher than the overlying water, indicating that the chemical and biological processes associated with the release of phosphorus to the interstitial water were proceeding at a greater rate than the mixing of the interstitial water with the overlying water.

Lee (1970) also reported that the classical picture of well-defined laminae or varves representing annual deposition layers in lake sediments may be a rare occurrence rather than the general situation. It appears that most lake sediments are mixed from a few cm to tens of cm in depth each year as a result of physical, chemical and biological processes. Based on these observations, it was felt that the classical work of Mortimer (1942) on Lake Windermere sediments may not present an accurate representation of the overall phosphorus release from lake sediments because of the experimental approach used which did not provide for an accurate simulation of the mixing processes that occur within the sediments and between the sediments and the overlying waters. It was therefore decided to conduct a series of studies on the release of phosphorus from Lake Mendota sediments under situations where mixing would not be the rate controlling step. A complete description of these studies and a comprehensive review of the literature on the exchange of phosphorus in water and sediments is presented in the Ph.D. dissertation of Spear (1970). Only an overall summary of the approach and results are presented here.

Laboratory studies

Experimental procedure

The experimental procedure for these studies consisted of taking samples of sediments from several locations in Lake Mendota using an Ekman sediment grab sampler. The sediments were placed in a reaction flask into which could be passed nitrogen gas, carbon dioxide, various mixtures of these two gases or air. The anoxic experiments involving N_2 or N_2-CO_2 mixtures were purified to remove traces of residual oxygen. The system was continuously stirred with magnetic stirrer and teflon-coated stirring bar. Distilled water was used as the leaching solution for the majority of the tests; however, after contact with the sediments, the water quickly dissolved some of the calcium carbonate present in the sediments. Therefore, it is best characterized as a calcium-magnesium carbonate leaching solution. The pH of the leaching solution was adjusted by the partial pressure of CO_2 in the gas which passed over the surface of the water-sediment slurry.

Two lakes were studied in this investigation– Mendota, a hard water eutrophic lake located in south central Wisconsin, and Trout Lake, a moderately soft water, mesotrophic lake located in north central Wisconsin. Part of the Lake Mendota data will be presented in this paper. This lake has a surface area of 38 square kilometers and a maximum depth of 24 meters. Thermal stratification becomes well established by late May-early June and persists through September. The hypolimnion becomes anoxic usually about mid-July.

For the anoxic studies it was found that the filtration of the samples of the slurry had to be conducted under anoxic conditions in order to prevent loss of phosphorus in the ferric hydroxide precipitate which rapidly formed upon exposure to air. This was done by passing purified nitrogen gas over the top of a covered funnel. Soluble orthophosphate was measured on all samples as a function of time using 0.45 micron pore size membrane filters to distinguish between soluble and particulate phosphorus. The phosphomolybdate method with stannous chloride as a reducing agent was used for phosphorus measurements in accord with Standard Methods, 12th Ed. (APHA, et al., 1965). Additional details on the experimental procedures are available in the dissertation by Spear (1970).

Results

Sediments were taken from three different locations within Lake Mendota - from the deep hole area (Station 1), from the slope of the deep hole (Station 2), and from University Bay (Station 3). University Bay is separated from the deep hole area by a sill. The sediments from all three areas were taken from depths which are normally below the thermocline during the summer stratification period. These sediments had 62 to 66 percent water, 31 to 36 percent carbonates, 12 to 15 percent organic matter and 51 to 52 percent clastics (defined as the difference between the organic content of the sediments and the carbonate content).

Figures 1, 2 and 3 show the rates of soluble orthophosphate release from these three locations under oxic and anoxic conditions at a temperature of 24°C. Several things are evident from these figures. First, as expected, anoxic release took place much more rapidly, reaching a plateau within about 200 hours after initiation of the leaching experiment. Oxic release, however, while initially slower, did, over the 1200 to 1400 hour incubation period, release soluble orthophosphate which appeared to plateau at approximately one half the concentrations reached in the anoxic tests. It is somewhat surprising to see the relatively large amount of oxic release that took place in these tests since Lake Mendota sediments from these locations typically contain from 10,000 to 20,000 ppm iron (Lee, 1962). It is evident that the ferric iron formed upon aeration of these sediments was not controlling phosphorus release. A number of other similar paired experiments were run by Spear (1970) utilizing sediments from these locations. Examination of the effect of temperature on the rate of phosphorous release under oxic and anoxic conditions showed that the rate of release was markedly affected by temperature under both conditions.

Under anoxic conditions, temperature affected not only the rate of release but also the apparent plateau, with approximately half as much phosphorus being released at 11°C as 24°C. Under oxic conditions the effect of temperature was substantially greater with an eight fold reduction in the rate of release during the first 800 hours. It does appear, however, that over extended periods of time the lower temperature runs could reach the same plateau as the 24°C run.

