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Phosphorus Release from Sediments in Lake Winona

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1. Introduction

The biogeochemical characteristics of phosphorus play a significant role in lake eutrophication. Phosphorus may accumulate in lake sediments during heavy loading periods and release from sediments into the overlying water under conditions such as changes in system redox potential and reduction in external loading. This phenomenon may cause deterioration of water quality and impair water uses. Phosphorus releases from sediments to the overlying water in a lake is important in Total Maximum Daily Load (TMDL) studies and in water resources management.

Lake Winona, located to the west and south of Alexandria, Minnesota, has been listed as an impaired water body by Minnesota Pollution Control Agency. As a result, a TMDL study is required for the lake (Section 303(d) of the federal Clean Water Act) primarily due to excess phosphorus. Lake Winona has a mean depth of only 4 feet and is believed to be vertically well-mixed much of the year due to wind. Nutrients including phosphorus may be released from the bottom sediments and enter the water column, thereby acting as an internal loading mechanism. As part of the TMDL study, it is desired to determine the rate of phosphorus release to the water column in order to estimate the internal loading for TMDL allocations. The purpose of this study is to determine the rate of phosphorus release to the water column. Multiple intact sediment cores were collected from Lake Winona and incubated in the laboratory to take measurements of phosphorus concentration in the water column under aerobic and anaerobic conditions.

2. Methods and Materials

Based on the size and layout of Lake Winona and recommendations of Earth Tech staff, a total of ten intact sediment cores, two at each of five stations, were collected from Lake Winona. The samples were collected on October 20, 2008 from Stations 1 - 5. The layout of the lake and locations of the sampling sites are shown in Figure 1. The sediment core samples were taken using an Aquatic Instruments corer sampler (Figure 2) by pushing the sampler down into the sediments from a boat. The depths of the sediment cores collected ranged from 40 to 50 cm. The collected cores were transported to laboratory and stored in a temperature-controlled room at 4 ^{o}C within several hours of collection. The overlaying water at the sampling locations was also collected with the sediment cores.

Dissolved oxygen and temperature at the sampling sites were measured during sampling. The observed results are listed in Table 1. Observed dissolved oxygen concentrations between at surface and above sediment-water interface were relatively close, indicating that the lake was close to well-mixed, and the sediment-water interface was exposed to aerobic conditions on the day of sampling.

Table 1 Observed Temperature and Dissolved Oxygen in Lake Winona

Station	Depth (ft)	Surface T (^{o}C)	DO (mg/L)	
			Surface	Bottom
1	6	8.3	12.5	12.4
2	6	8.4	13.3	12.8
3	4	8.7	13.2	12.2
4	7	8.7	14.4	13.1
5	7	9.1	14.3	13.4

