PHOSPHORUS RELEASE FROM SEDIMENTS
IN SHAWANO LAKE, WISCONSIN

by

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A thesis submitted in partial fulfillment
of the requirements for the degree of

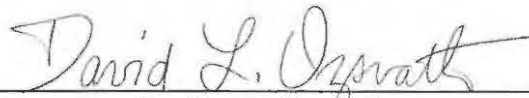MASTER OF SCIENCE

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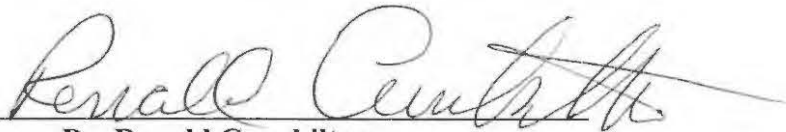UNIVERSITY OF WISCONSIN
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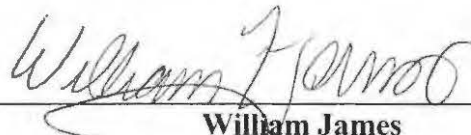APPROVED BY THE GRADUATE COMMITTEE OF:

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ABSTRACT

The release of phosphorus (P) from lake sediments to the water column is important to lake water quality. Previous research on sediment P release has largely been in deeper, stratified lakes where hypolimnetic anoxia can lead to very high sediment P release rates. Recent studies suggest that sediment P release may also be important in large shallow lakes. Sediment P release in shallow lakes is poorly understood, and it is important that lake managers have a better understanding of how it influences lake nutrient budgets. This research developed a P budget for Shawano Lake, a large shallow lake in north central Wisconsin, and used the sediment P release to explain the difference between measured loads and summer P increases in the lake. Laboratory derived P release rates from intact sediment cores taken from littoral areas of Shawano Lake exhibit mean P release rates that are high under anoxic conditions (1.25 mg m^{-2} d^{-1}) and lower, although still significant, under oxic conditions (0.25 mg m^{-2} d^{-1}). When compared to the other components of the summer P budget, internal sediment P load accounted for 71% (46% to 81% range) of the summer P budget. This P release could be explained with an oxic P release rate of 0.31 mg m^{-2} d^{-1} (0.10 to 0.49 mg m^{-2} d^{-1} range). Sediment P release was clearly important to P concentrations in Shawano Lake as it accounted for the largest source of P in the monitored summers. This internal P source is a vital P pathway to the lake and should be considered when attempting to manage P cycling in Shawano Lake and other shallow lakes.

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1.0 Introduction

The transfer of phosphorus (P) across the sediment-water interface may be important to water quality. Where P moves from the water to the sediment it reduces the P available for algae and other aquatic organisms. When P from the sediment is released back to the water, it becomes readily available for these same organisms, particularly the phytoplankton community, which can increase in productivity (Sondegaard 2001 and 2003, Welch 2005). Because P sedimentation removes particulate and detrital P and P release is largely soluble P, the sedimentation and release is converting P to a more algal available form.

P release from the anoxic sediment in deep lakes has been the subject of research for many years, but less is known about the importance of P release from oxic sediments in shallow lakes. Understanding P transfer across the sediment-water interface has become more important as management efforts to reduce external P loads have not led to the anticipated improvement in water quality in many shallow lakes. In some cases, this delayed lake response has been attributed to P release from the sediment. In those lakes, the P that accumulates in the sediment during periods of high external load may provide a source of phosphorus to the lake that continues after external loading has been reduced. This P can be released to the lake slowly over time and take many years to deplete. It is important that lake managers develop a better understanding of sediment P release, its impact on lake nutrient budgets, and its importance to improving water quality. It is hoped that the research on sediment P

release described in this thesis will assist lake managers better understand the role of

sediment P transfer in lake systems.

2.0 Literature Review

P release from sediment is influenced by many factors. For example, the release of P from the sediment increases with warmer water temperature, lowered dissolved oxygen, high or low pH, and a lower redox potential. The influence of these different P release mechanisms may vary over time and between lakes.

Increased summer water temperatures can increase microbial activity and stimulate mineralization. Increased microbial activity increases decomposition at the sediment/water interface thereby releasing organic bound P (Gachter et al. 1993, Jensen 1992, Holden and Armstrong 1980). Increased microbial activity also consumes oxygen and studies have shown particularly high P release when overlying water becomes anoxic and a redox-mediated release of P bound to iron occurs (Mortimer 1941, 1971). Oxygen from the overlying water is consumed through microbial activity and organic decomposition. In stratified lakes with an anoxic hypolimnion, P release can become an extremely large source of internal P for a lake (Nürnberg 1984, 1987). This anoxia at a smaller scale, such as during micro-stratifications and localized changes in oxygen, can also enhance P mobilization (Penn et al. 2000).

Research has shown that sulfur can enhance sediment P release under anoxic conditions (Caraco et al. 1993). When lower redox potentials are sustained, sulfides and iron are reduced. Sulfides can then remove iron from anoxic water as an iron sulfide (FeS) precipitate. Ferrous iron that was in the pore water is no longer available to precipitate as a P adsorbing iron oxide upon reoxygenation. P that would have formed with iron oxides is now more available for release. Anthropogenic enrichment

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of sulfur in lakes worldwide may be enhancing this mechanism as industrial release of sulfur eventually is deposited back on the earth's surface and leads to increased sulfur concentrations in water bodies (Caraco et al. 1993).