In order to investigate the potential impact of pH and addition of air on the release of phosphorus from Lake Mendota sediments under anoxic conditions, an experiment was conducted in which the sediments were kept anoxic for approximately 480 hours by bubbling purified nitrogen gas through the solution. At this time the gas used to maintain anoxic conditions was changed to a mixture of N_2-CO_2, which resulted in the pH decreasing from about 8 to approximately 7. Examination of Figure 4 shows that the typical anoxic release pattern was

Figure 1. Phosphorus released from Lake Mendota sediments under oxic and anoxic conditions - Station 1

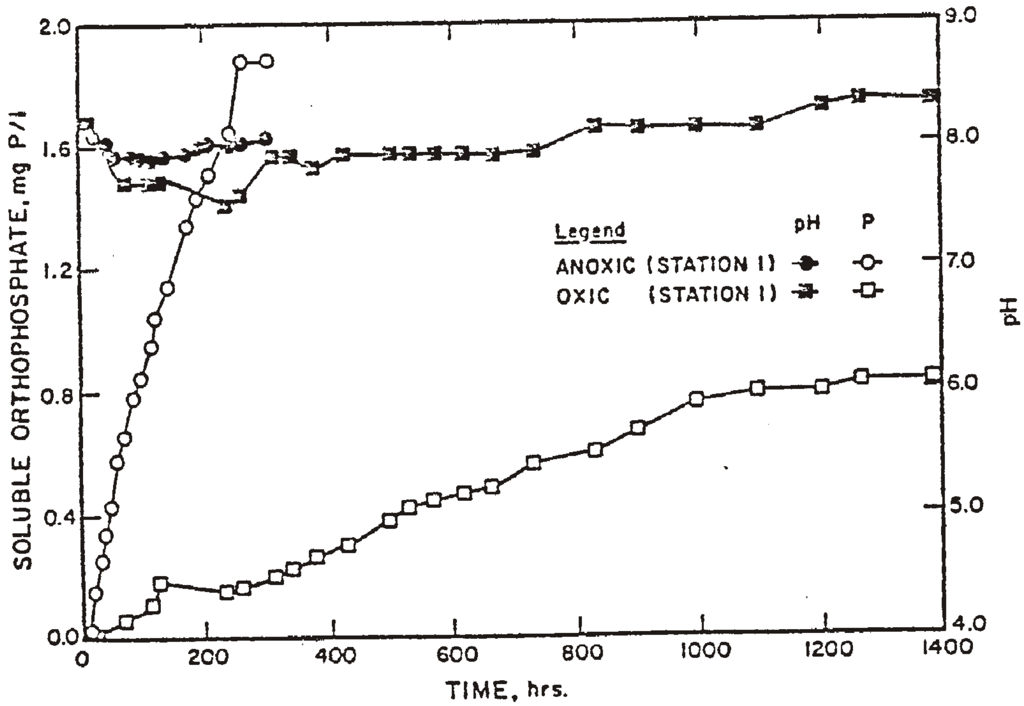


Figure 2. Phosphorus released from Lake Mendota sediments under oxic and anoxic conditions - Station 2

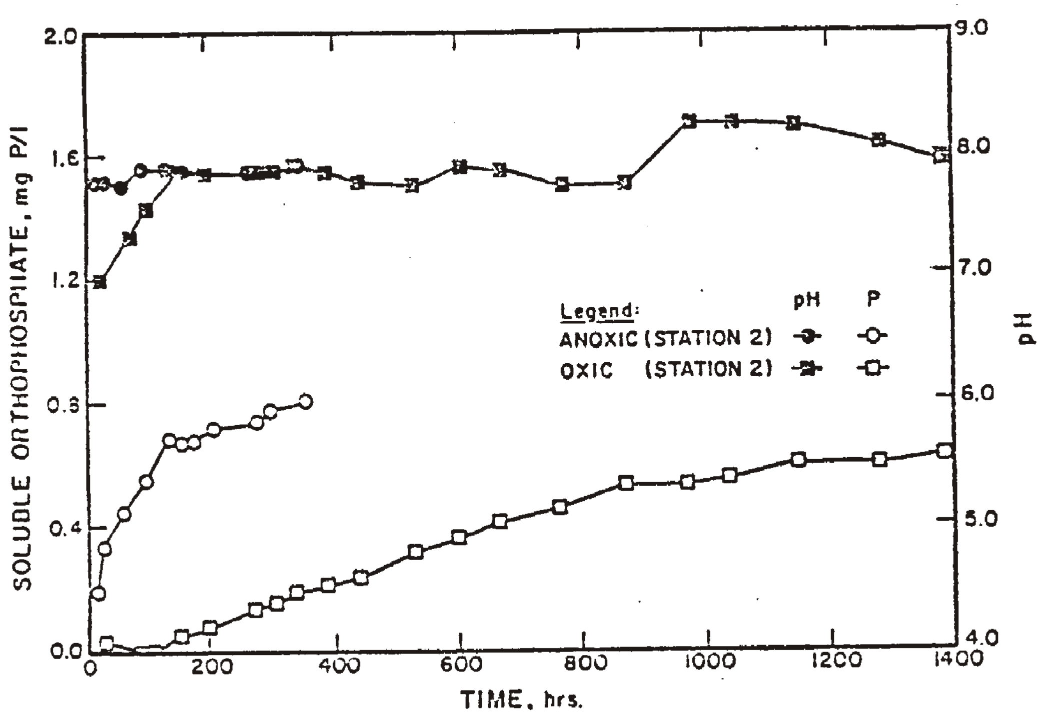


Figure 3. Phosphorus released from Lake Mendota sediments under oxic and anoxic conditions - Station 3