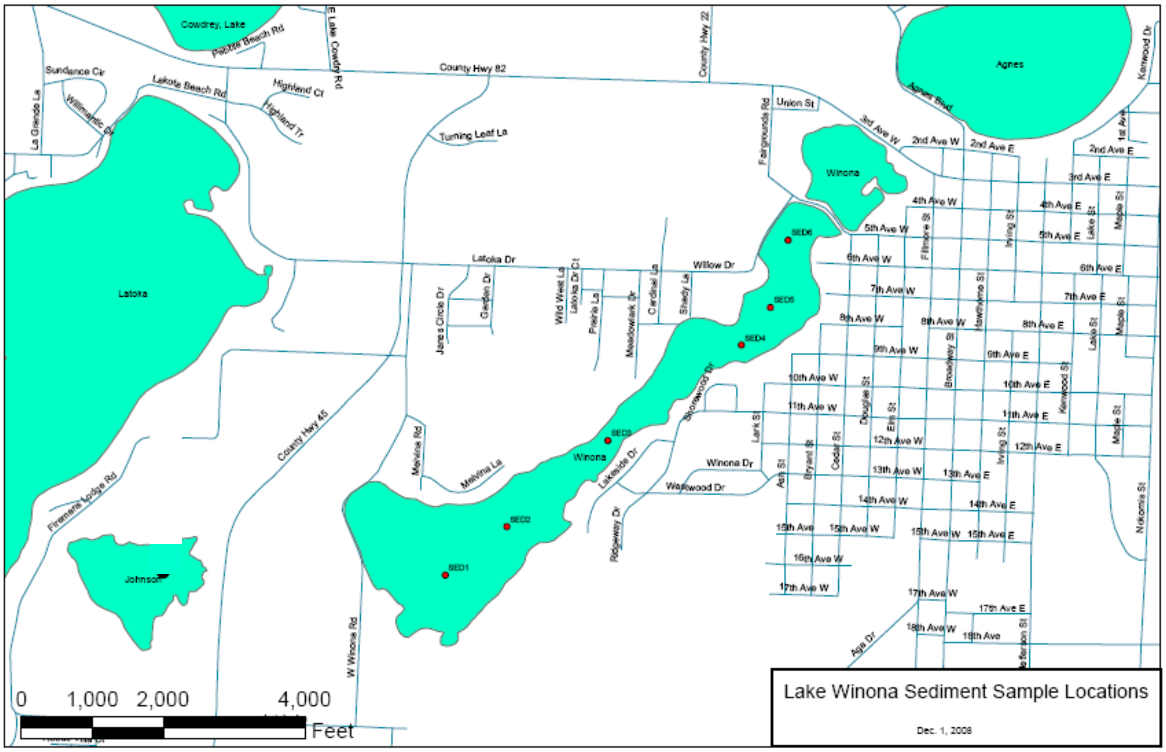

Figure 1 Lake Winona and Locations of the Sampling Sites

A series of 10 column stands were constructed and installed in a temperature-controlled room of the Department of Civil Engineering, University of Minnesota. Each of the ten columns contained a sediment core taken from Lake Winona. Water collected from Lake Winona was placed on top of each sediment sample to a depth of approximately 80 cm. The columns were incubated at 20 ^{o}C +/- 2 ^{o}C without light throughout the entire test. Five column stands were used to test phosphorus release from the five sediment sampling locations under aerobic conditions. The remaining five columns, which were from the same five sampling locations, were tested under anaerobic conditions. The test setup followed the designs by Wang et al. (2002). A schematic of the laboratory setup is provided in Figure 3. The setup consists of a sediment core with the lake water above the core acting as a reaction chamber. Both the top and bottom of the reaction chamber were sealed with rubber stoppers. At the top of the chamber, inlet and outlet tubes provided manipulation ports for the oxygenation/de-oxygenation of water above the sediment core using compressed air and nitrogen gas. The first group of five columns was oxygenated by bubbling air through the water column and the second group of five columns was deoxygenated by bubbling nitrogen gas through the water column.

Figure 2 Sediment Core Sampling by Ben Erickson Using an Aquatic Instruments Corer

The experiments ran for over 14 days from Oct 21 to Nov 3, 2008. During the test period, 5 mL water samples were collected from each reaction chamber at different intervals. The water samples collected were stored at 4 ^{o}C in dark conditions and then delivered to the Research Analytical Laboratory at the University of Minnesota for analysis of dissolved reactive phosphorus (ortho-phosphorus) concentrations. Dissolved oxygen concentrations (DO) in the water column of the ten reaction chambers were also monitored during the test period. The results were used to determine the phosphorus release rates from the sediments under aerobic and anaerobic conditions.