Changes to pH have a profound impact on the mobilization of P in lake sediment (Bostrom et al. 1982; Drake and Heaney 1987; James and Barko 1991; James et al. 1996, Fischer 2001). Changes in the lake pH can result from photosynthetic activity in which plants and algae remove carbon dioxide (CO_2) from the water column, thereby raising the pH. Photosynthesis can increase pH to values of 10 or more (Boers 1991, Frodge 1991). At high pH, the rate of sediment P release can increase. This has been related to desorption of P from ferric hydroxide by the replacement of phosphate with hydroxide (Jensen et al. 1992; Boers, 1991; Drake and Haney 1987). Jensen et al. (1992) determined that Fe:P ratios in the surface sediment can also be used indicate the likelihood of P release from oxic sediments. They showed P release was negatively correlated with the surface sediment at a high Fe:P ratio as more iron provided more free sorption sites for P. Oxic P release was important as increased release rates were observed when Fe:P ratios were less than 15. In contrast to the reactions of P with iron, the coprecipitation or adsorption of P on calcium solids can increase with increasing pH. If conditions change and the pH is reduced, this may be released.

Changes in pH and oxygen from photosynthesis and respiration may be particularly important in littoral regions of a lake. Fluctuations in pH and oxygen may result diurnally and seasonally, during respiration and photosynthesis and especially under periods of limited water column mixing (James et al. 1996). If frequent and large

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enough, these variations in oxygen and pH can stimulate P release (Bostrom et al. 1982; Drake and Heaney 1987; James and Barko 1991b; James et al. 1996). Dense canopies of aquatic macrophytes can be regions of high P release. P release under dense mats of green filamentous algae has also been reported when dissolved oxygen concentrations reach 20 mg/L and pH is greater than 9 (Frodge 1991).

One aspect of sediment P release that is poorly understood is the role of calcium. Hardwater lakes with natural calcium carbonate ($CaCO_3$) particulate formation are often low in nutrients and productivity (Koschel 1990, Murphy et al. 1983). $CaCO_3$ forms during the uptake of carbon dioxide or bicarbonate by phytoplankton or aquatic macrophytes that cause an increase in pH and over-saturation with respect to $CaCO_3$. Research has shown that P can be adsorbed or co-precipitated with $CaCO_3$ (Otsuki and Wetzel 1972, Murphy 1983, House 1990). Increased sorption and co-precipitation of P and $CaCO_3$ is favored by an increase in pH. In the sediment, the $CaCO_3$ may also act as a barrier to diffusive transport of P and reduce release rates from the sediment. $CaCO_3$ and the sorbed or co-precipitated P can settle in the lake. There is evidence that the dissolution of $CaCO_3$ and/or Ca-P minerals occur in the sediment that may lead to P release even under oxic water conditions (Driscoll et al. 1993, Penn et al. 2000).

Some insight into the role of $CaCO_3$ in reducing the release of P from the sediment may come from the use of $CaCO_3$ to remove and inactivate P and control internal P loading from the sediment. Murphy et al. (1988) and Murphy and Prepas (1990) applied slaked lime ($Ca(OH)_2$) to the surface of Frisken Lake, B.C. (Canada) to

co-precipitate $CaCO_3$ and P. The solids settled into the hypolimnion, but they later dissolved and limited the longevity of the treatment. Babin et al. (1994) preformed a similar study upon Half Moon Lake, Alberta (Canada) in which lime was also used and applied to the surface water. Treatments preformed in 1989 and 1990 showed decreases of 53% and 63% respectively in the mean summer total P. These decreases were attributed to P co-precipitation with $CaCO_3$. It was further hypothesized that the presence of $CaCO_3$ on the sediment surface was responsible for reduced sediment P loading.

It is clear from this review that increased P release can occur under both anoxic and oxic conditions. Because shallow lakes have large areas of sediment relative to the volume of lake water, release of sediment P may be a major source of P in shallow lakes (Jensen and Andersen 1992, Ryder 1985). In shallow polymictic lakes, oxic sediment release may be much more important than anoxic sediment release because frequent mixing and only brief, if any, stratification occurs. Only a few studies have documented the internal P release from the littoral, well oxygenated region as an important contributor of P to the open water column (Nurnberg 1984). Anoxic sediment P release is better understood, likely because it leads to pronounced increases in P concentrations in the hypolimnion of stratified lakes. As a result, oxic P release has largely been left out of many mass balance P budgets. Several studies have documented internal P release under oxic conditions (James 2006, Haggard et al. 2005, James et al. 2005, James et al. 2002, James et al. 1996, James et al. 1995, James et

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al.1991, Boers 1991, Drake et al. 1987). A summary presented in Table 1 shows a range of P release rates from different lakes under oxic conditions.

The release of phosphorus from oxic sediment in shallow, mixed lakes could be an important contribution to growing season phosphorus concentrations in shallow lakes. Unfortunately, little is known about its importance to P budgets in many lakes, nor has it been linked to summer P concentrations in many lake studies. In this study, the importance of oxic sediment P release will be characterized for a large shallow lake.

Table 1. Examples of oxic P release rates reported for nine shallow lakes.

Lake	pH	mean oxic P release rate (mg P m^{-2} d^{-1})
Lake Esthwaite (Drake et al. 1987)	10.6	75
	9	2
Lake Veluwe (Boers, 1991)	9.3	4
Lake Pepin (James et al. 1995)	8.3	4
Half Moon Lake (James et al. 2002)	8.5	~ 2 - 3
	7.7	.12 - .22
Mead Lake (James et al. 2005)	8.5	.53 - .96
Eau Galle Reservoir (James et al. 1991)	8-10	3.6
Lake Delavan (James et al. 1996)	8.5	3.4
	9.1	7.1
Lake Eucha (Haggard et al. 2005)	-	1
Shawano Lake (James, 2006)	8	*0.215 (.07)
	> 9	< .01

* Includes a single core with a release rate of 2.9 mg m^{-2} d^{-1}, mean of the other 19 cores was .07 mg m^{-2} d^{-1}

3.0 Methods and Material

3.1 Study location and description: Shawano Lake, Wisconsin

Shawano Lake in Shawano County, Wisconsin is a 25 km^2 lake with an average depth of 9 ft (Figure 1). It is a mesotrophic to moderately eutrophic lake (total P range = 12-48 μg L^{-1}; secchi transparency range = 3-20 feet; and chlorophyll *a* range = 2-21 μg L^{-1}) in the North Central Hardwoods of Wisconsin. Shawano Lake is a hard water lake with a total hardness of 125 mg L^{-1} as CaCO$_3$. That is similar to many lakes in central Wisconsin where dolomitic glacial till in the watershed leads to relatively hard groundwater. It is one of the most heavily used lakes in the state with a long history of human activity. It has experienced many years of shoreland and in-lake disturbances, introduced invasive species, and an increase in recreational uses. Concern over the long term biological productivity of the lake has led to a need to quantify the role of sediment in nutrient loading in the water.