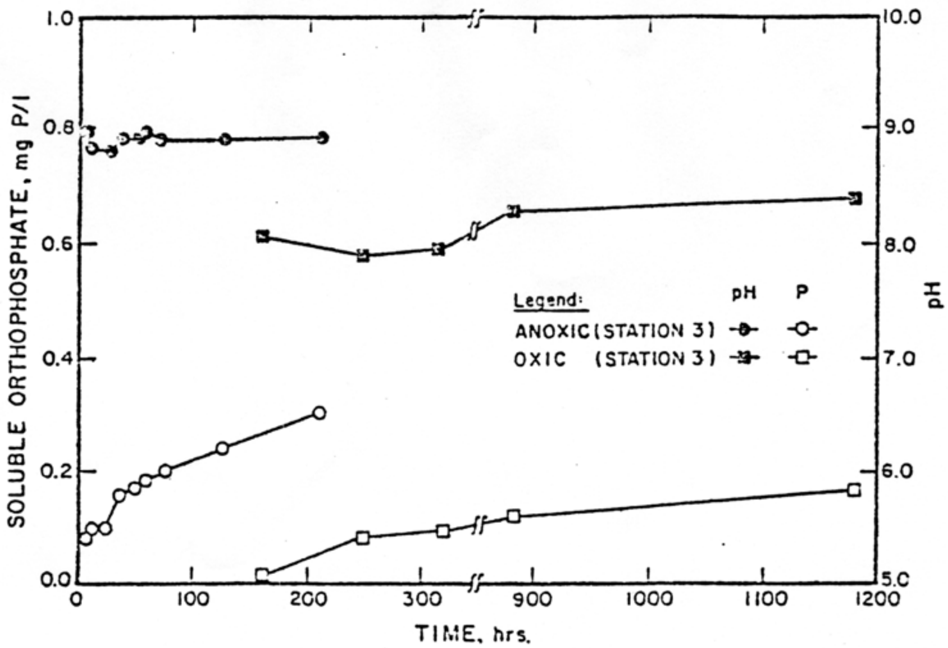
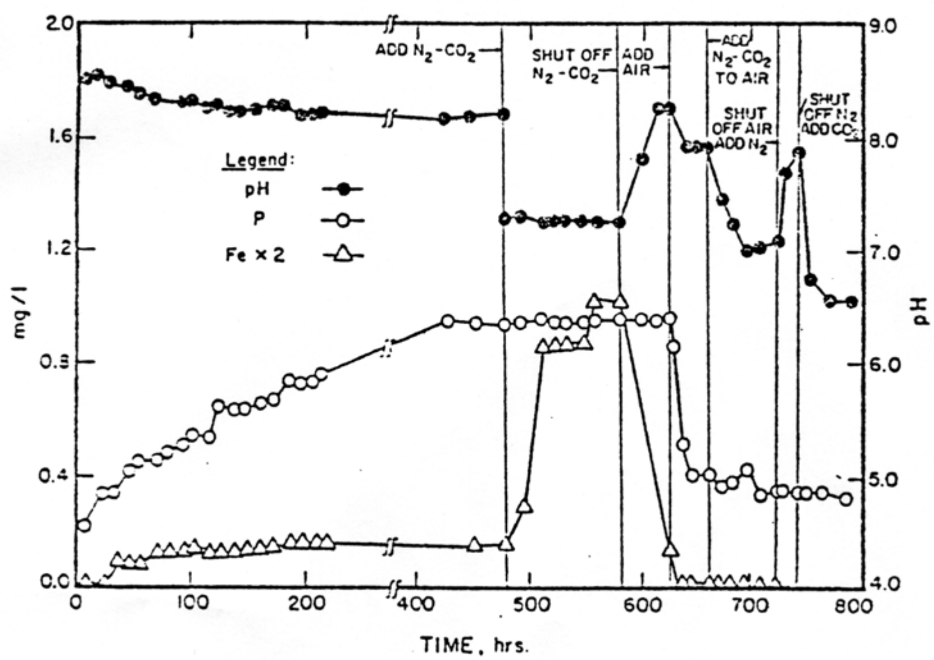


Figure 4. Effect of selected parameters on phosphorus release from Lake Mendota sediments, anoxic-oxic conditions - Station 1



obtained during the first 480 hours. Changing the pH from 8 to 7 had no effect on the orthophosphate content of the solution. It did, however, markedly affect the amount of iron present in solution. At about 620 hours air was introduced into the test system. This resulted in a marked decrease in the orthophosphate and iron. This system was again made anoxic and the pH again adjusted to 7. This time, as in the past, there was no effect on the release of phosphorus.