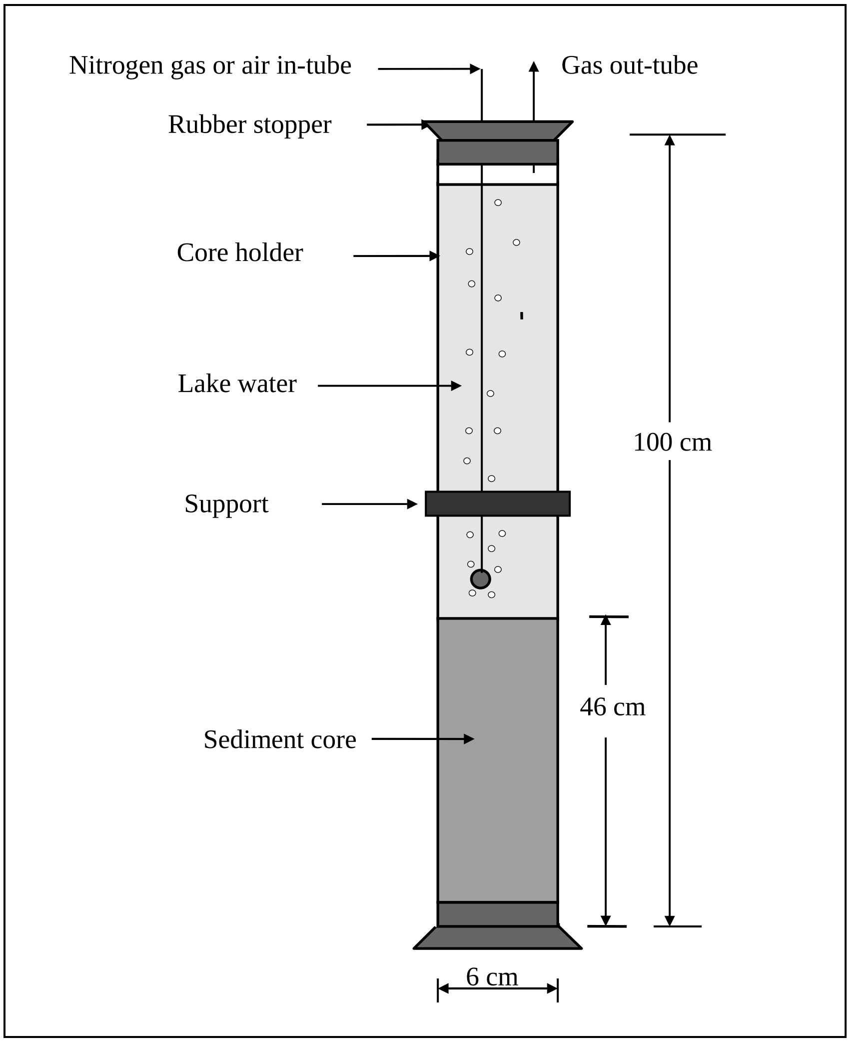

Figure 3 Phosphorus Release Test Setup (Wang et al., 2002).

3. Results

The laboratory columns with sediment cores in the temperature control room are shown in Figure 4.

Figure 4 Setup of Columns for Phosphorus Release Tests in Temperature-Controlled Room

In the reaction chambers (i.e. columns) that were bubbled with air (i.e. aerobic conditions), the overlying water DO concentrations varied from 9.2 to 9.9 mg/L (Figure 5), which are sufficient to consider the sediments to be exposed to an aerobic water body. Dissolved phosphorus concentrations (Figure 6) varied from station to station. No changes in dissolved phosphorus concentrations were observed in the reaction chamber containing the sediment core of Station 1 during the course of the tests except from Day 13 to Day 14. In the reaction chambers of Stations 2, 3, 4 and 5, the dissolved phosphorus concentrations were relatively stable during the first three days, increased up to 0.035

mg/L, 0.027 mg/L, 0.024 mg/L and 0.022 mg/L respectively in Days 4 or 5, and then reduced to 0.005 mg/L at Days 6 or 8. This period from Day 1 to Day 8 will be referred to Phase I of phosphorus release.