Figure 1. Shawano Lake, Shawano County, Wisconsin and core sampling locations

3.2 Shawano Lake and watershed water quality evaluation

Shawano Lake was studied in 2004-2007 to develop a management plan for the lake. A monitoring plan was designed to estimate the P budget for Shawano Lake as part of the Shawano Lake study (CWSE 2007). This study is described in detail in the final report and only aspects of the study relevant to the sediment P release are described here. This study was conducted by the Shawano Lake Area Waterways Association, the Wisconsin Department of Natural Resources, the United States Army Corp of Engineers (USACOE), and the Center for Watershed Science and Education at UWSP. Five tributaries to the lake (Loon Creek, Dutchess Creek, Pickerel Creek, No Name Creek, and Murray Creek) were monitored for flow using water level loggers (Solinst, Georgetown, Ontario) and for quality using siphon and grab samples. Near-shore groundwater inflow and outflow was measured using mini-piezometers and seepage meters. Lake water quality was measured at two locations (east and west sites) every 2-3 weeks with depth profiles for temperature, dissolved oxygen, specific conductivity, and pH using a portable water quality unit (Hach Environmental, Hydrolab Quantra). Vertical integrated water samples were taken in the epilimnion and about 2-3 feet above the lake bottom in the hypolimnion when present. An aquatic plant survey and P estimate from curly leaf pondweed (*Potamogeton crispus*) was performed to evaluate the aquatic macrophyte P contribution.

To identify the water quality conditions that might influence P release from the sediment, oxygen and pH were measured in the lake. Daily and seasonal fluctuations in oxygen and pH were measured with a recording water quality monitor (YSI, Model

6600; Yellow Springs Instruments) deployed by the USACOE. The monitor was located in a shallow, submersed, densely populated aquatic macrophyte bed. It recorded temperature, pH, and dissolved oxygen multiple times during the day. In addition, water chemistry within aquatic macrophyte beds was sampled at fourteen locations in the early morning (~ 4:00 – 6:00 am) on several days during periods of very little wind disturbance. Sampling locations are shown in Figure 2 for in-lake monitoring.
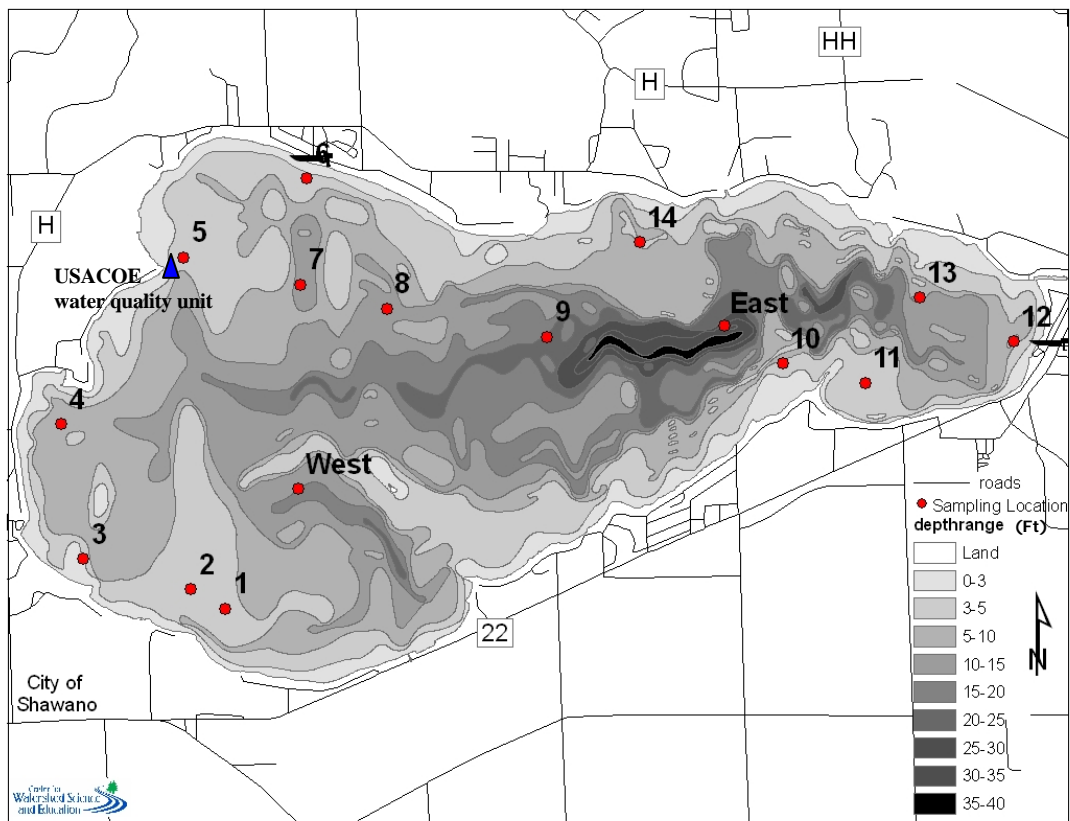
Figure 2. Locations of the two in-lake water quality sampling locations (east and west), fourteen aquatic macrophyte bed sampling locations, and USACOE water quality unit deployment location

3.3 Phosphorus Release Experiments

An environmental growth chamber (Controlled Environments, model 20D0018) was used to house a sediment core incubation system constructed for this project. Figure 3 shows several parts of the core incubation system. The environmental chamber was kept dark and at 20° C to replicate conditions at the sediment surface during the summer months of July and August. The oxidation–reduction environment in the water above the sediment was controlled by bubbling air (oxic) or nitrogen (anoxic) through an air stone just above the sediment surface. The amount of air was regulated with valves (Ultra Plastic 4-way) to mix the water but not to suspend the sediment. Prior to entering the environmental chamber, the air was hydrated by passing it through deionized water (Figure 3). Carbon dioxide was mixed with compressed atmospheric air using a 65 and 150 mm air flowmeter (Manostat Inc.) to mimic lake pH values. A mini-pH electrode (Orion Ross) was used to monitor and track changes in pH.