This experiment demonstrates the classical limnological model for iron and phosphate behavior where under anoxic conditions phosphorus is released with the amount of release independent of pH in the neutral to slightly alkaline region. The introduction of air into the system caused the precipitation of ferric iron with the concomitant removal of the soluble orthophosphate. Based on these experiments, it is clear that the classical limnological model for iron control of phosphate holds for short periods of time. However, with extended periods of time, i.e., hundreds of hours, phosphorus is released under oxic conditions. This release appears to be related primarily to mineralization reactions of organic phosphorus. Measurements of the calcium content of the oxic test showed that it increased throughout the incubation period. This is believed to be due to a solubilization of calcium carbonate present in the sediments. Mineralization reactions result in the production of CO_2 which would interact with the solid calcium carbonate present in the sediments to form calcium bicarbonate. As noted in Figures 1 through 3, the pH during the course of the various tests did not change significantly. The sediments contained approximately 30 percent calcium carbonate and therefore represent a well buffered pH system.

Discussion

The implications of these results to the lake are significant. They indicate that potentially large amounts of phosphorus release could be occurring under oxic conditions. This is somewhat contrary to what is generally believed. If one examines the basis of the general position that anoxic release is of major significance, the conclusion is drawn that the reason for this position is primarily based on the fact that the thermocline acts as a trap for anoxic release. On the other hand, under oxic conditions, the lake is normally well mixed with the result that any phosphorus released from the sediments due to mineralization processes is circulated throughout the water column and therefore not readily detected because of the much greater dilution and uptake by algae.

Interestingly, the rates of phosphorus release under oxic conditions, while slower than anoxic conditions, are still sufficiently rapid to be of significance in internal cycling of nutrients. Also the rates of release under both oxic and anoxic conditions from these sediments are much more rapid than would be expected under quiescent conditions such as those frequently used by various investigators (a sample of sediment placed in a carboy and the phosphorus released to the overlying waters measured as a function of time). The lake probably behaves somewhere between the quiescent conditions and the completely slurried conditions used in these studies. During periods of storms shallow water sediments often are readily suspended and thereby provide the opportunity for oxic release of phosphorus associated with the particulate material as well as from the interstitial waters.

Since it is impossible to simulate the hydrodynamic conditions that exist in lakes in the laboratory with a known degree of reliability, it was felt that further laboratory studies on the potential significance of the overlying waters would be of limited value. Therefore, the whole lake mass balance approach was used, the results of which follow.

Field studies-mass balance

It was felt that the best approach to take for assessing the actual role of lake sediments in controlling phosphorus in the overlying waters is the mass balance approach where the total phosphorus present in the water column can be examined as a function of time. By correcting the total water column phosphorus for the net phosphorus input, it should be possible to determine the net fluxes of phosphorus to and from the sediments. This was the approach used by Sonzogni (1974). At periodic intervals over a three year period measurements were made of the total phosphorus content of Lake Mendota waters. Also, soluble orthophosphate was measured as well as various nitrogen species. This paper will present a summary of the phosphorus data. The complete data are available in Sonzogni (1974).

Coincident with measurement of the total phosphorus content of the lake, estimates were made of the phosphorus input to the lake. Table 1 presents a summary of these estimates. According to these estimates Lake Mendota receives approximately 60,000 kg/yr of total phosphorus of which slightly over half is in the dissolved reactive form. The principal source of phosphorus for this lake is rural runoff, with a substantial part of this runoff derived from dairy manure spread on frozen land. The amount of phosphorus contributed to the lake each year via this source is highly variable, dependent primarily on the climatological characteristics of the spring snow melt period. If the spring rains and snow melt occur at a time when the subsoil is frozen, then most of this phosphorus is transported over the surface of the soil to nearby tributaries which eventually reach Lake Mendota. However, under conditions where the subsoils are not frozen at the time of snow melt and spring rains, a substantial part of the phosphorus will go into the soil and become fixed on soil particles. In order to account for the yearly variability of phosphorus loading, a range of possible values is given in Table 1 for total phosphorus loading.

Table 1 is based on prediversion wastewater figures. In 1971 the wastewaters from several small towns located in the Lake Mendota watershed were diverted around the lake. Following diversion, wastewater discharges of total P decreased from 24 percent of the total (Table 1) to approximately 2 percent. The rural runoff post-diversion figures increased to 63 percent of the total P input to the lake.

Sonzogni (1974) has estimated that approximately 15,000 kg of total P leaves Lake Mendota each year via its outlet. Of this, approximately 11,000 kg is in a dissolved reactive (DRP) form. Therefore, the net phosphorus input to Lake Mendota each year is on the order of 46,000 kg/yr total P (TP).

Procedure

Water samples were taken in the region of the deep hole at 1 m intervals during the spring, summer and fall and at 2 m intervals during the winter. Measurements were made of Secchi depth, dissolved oxygen and temperature. The lake was sampled approximately weekly, except during the winter, when sampling was conducted at bi-weekly intervals. The sampling program was initiated in the summer of 1970 and continued until July, 1973. Dissolved reactive phosphorus was measured by filtration through 0.45 µm pore size membrane filters followed by the Murphy and Riley (1952) procedure. Total phosphorus was initially digested with persulfate in accord with the procedures presented in Standard Methods, 13th Ed. (APHA *et al*., 1971).