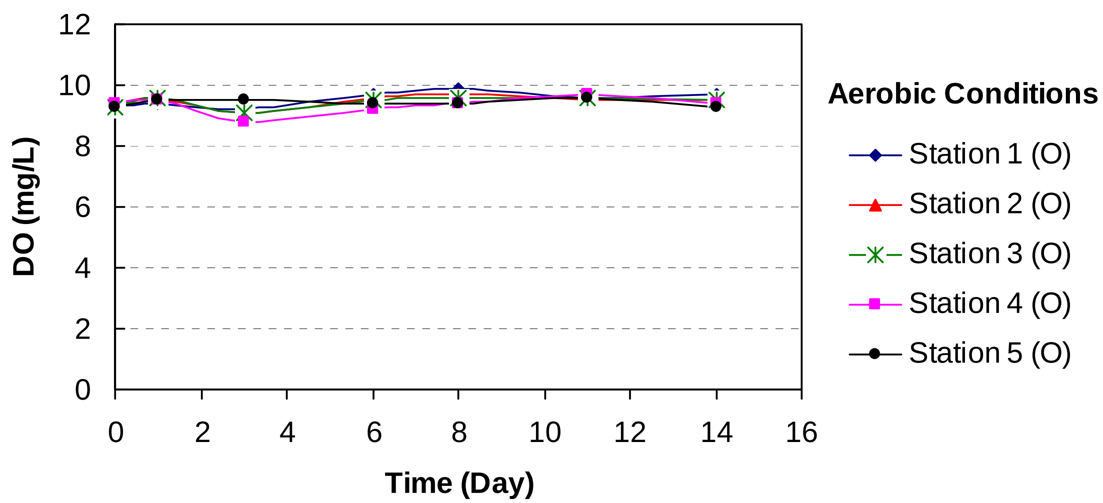

Figure 5 Overlying Water Dissolved Oxygen in Aerobic Tests for Lake Winona

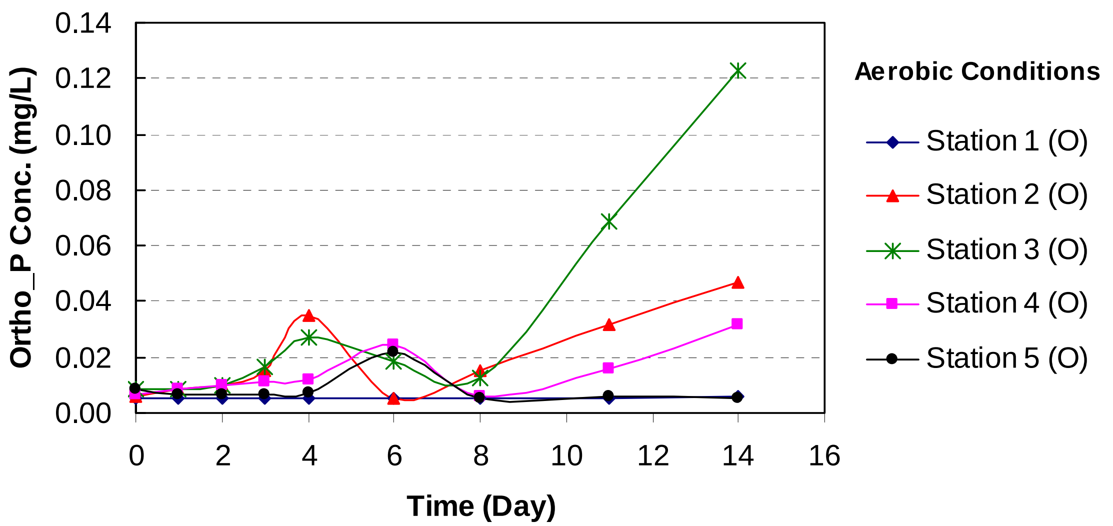

Figure 6 Overlying Water Dissolved Phosphorus in Aerobic Tests for Lake Winona

The remaining (from Day 8 to Day 14) of the tests will be referred to as Phase II. During this period, the dissolved phosphorus concentrations in the reaction chamber of Station 1 had a slight change from 0.005 mg/L at Day 11 to 0.006 mg/L from at Day 14. Slight change of the dissolved phosphorus concentrations during the test course indicates that there was little phosphorus release from Station 1 in Lake Winona under aerobic conditions. After day 8, the dissolved phosphorus concentrations in Stations 2, 3 and 4, started to increase linearly. The dissolved phosphorus concentrations in station 2 started to linearly increase from 0.005 mg/L at Day 6 to 0.047 mg/L at Day 14. Station 3 started to increase from 0.012 mg/L at Day 8 to 0.123 mg/L at Day 14. Station 4 started to increase from 0.005 mg/L at Day 8 to 0.032 mg/L at Day 14. The dissolved phosphorus concentrations in Station 5, however, unexpectedly reduced to a range around detection limit of 0.005 mg/L during Phase II.

In the reaction chambers that were bubbled with nitrogen (i.e. anaerobic conditions), the overlying water DO concentrations varied from 0.4 to 0.6 mg/L (Figure 7). Similar to the tests performed under aerobic conditions, the dissolved phosphorus concentrations in the reaction chamber of Station 1 show a slight change during the 14-day test period. This indicates that there was little phosphorus released from the sediments at Station 1 in Lake Winona under anaerobic conditions (Figure 8).

Similar to the aerobic tests, the phosphorus concentrations in Stations 2 and 5 (Figure 8) displayed two release phases; the phosphorus concentrations increased to 0.017 mg/L and 0.036 mg/L respectively after a relatively stable period of 2 or 3 days, decreased and then increased again. Results from stations 3 and 4 were different from the aerobic condition results; however, as phosphorus release processes at these stations did not exhibit two-phases. Dissolved phosphorus concentrations in Station 3 increased slightly during first 2 days, then decreased to 0.032 and 0.033 mg/L in Days 3 and 4. Station 4 increased slightly reaching a maximum of 0.012 mg/L at Day 6 after a relatively stable period in the first 2 days. After this maximum, dissolved phosphorus concentration decreased through the last day of the test.