Intact sediment cores were collected from littoral areas in Shawano Lake in 2007 on February 21, March 25, and August 20 (Figure 4). Sampling was done using a sediment corer equipped with an acrylic or clear PVC core liner (3.5 inch ID, 4.0 inch OD, and 18 inch length) in approximately 10 feet of water. This method minimized disturbance at the sediment/water interface during sampling. Lake water was collected at the sampling locations for use as incubation and replacement water.
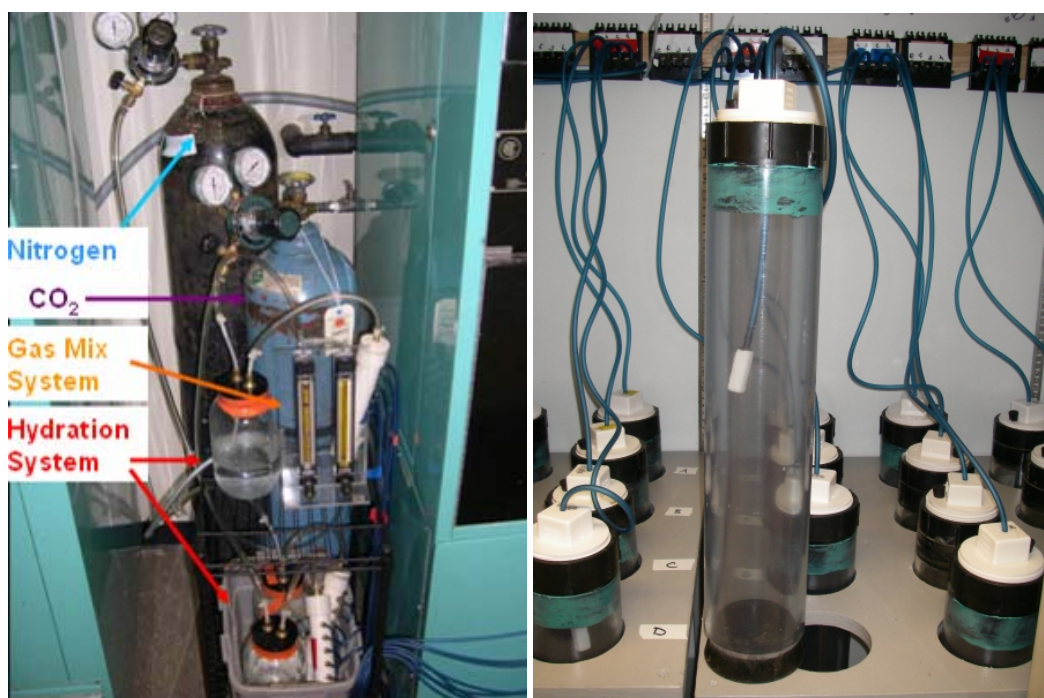
Figure 3. Environmental chamber used to house sediment cores, a mixing / hydration system, and a controlled environment.

Figure 4. Sediment cores taken in Shawano Lake

The sediment cores were taken to the laboratory and processed within 24 hours. The overlying core water was replaced with 600 ml of 1.2 μm glass fiber filtered lake water taken from the same location where the cores were collected. Care was taken to not resuspend sediment when replacing the water. The cores were randomly assigned different treatments and then incubated for a 7-9 days. Water samples were collected daily from the center of the bulk water and pH was monitored in the incubation system. Water samples were filtered through 0.45 μm cellulose nitrate membrane filters and analyzed for soluble reactive phosphorus (SRP) using the automated colorimetric method on a Lachat auto-analyzer at the University of Wisconsin, Stevens Point, Watershed and Environmental Analysis Laboratory. The water removed by the sampling was then replaced by lake water that was kept under the same conditions as the cores. Rates of SRP exchange from the sediment (mg m^{-2} d^{-1}) were calculated as a change in concentration in the overlying water divided by time and the area of the incubation core with a minor adjustment for the dilution with replacement water. A sample of water was also analyzed for calcium using a flame photometer (Geneq Inc. Model 410).

The cores were incubated under different environmental conditions. P release rates were maintained under oxic and anoxic conditions. Another experiment also studied the effect of pH by adjusting CO_2 concentration of the bubbled air.

Dissolved oxygen and pH data obtained during the summer of 2006 were used to determine the range in environmental conditions at which to control sediment core environments. Daily variations in dissolved oxygen and pH in the field consisted of

increases during the day and decreases during the night, which were attributed to photosynthesis and respiration, respectively. Dissolved oxygen concentrations never fell below 5 mg L^{-1} (min. = 5.5 mg L^{-1}) and pH ranged from 7.3 to 9.5 at the monitoring location deployed by the USACOE (James et al. 2006). Daily variations monitored at 14 aquatic macrophyte beds showed dissolved oxygen concentrations fell below 5 mg L^{-1} only once (site 5 = 3.8 mg L^{-1}) and pH ranged between 7.6 and 10.0.