When a thermocline was present, the depth of the thermocline was determined by examining the temperature and chemical profile. In subsequent computations of hypolimnion volume, the metalimnion was considered to be part of the hypolimnion. During periods of ice cover the lake was arbitrarily divided into two layers consisting of the top 17 m and bottom 5 m.

Figures 5 through 8 present the results of the total and dissolved reactive phosphorus content of Lake Mendota from August, 1970 through November, 1973. In addition, where appropriate, the two forms of phosphorus present in the hypolimnion and epilimnion are also presented. Table 2 presents the average content per month for the study period for each of the two

Table 1. Summary of pre-diversion phosphorus sources for Lake Mendota

Source	DRP	TP	%Estimated Contribution
	kg/yr		TP
Wastewater discharge	9,500	15,000	24
Urban	4,000	7,000	11.5
Rural	15,000	30,000 (4,500-46,500)	48.5
PPt	1,000	1,000	1.5
Dry fallout	500	3,000	5
Groundwater seepage	300	300	0.5
Base flow	5,500	5,500	9
Woodland runoff	0	0	0
Marsh drainage	0	0	0
Total	35,800	61,800	

After Sonzogni (1974).

Table 2. Mean monthly, winter and annual phosphorus contents for Lake Mendota

Mean Content	1970-1971		1971-1972		1972-1973	
	kg x 10^{-4}		kg x 10^{-4}		kg x 10^{-4}	
	DRP	TP	DRP	TP	DRP	TP
Aug	5.7	7.0	5.3	6.9	6.2	8.1
Sept	5.5	7.2	6.3	8.0	6.2	7.6
Oct	5.8	7.2	5.6	7.3	6.4	7.7
Nov	5.3	5.9	5.5	6.9	6.1	6.9
Dec	4.9	5.8	5.2	6.4	6.2	6.9
Jan	5.2	5.9	4.2	6.0	6.2	7.1
Feb	5.0	5.8	4.3	5.4	6.5	7.1
March	5.3	6.1	4.7	5.6	7.2	8.4
April	1.7	4.6	4.9	6.4	7.1	8.1
May	1.9	3.0	4.6	6.0	6.4	7.2
June	3.6	4.8	4.2	5.8	4.5	6.6
July	4.8	6.3	5.1	6.9	3.9	6.2
Winter[a]	5.1	5.8	4.6	5.9	6.3	7.0
Annual[b]	4.6	5.8	5.0	6.5	6.1	7.3

[a]Average for Dec, Jan and Feb

[b]Average for Aug through July

After Sonzogni (1974)

forms of phosphorus measured. Examination of these figures and this table shows that the total phosphorus in August 1970 and 1971 was .approximately 7 x 10^4 kg. Examination of the three years of record shows that approximately 80 percent of the phosphorus present in the lake at any time is in the dissolved reactive form.

The greatest year-to-year variability of the phosphorus at any time of the year occurred shortly after ice-out. In the spring of 1971 a massive diatom bloom occurred in Lake Mendota which caused the total phosphorus content of the lake to decrease from slightly over 5 x 10^4 kg to about 1.7 x 10^4 kg in association with the settling of this bloom. Following the bloom, Figure 6 shows a more or less linear increase in phosphorus through September. In the period mid-April through early July the bottom waters of the lake were oxic. This year was a particularly dry year in which there was below normal precipitation in the spring and early summer. Lake Mendota had the best water quality during that period that it has had in many years. This appears to be the result of the diatom bloom tying up the phosphorus in the cells and transporting it to the sediments. It is evident from Figure 6 that there was significant oxic phosphorus release arising from mineralization reactions of the phosphorus present in the sediments in the form of algal cells.

Examination of the spring 1972 and 1973 shows that the 1971 pattern was not repeated. In 1972 ice-out was accompanied by an increase in the phosphorus content, probably due to transport from the lake's watershed. In 1973 the total phosphorus content of the lake was the greatest of any of the four spring seasons monitored. This spring was one of the wettest springs in many years and the high phosphorus represents transport from the watershed.

During periods of summer stratification, usually beginning in late August, there is an inverse relationship between the total mass of phosphorus in the hypolimnion compared to the epilimnion. This is the result of thermocline migration, where during this time rapid downward movement of the thermocline results in the transport of phosphorus from the hypolimnion to the epilimnion. This downward movement was accompanied by a decreased hypolimnetic volume accounting for the decrease in the total mass of total and soluble orthophosphate present in the hypolimnion during this time.

The year-to-year variability in the phosphorus content of the lake as shown in Table 2 is strongly influenced by algal population dynamics and input from the watershed. The primary factor controlling the phosphorus input to Lake Mendota is the precipitation and snow melt with the associated runoff to tributaries of this lake. It is important to emphasize that during this period Lake Mendota received in excess of 98 percent of the total phosphorus input from diffuse sources such as urban stormwater drainage, rural runoff, atmospheric precipitation and dustfall. Interestingly, the annual average total phosphorus content of Lake Mendota, 4 to 6 x 10^4 kg, is approximately equal to the normal annual input. This results in phosphorus residence time for Lake Mendota of about one year (Sonzogni et al., 1976).