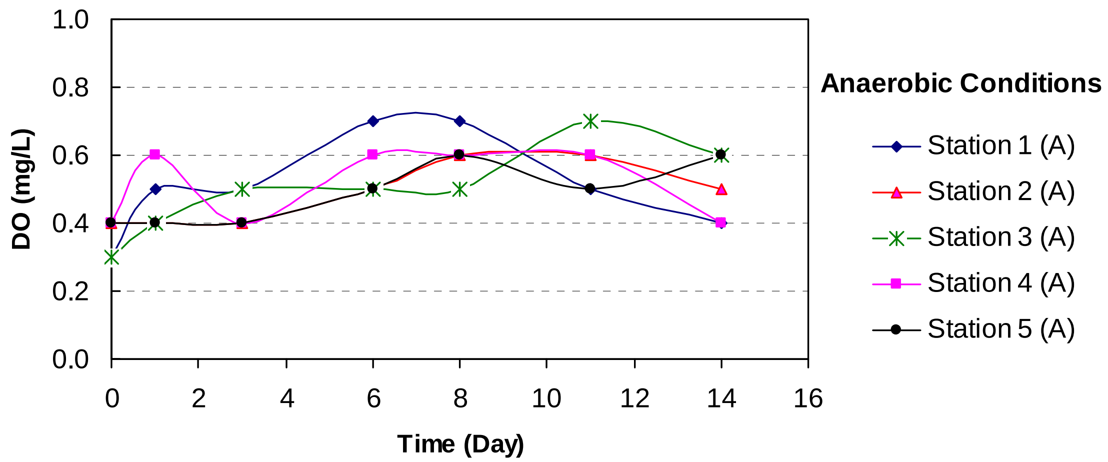

Figure 7 Overlying Water Dissolved Oxygen in Anaerobic Tests for Lake Winona

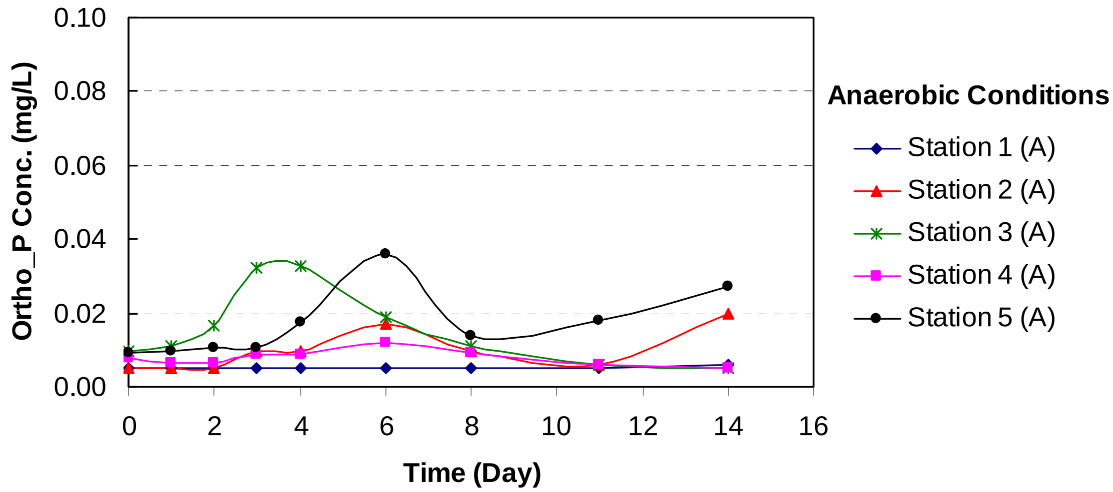

Figure 8 Overlying Water Dissolved Phosphorus in Anaerobic Tests for Lake Winona

4. Discussion

There are several mechanisms that regulate the release of phosphorus from lake sediments. The primary two mechanisms are bacterial breakdown of organic particles and chemical redox reactions of phosphorus-bond metals. Bio-decomposition of organic particles (such as dead algae) provides a continuous source of dissolved phosphorus in sediments for release to the overlying water (Boers, 1988; Di Toro and Fitzpatrick, 1993). In addition, phosphorus has a strong affinity to oxide iron and aluminum. Reduction and oxidation (redox) of these metals in sediments can regulate the dynamics of phosphorus release (Holdren and Armstrong, 1980; Nakajima, 1983).

The release rate of phosphorus can be estimated according to changes of the dissolved phosphorus concentrations in a reaction chamber with time as:

$$F_{rel}(t) = \frac{V_w}{A_s} \frac{d(DP)_w(t)}{dt} \tag{1}$$

where F_{rel} *(t)* is the phosphorus release flux (mg/m^2-day), which varies with time *t*, V_w is the total volume of the overlying water in reaction chamber (m^3), A_s is the area of the sediment-water interface of sediment cores (m^2), and $(DP)_w(t)$ is the accumulated dissolved phosphorus concentrations at the time *t* in the overlying water (mg/m^3), *dt* is the time step. Equation (1) can be written as

$$F_{rel} = \frac{V_w}{A_s} \frac{\Delta(DP)_w}{\Delta t} \tag{2}$$

where F_{rel} is the constant release rate during the time span time, Δt and $\Delta(DP)_w$ is the phosphorus concentration difference.

To understand the column data, the conditions to which the sediments were exposed in the field should be compared to those of the laboratory. The field conditions were an aerobic water column at 8 – 9 ^{o}C. The aerobic columns in the temperature-controlled room were maintained at 20^{o}C, so the bacteria in the columns would need to adjust to a new temperature. In addition, because the sediment samples were collected from Lake Winona when the sediment-water interface was exposed to aerobic conditions on the day of sampling (Table 1), the anaerobic bacteria in the anaerobic chamber would need a longer period than in the aerobic chambers to develop a substantial population before organic degradation and phosphorus release would occur. Anaerobic bacteria are known for a slower development of population density than aerobic bacteria. This is presumed to be the reason for the conditioning period, Phase I.