3.4 Core Sediment Analysis

After the sediment P release experimentation, the top 3-4 cm of sediment was homogenized and analyzed for multiple forms of P. A sequential P extraction detailed in Hieltjies and Lijklema (1980) was used to determine the fractional composition of inorganic P. The P extraction involved using 1.0 M ammonium chloride (NH_4Cl), 0.1 N sodium hydroxide (NaOH), and 0.5 N hydrochloric acid (HCl) in sequence. The extraction determined the fraction of P-NH_4Cl (loosely bound, interstitial P, and $CaCO_3$ adsorbed P), P-NaOH (iron and aluminum bound P), and P-HCl (calcium bound P). The sequential extraction procedure used a measured portion of wet sediment (6.0 – 8.0 g). The sample was placed in a 50 ml centrifuge tube and 40 ml of 1 M NH_4Cl extraction solution was added and agitated for 2 hours using a rotating mixing apparatus (Figure 5). The solution was then decanted and the same procedure was repeated for another 2 hours with another 40 ml of the same extraction solution. 40 ml of 0.1 N NaOH solution was then added and agitated using the same process for 17 hours. A final 40 ml of 0.5 N HCl was added and agitated for 24 hours. Each sample was filtered with glass fiber filter and a 0.45 μm cellulose nitrate membrane filter and analyzed for SRP using the automated colorimetric method. Subsequent total phosphorus (TP) analysis was preformed upon the NaOH extractant that was not filtered to determine a portion of organic bound P that was also removed during the NaOH extraction. A final P digestion with sulfuric acid, potassium sulfate, and red mercuric oxide was used to extract any remaining P. The filtered NaOH extractable P fraction was then added to this fraction and the total was considered organic bound P.
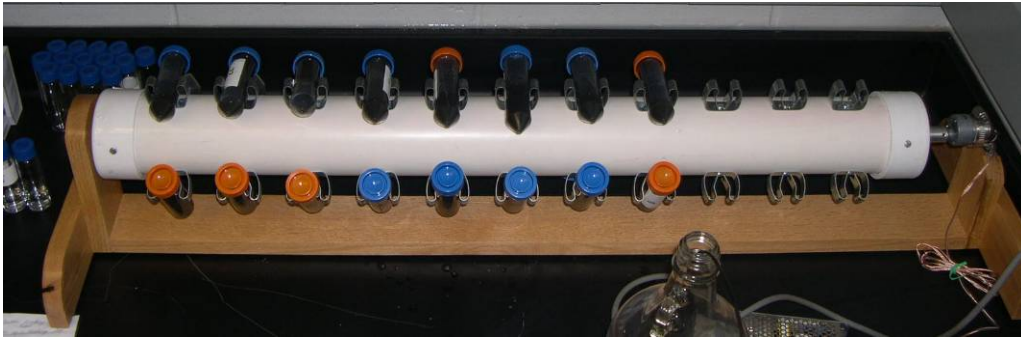
Figure 5 Sediment agitation apparatus.

Six sediment cores (10-12 and 20-22) were analyzed for a P, iron, calcium, aluminum, magnesium, manganese, potassium, copper, lead, sodium, sulfate, and zinc using microwave digestion and a inductively coupled plasma atomic emission spectroscopy (ICP-EAS) analysis. Percent moisture, total organic matter, and total carbonates were determined by weight loss after drying at 105° C, and loss on ignition at 550° C and 950° C respectively (Heiri et al. 2001).

4.0 Results and Discussion

4.1 Shawano Lake Phosphorus Budget

A phosphorus budget for Shawano Lake was developed to determine the importance of sediment P release. The P budget quantified P inputs and outputs and the change in P stored in the lake. The increase in P mass in the lake should be equal to the difference between the rate P enters and the rate P leaves for any given period of time. P inputs include tributaries (P_{trib}), groundwater (P_{gw}), precipitation (P_{precip}), aquatic plants (P_{plant}), hypolimnion sediment release ($P_{hypo-sed}$), and epilimnion sediment release ($P_{epi-sed}$). P outputs from the lake include outflow ($P_{discharge}$) to the Wolf River and settling ($P_{sedimentation}$) in the lake. The P budget for the epilimnion can be written as:

Rate of P change =

$$(P_{trib} + P_{gw} + P_{precip} + P_{plants} + P_{hypo-sed} + P_{epi-sed}) - (P_{discharge} + P_{sedimentation})$$

where all terms are mass over time (e.g. kg/month).

The terms of the P budget were measured or estimated and compared with the change in the mass of P within the lake. The change of the P mass within the lake was estimated by the difference in P concentration over time using near surface epilimnion concentrations taken at the east sampling location. Lake P concentrations were assumed uniform lake-wide and were multiplied by the entire epilimnion volume. The change in P mass within the epilimnion constituted an increase of approximately 1100 kg of P (Figure 6). The phosphorus enriched anoxic hypolimnion was not included in

the epilimnion concentration as it was considered separately as a source of P to the lake.