During the summer stratification period the primary controlling factor for algal blooms has been found by Stauffer and Lee (1973) to be the passage of cold fronts, in which high intensity winds tend to sharpen and lower the thermocline. Each time the weather frontal system passed, there was generally a period of high intensity wind which sharpened the thermocline and moved it downward, 0.5 to 1 m. This migration downward results in the transfer of sufficient amounts of available phosphorus from the hypolimnion to the epilimnion to cause a phytoplankton bloom about a week after passage of the front.

Some of the variability noted in Figures 5 through 8 during the summer reflects these algal blooms. Following the bloom, Secchi depth increases and total phosphorus content decreases due to the uptake of phosphorus by the algae and their subsequent settling to the bottom of the lake.

Table 3 presents an estimate of the net increase of the total phosphorus content of Lake Mendota during summer stratification for 1971, 72 and 73. In 1971 the average daily total phosphorus increase was about 187 kg/day; for 1973 it was approximately half this amount (92 kg/day). These differences probably reflect the fact that 1971 was a somewhat peculiar year in terms of typical phosphorus input from the watershed and the massive diatom bloom that occurred at ice-out. The bloom probably removed the phosphorus entering the lake in the spring providing the opportunity for an overall greater increase in phosphorus during summer stratification than was possible in the other years. Also, the overturn, which usually occurs in October, did not result in a significant change in the total phosphorus content of the lake. This is significant since classical models of phosphorus dynamics indicate that

Figure 5. Dissolved reactive phosphorus and total phosphorus content of Lake Mendota , 1970

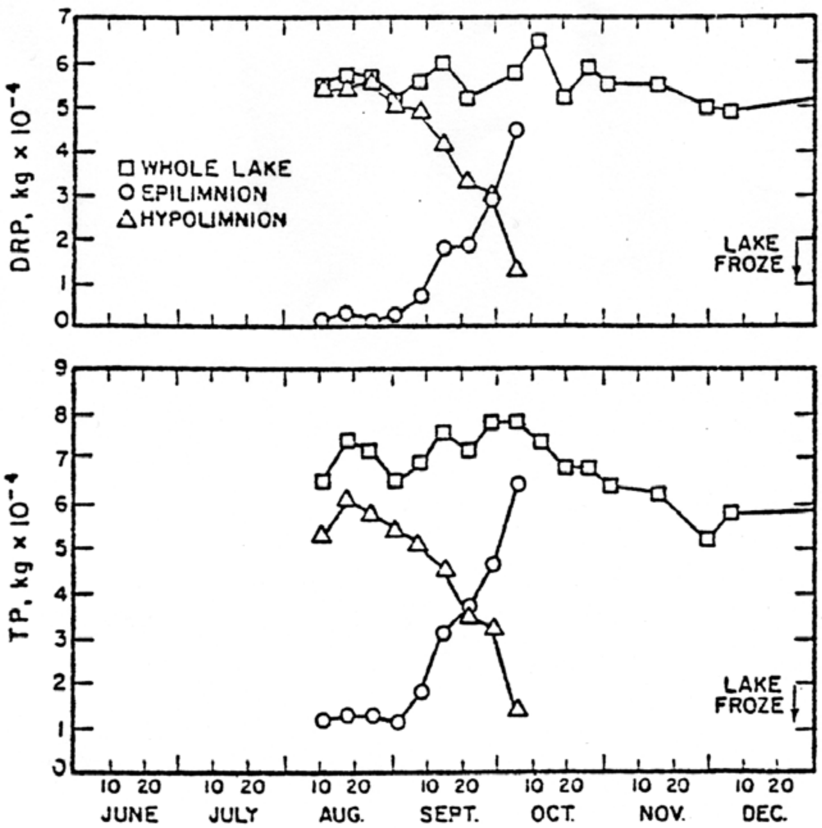


Figure 6. Dissolved reactive phosphorus and total phosphorus content of Lake Mendota, 1971