Following the Phase I period, phosphorus concentration increased linearly in most cases during Phase II. Phase II was therefore used to estimate phosphorus release rates, because Phase I is assumed to be a conditioning period where bacterial population density is developing into a relatively steady population. Table 2 lists the release rates of phosphorus estimated for the five sampling stations of Lake Winona under aerobic and anaerobic conditions. The estimated phosphorus release rates from the sediments of Lake Winona ranged from 0.1 to 14.7 mg/m^2-day for aerobic conditions and 0.1 to 1.8 mg/m^2-day under anaerobic conditions. The phosphorus releases of the five sampling locations were substantially different.

Station 1 had low phosphorus release under both aerobic and anaerobic conditions. As observed from the sample photographs (Figure 4), the sediment cores of Station 1 had less than 2 inches of silt with the remaining material being sand. Dissolved phosphorus release generally occurs due to the breakdown of organic material by bacteria in the sediments. The sandy character of the sediment cores taken from Station 1 indicates minimal organic contents in the sediments and therefore little release of dissolved phosphorus, as observed. There are phosphorus releases from Stations 2 through 4, under aerobic conditions, with variable magnitudes.

Table 2 Estimated Release Rates of Phosphorus from Lake Winona Sediments at 20º C. Samples were collected on October 20

Station	Phosphorus Release Rate (mg/m^2-day)	
	Aerobic Conditions	Anaerobic Conditions
1	0.1	0.1
2	4.4	1.4
3	14.7	NA
4	3.7	NA
5	ND	1.8

ND: no detection of phosphorus release in the period for estimation (Phase II).
NA: not available. Data could not be used to determine a release rate.

No detection of phosphorus release rate was assigned to Station 5 under aerobic conditions, because most dissolved phosphate concentrations during period II were below the detection limits of 0.05 mg/L. In addition, Stations 3 and 4 under anaerobic conditions are listed as "not available" because they had unexpectedly a decrease in phosphorus concentration over Phase II. This may be due to sorption of dissolved phosphorus with a slight increase of dissolved oxygen in the system during Phase II (Figure 7). The relatively smaller phosphorus releases from Stations 1, 2 and 5 under anaerobic conditions than those under aerobic conditions are contrary to what are found in most lakes, where higher phosphorus release rates are typically found under anaerobic conditions.

If the release rate at station 5 is assumed to be 0.0 mg/m^2-day, the mean aerobic phosphorus release rate is 4.6 +/- 3.7 mg/m^2-day (67% confidence interval). No mean was computed for anaerobic release rates because of difficulties in the community adapting to anaerobic conditions during the period of the tests.

As discussed previously, phosphorus concentrations in the water above the sediments displayed a relatively stable period before the phosphorus started to release. We believe that this was due to the bio-decomposition of organic phosphorus in sediments, which typically requires a lag time to adapt to the new water temperature. Higher phosphorus releases were also observed in aerobic conditions than in anaerobic conditions probably due to several factors. First, the tests incubated in the laboratory under aerobic conditions were close to the field conditions. The adaptation of bacteria to the aerobic environment should occur more quickly than adaptation to an anaerobic environment. Second, phosphorus release will quickly respond to the changes in redox conditions only if the iron and other phosphorus-bonding metal contents are relatively high in the sediments of Lake Winona. With this hypothesis, Lake Winona would not demonstrate a higher phosphorus release rate from the sediments under anaerobic conditions than under anaerobic conditions, as long as the phosphorus-binding metal content is low in the sediments. The phosphorus dynamics in sediments would not be regulated by the oxidation-reduction processes of the iron and other phosphorus-bonding metals when system redox conditions change.

The hypothesis that iron and other phosphorus-bonding metal contents are low in the sediments of Lake Winona is supported by chemical analysis of sediments collected at the same time with the sediment samples used for the release tests. The chemical analysis results were provided by Earth Tech Inc. The analyzed Fe contents ranges from 1120 to 1550 mg/kg, Al ranges from 489 to 966 mg/kg and Ca ranges from 22900 to 42800 mg/kg. Total phosphorus ranges from 4.69 to 7.49 mg/kg.