Figure 6 shows the time frame for the P budget and the change in P mass in the lake from July to September. By subtracting the difference between P inputs and outputs from the change in P mass within the lake it could be determined if any P was unaccounted for. From this unaccounted P, an estimate of the epilimnion sediment ($P_{epi-sed}$) contribution could be calculated. Since internal P loads associated with the anoxic hypolimnion and the other P loads were included in the P budget, the surplus P is most likely coming from epilimnion sediment P release.
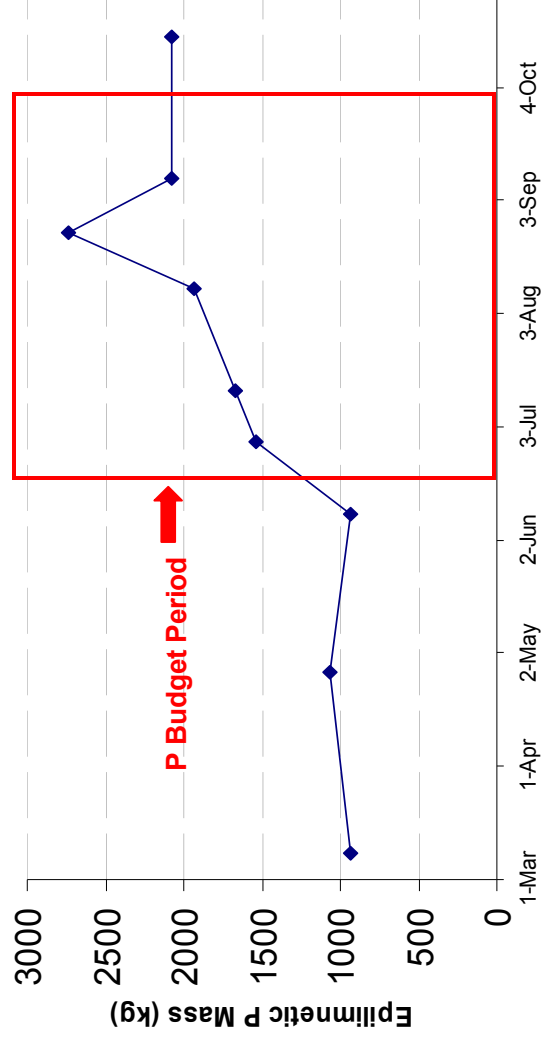
Figure 6. P mass (kg) in the epilimnion of Shawano Lake over time in 2006.

A level of uncertainty surrounds each estimate in the P budget. To remedy this, three P budgets were developed: a lower estimate, a most likely scenario, and an upper estimate. The lower estimate used the lowest inputs and the largest outputs. The upper

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estimate used the largest inputs with the lowest outputs. These were used to determine a range of sediment P release rates that could account for the change in summer P mass within the lake.

A P load from tributaries (P_{trib}) was estimated using daily flow and P concentration measurements. P loads were calculated with FLUX, a model designed to estimate nutrient loads through a flow-concentration relationship (Walker 1996). Each of the monitoring stations was modeled individually using a continuous record of mean daily flow and nutrient concentrations, measured during the 2005 and 2006 field seasons. Nutrient concentrations were analyzed from grab and siphon samples. A P load from the unmonitored tributaries was quantified using landuse-based P export coefficients derived from the monitored areas. P loads of 90, 108, and 126 kg of P were modeled as the lower, most likely, and upper estimates of P input from the tributaries during the ninety day summer period. Annually, P_{trib} is likely a large source of P to the lake. During the summer of 2006 when flow was decreased, the P input from the tributaries was also decreased, and P_{trib} was a small part of the P budget. A more detailed description and results of the P contribution from tributaries is presented in the Comprehensive Lake and Watershed Assessment of Shawano Lake, Wisconsin (CWSE, 2008).

Groundwater (P_{gw}) was quantified using groundwater inflow and P concentrations measured during the 2006 field season. Mini-piezometers and seepage meters were used to quantify groundwater inflow. P concentrations were analyzed from samples taken from mini-piezometers. They were combined with flow data to

determine the P input from groundwater. P loads of 13, 39, and 150 kg were calculated as the lower, most likely, and upper estimates of P input from groundwater. The lower P estimate was derived from the lowest groundwater inflow estimate and P concentrations collected. The most likely estimate considered the measured groundwater inflow and an area-weighted P concentration. The upper estimate assumed ten inches of groundwater infiltration across the watershed, typical for east-central Wisconsin soils, and an average measured P concentration. This likely overestimated the actual contribution of P_{gw} because some groundwater would have been accounted for in P_{trib}. Again, a full description and results of the P contribution from the groundwater is detailed in the Comprehensive Lake and Watershed Assessment of Shawano Lake, Wisconsin (CWSE, 2008).

A P load from precipitation (P_{precip}) was quantified using total rainfall for the given time period and rainwater P concentrations. Rainwater P concentrations of 4, 7, and 12 $\mu g\ L^{-1}$ were used for the lower, most likely, and upper estimates. Total rainfall was kept constant for the P_{precip} range estimated. Data collected in Shawano County by the National Atmospheric Deposition Program was used for the lower estimate (19 kg). Average collected P concentration was less than concentrations used by others in the state, which is why it was used for the lower estimate of P_{precip}. The most likely (33 kg) and upper (94 kg) estimates were based on results from other researchers (D. Robertson, personal communication). The most likely estimate was indicative of mixed agriculture/forested region in central Wisconsin, such as the Shawano Lake region. The upper estimate was indicative of an agriculture region.