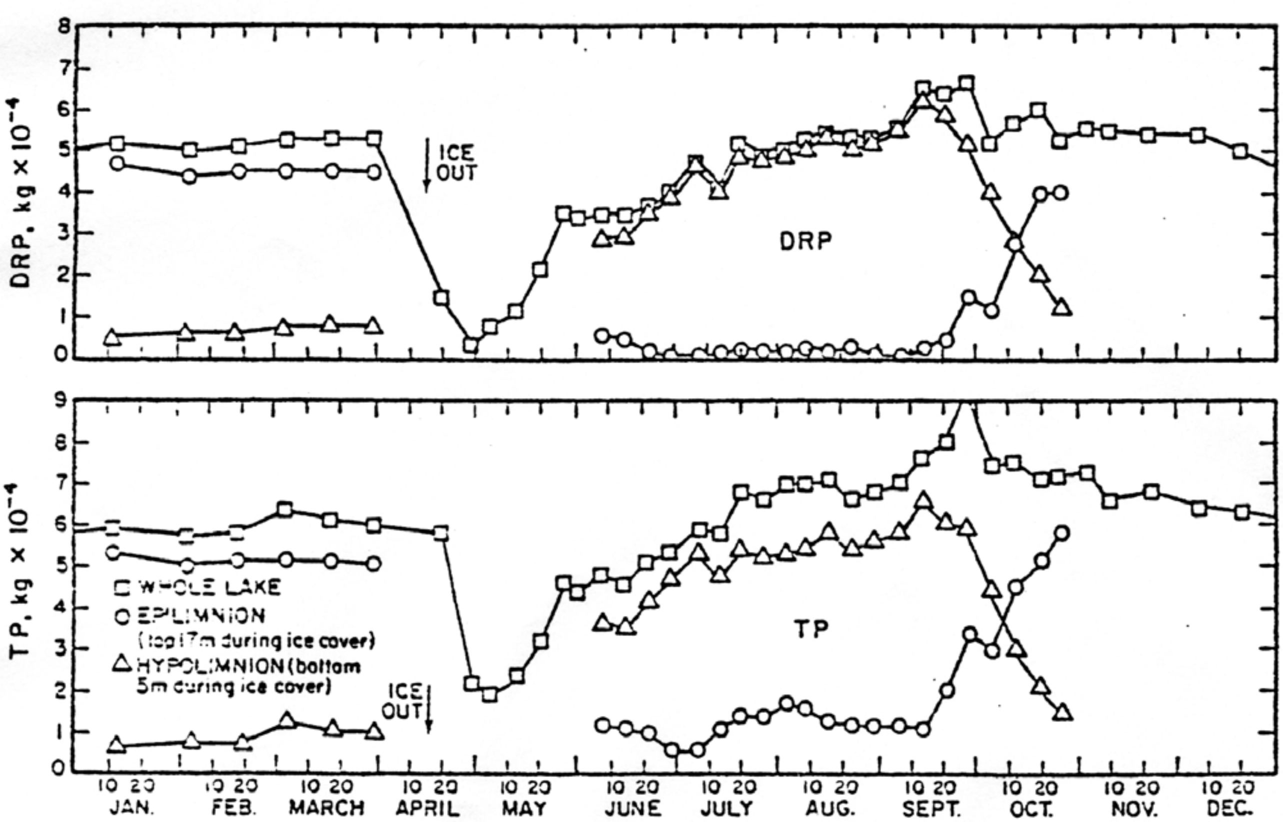


Figure 7. Dissolved reactive phosphorus and total phosphorus content of Lake Mendota, 1972

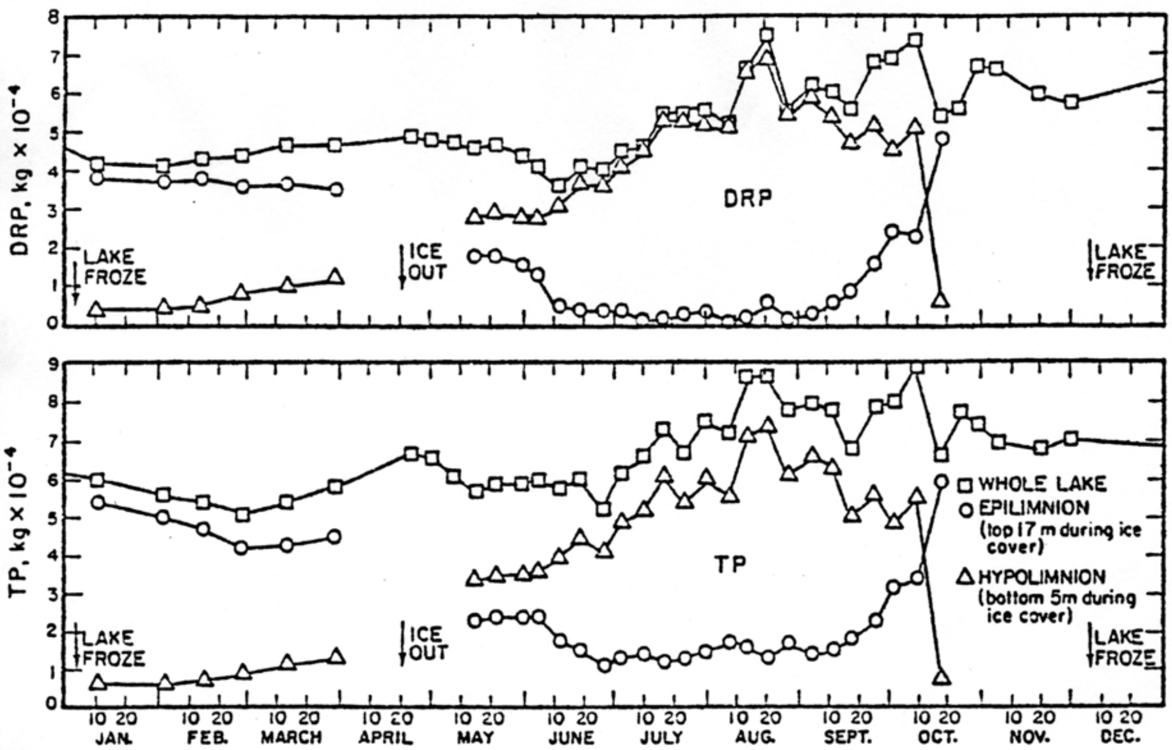


Figure 8. Dissolved reactive phosphorus and total phosphorus content of Lake Mendota, 1973