Table 3 provides a comparison of phosphorus-bonding metals in Lake Winona versus other aquatic sediments. The contents are given in mean values of the measured content ranges. Lake Winona has relatively low Fe, Al and Ca contents in the sediments compared to other water body sediments (Williams et al.,1971 and 1976, Reddy et al., 1995, Ting and Appan, 1999, Perkins and Underwood, 2000 and Wang et al., 2002). Low Fe and Al contents in sediments provide Lake Winona with a relatively low holding capacity of phosphorus in the sediments and less response to changes in sediment-water interface redox conditions. Compared to other Minnesota lakes, such as Lake Jessie, Lake Winona has a slightly higher sediment Ca content, which indicates that most sediment phosphorus in Lake Winona could be precipitated as a stable fraction without release into the water column.

Table 3 Phosphorus-Bonding Metals in Lake Winona versus other Water Body Sediments (g/kg)

Water Body	Fe	Al	Ca	Reference
Lake Winona, USA	1.31	0.74	29.93	This study
Lake Jessie, USA	6.53	1.61	16.09	Wang et al. (2002)
Okeechobee Basin, USA	1.62	1.11	-	Reddy et al. (1995)
12 Wisconsin Lakes, USA	26.53	28.73	-	Williams et al. (1971)
Alton Reservoir, UK	95.50	-	133.25	Perkins & Underwood (2000)
Lake Erie, Canada	38.22	-	-	Williams et al. (1976)
Kranji Reservoir, Singapore	34.73	-	-	Ting & Appan (1999)

Finally, the following considerations should be noted when applying these results:

- Phosphorus release rate from lake sediments tends to vary seasonally, due to algae blooms in the water column and settling to the sediments, different temperatures and dissolved oxygen concentrations (Hakanson and Jansson, 1983, Wang, et al, 2002).
- Annual release rates also tend to differ, due to differences in temperature profile and dissolved oxygen concentration above the sediments (Kelderman et al., 1982, Boers, 1988, Di Toro and Fitzpatrick, 1993).
- The water concentration of phosphorus will be impacted by changes in external loading because of the relatively small volume of Lake Winona. Thus, the phosphorus release rate will be affected by changes in overlying water concentration of phosphorus (Holdren and Armstrong 1980, Hakanson and Jansson, 1983).

5. Conclusions

Various phosphorus release rates of Lake Winona sediment samples were estimated by laboratory simulation tests. The tests used intact sediments cores collected from five locations in the lake, which were incubated in laboratory under aerobic and anaerobic conditions at approximately 20 ^{o}C.

Spatial variations in phosphorus release rates were apparent in Lake Winona. The estimated phosphorus released rates from the sediments of Lake Winona raged from 0.1 to 14.7 mg/m^2-day for aerobic conditions and 0.1 to 1.8 mg/m^2-day under anaerobic conditions. The mean aerobic phosphorus release rate is 4.6 +/- 3.7 mg/m^2-day (67% confidence interval). The work plan to sample from various locations in Lake Winona was justified.

Station 1 has little phosphorus release under both aerobic and anaerobic conditions. The phosphorus release results may be explained by biological decomposition of organic phosphorus and the low content of phosphorus-bonding metals in Lake Winona sediments.

The following caveats should be considered when performing load calculations:

1. Phosphorus release rate from lake sediments tends to vary seasonally, due to algae blooms in the water column and settling to the sediments, different temperatures and dissolved oxygen concentrations.
2. Annual release rates also tend to differ, due to differences in temperature profile and dissolved oxygen concentration above the sediments.

3. The water concentration of phosphorus will be impacted by changes in external loading because of the relatively small volume of Lake Winona. Thus, the phosphorus release rate will be affected by changes in overlying water concentration of phosphorus.

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