Curly-leaf pondweed (*Potamogeton crispus*) contributes P to the lake following senescence, usually in late June through early July. Data collected in 2005 and 2006 by the USACOE quantified plant abundance, density, total biomass, and P associated to this biomass (Owens et al. 2006). Using this data, P_{plant} was quantified as a release from dead and decomposing plant material. P release is believed to take place rapidly following senescence and becomes depleted after 30 days (James et al. 2002). Increased P concentrations were observed in the lake following curly-leaf pondweed senescence when monitoring for water chemistry changes in large, shallow aquatic plant beds. At times P concentrations greater than 200 µg L^{-1} were observed (Figure 7). P_{plant} was estimated to be 178 kg (James et al. 2006). To calculate a lower, most likely, and upper estimate of P from curly-leaf pondweed senescence, it was assumed that the population may fluctuate 20% in either direction of the 2006 estimate. This results in a lower estimate of 142 kg of P and an upper estimate of 214 kg of P.
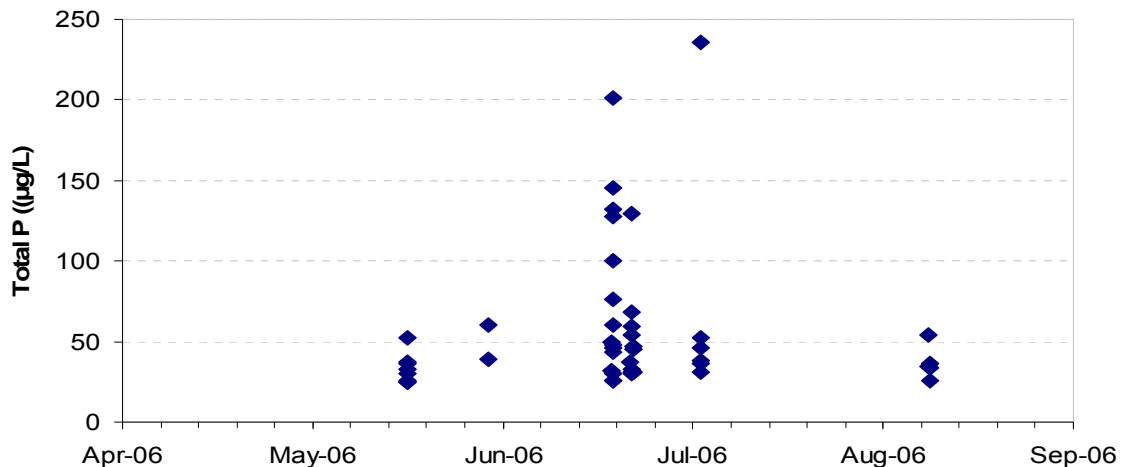
Figure 7. TP concentrations (µg L^{-1}) collected during early morning sampling near dense aquatic plant beds. An increase in late June follows the senescence of curly-leaf pondweed.

High concentrations of P in the hypolimnion (Figure 8) followed stratification in 2006 (Figures 9 and 10) that led to anoxia (dissolved oxygen < 1 mg L^{-1}) above the sediment surface. To evaluate the P loading from the sediment under anoxic conditions, two methods were compared. The first method uses the Nürnberg (1995) anoxic factor and the second method uses the hypolimnion volume and P concentration.

For the first method, an estimation of the areal extent and time period of anoxia in both shallow and deeper regions of the lake is used to calculate the anoxic factor. Shawano Lake only exhibited anoxia in the hypolimnion, so shallow regions were not included. From this, an anoxic factor (AF) of Nürnberg (1995) for the lake can be calculated:

$$AF = \frac{t_i a_i}{A_o}$$

where t_i is the period of anoxia (days), a_i is the area (m^2) of the hypolimnion, and A_o is the lake surface area (m^2). The anoxic factor is equivalent to the days of anoxia an area the size of the entire lake that would be releasing P from the sediment under anoxic conditions. A lake wide anoxic internal P load from the sediment (mg m^{-2} summer period^{-1}) can then be calculated using the anoxic factor and a measured anoxic sediment P release rate:

Anoxic sediment P load = AF (days) · anoxic P release rate (mg m^{-2} d^{-1})

The temperature and dissolved oxygen profiles (Figures 9 and 10) collected in 2006 were used to estimate the anoxic period, hypolimnetic depth, and anoxic area. An anoxic period of 60 days was estimated from the onset of anoxia in early July and to breakup of stratification in late August. The resulting anoxic area was 530,000 m^2 and the anoxic water volume was approximately 0.9 hm^3. An AF of 0.46 days was calculated for 2006. Using the AF and lower (2 mg m^{-2} d^{-1}), most likely (6 mg m^{-2} d^{-1}), and upper (8 mg m^{-2} d^{-1}) anoxic P release rates derived from this research and James et al. (2006), an anoxic sediment P load was calculated. The $P_{hypo-sed}$ release was estimated to range from 64 kg (lower), to 190 kg (most likely), and 254 kg (upper). These were based on the lower, most likely, and upper anoxic sediment P release rates of 0.92 mg m^{-2}, 2.76 mg m^{-2}, 3.68 mg m^{-2}, respectively.

The second method for calculating anoxic sediment P release used the change in the hypolimnion P concentration and the hypolimnion water volume. The volume of water in the hypolimnion was approximately 0.9 hm^3 and the maximum measured P concentration was 223 μg L^{-1}. These led to an estimated $P_{hypo-sed}$ release of 200 kg.

Estimates of $P_{hypo-sed}$ release obtained using these two methods were similar. The first method used an anoxic P release rate of 6 mg m^{-2} d^{-1}, a relatively high anoxic sediment P release rate. This rate was reported for the deeper hypolimnetic sediment cores taken by James et al. (2006) in Shawano Lake.

Difficulties arise when determining the portion of released sediment P that is transported to the epilimnion. In this P budget for Shawano Lake, it is assumed that the entire anoxic P load from the hypolimnion would be mixed with the epilimnion. This