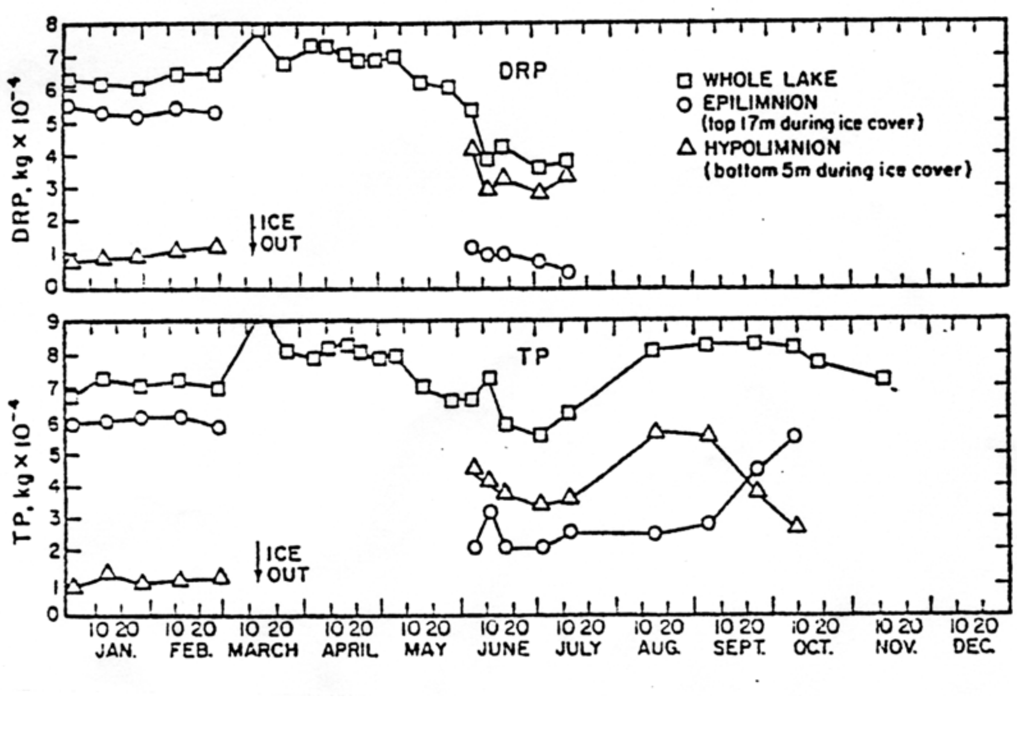


Table 3. Net increase in the TP content of Lake Mendota during summer stratification

Year	Duration of stratification (days)	TP increase (kg)	Average daily TP increase (kg/day)
1971	155	29,000	187
1972	146	16,000	110
1973	120	11,000	92

After Sonzogni (1974).

phosphorus tends to be removed during fall overturn in association with the oxidation and precipitation of iron.

Discussion

The mass balance approach for Lake Mendota and the laboratory results of Spear (1970) both indicate that under certain conditions, mineralization processes occurring under oxic conditions can result in significant release of phosphorus from lake sediments. As discussed earlier, in both the laboratory and in the lake, the ferric iron present in the surface sediments does not appear to be controlling the release of soluble orthophosphate. It further appears that at fall overturn the mixing of the ferrous iron-rich hypolimnetic waters in Lake Mendota does not have a major influence on the total phosphorus present in the water column.

The phosphate scavenging power of hydrous ferric oxide appears to be dependent on a number of factors. It has been found (Lee, 1975) that the formation of the ferric hydroxide floc in the presence of the phosphate was much more effective than a preform floc. This phenomenon likely accounts for the fact that the ferric hydroxide floc is formed relatively rapidly upon aeration of the sediments and therefore the phosphorus that is released under periods of days to weeks later comes in contact only with an aged floc. The same kind of phenomenon would be occurring in the surface sediments where the overlying waters are oxic.

Conclusions

It is concluded from these studies that at least for Lake Mendota sediments and quite possibly for many other lake sediments, the classical limnological model of ferric iron controlling phosphorus release from sediments and phosphorus content of the overlying waters is inappropriate to explain major phosphorus fluxes within the water body. It is further evident that while the sediments of lakes represent potentially significant sources of phosphorus over limited periods of the year, on an annual cycle the sediments of most lakes are sinks for phosphorus. Therefore, significant reductions of the input phosphorus from external sources will likely result in significant improvement in water quality arising from a decrease in the frequency and severity of noxious algal blooms in those water bodies where phosphorus is the key limiting nutrient or can be made so by input reduction.

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