was a reasonable assumption as the complete mixing of Shawano Lake did occur in late August 2006. Because the anoxic hypolimnion was small, confined, and strongly stratified prior to mixing, the ability to transfer P to the epilimnion was likely limited. If any portion of the estimated P load was transported to the epilimnion prior to mixing, the P mass in the hypolimnion would have been depleted, if only slightly. This would have increased P concentrations in the epilimnion and affected the estimate of $P_{hypo-sed}$.
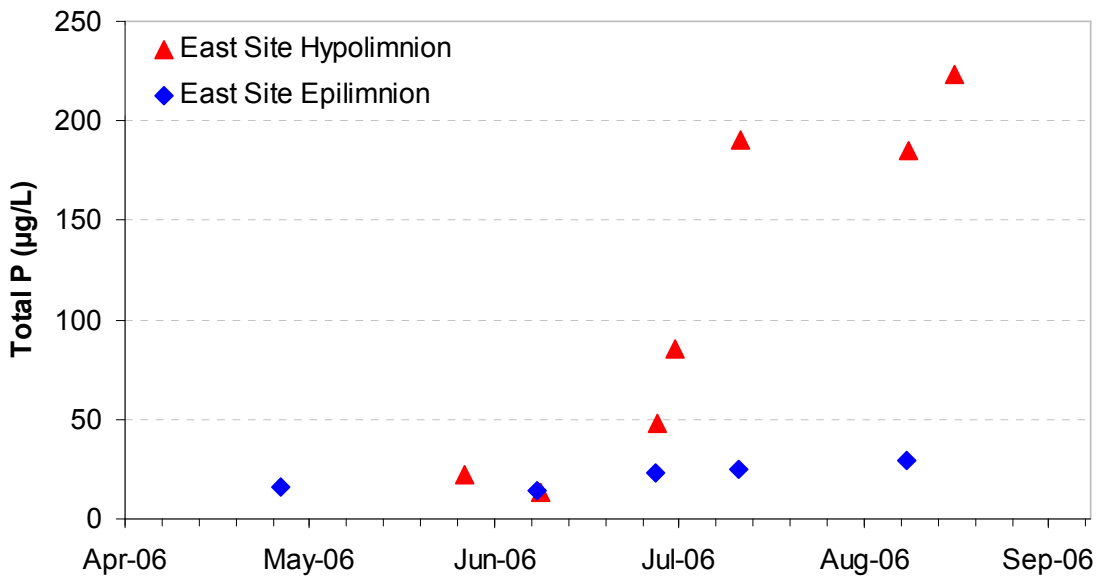
Figure 8. 2006 hypolimnion and epilimnion P concentrations (μg L^{-1}).
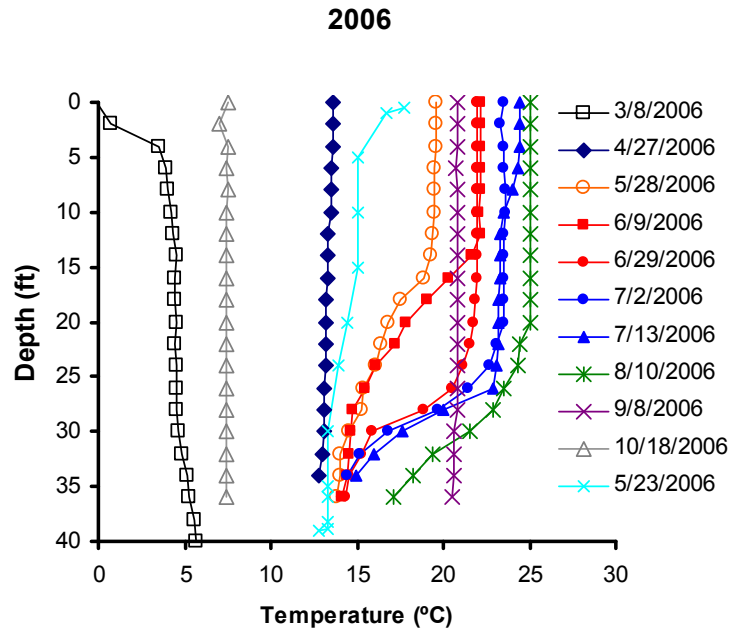
2006

Figure 9 Temperature profiles in Shawano Lake in 2006 collected at east location.
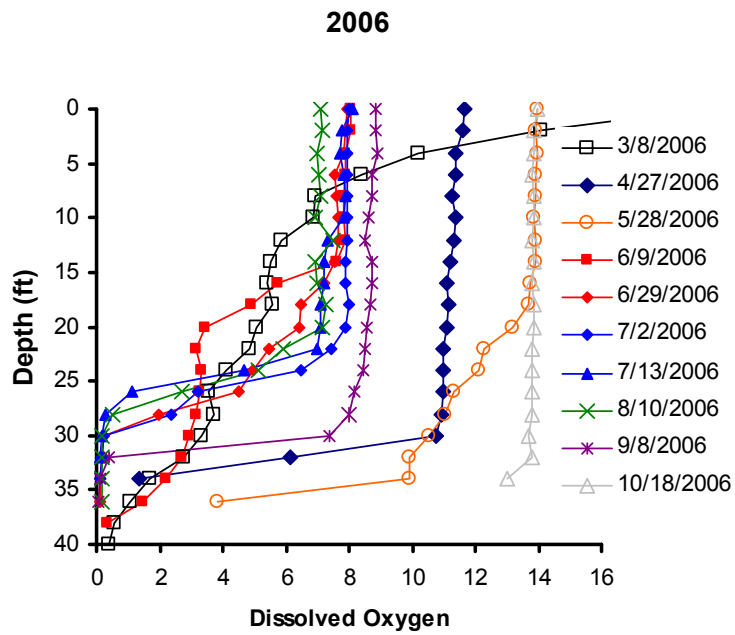
2006

Figure 10. Dissolved oxygen (in mg/l) profiles in Shawano Lake in 2006 collected at east location.

The outflow from the lake, $P_{discharge}$, was assumed to be very low. The outflow was observed to flow very slowly, if at all, and flow direction varied (in and out) as water levels changed in the Wolf River just downstream of the Shawano Lake outlet. This was consistent with high evaporation from the lake during the summer and low flow from its tributaries. A conservative estimate of average groundwater inflow from the watershed was based on a recharge of 10 inches/yr. That would lead to an average groundwater flow of 12.3 cubic feet per second (cfs) entering the lake. If evaporation minus precipitation is approximately 1 ½ feet of loss across the lake surface for the three summer months, it would be equivalent to 12.4 cfs during the summer. This suggests that groundwater discharge to the lake approximately equals evaporation loss during the summer. This would lead to a most likely $P_{discharge}$ estimate of zero kg from the outflow. Hypothetical scenarios were used to provide the lower and upper estimates. Assuming -4 cfs and 4 cfs at the outflow and an average P concentration of 30 μg L^{-1}, a lower estimate of -25 kg and a upper estimate of 25 kg was calculated.

A net P settling rate approach was used to estimate the deposition of P ($P_{sedimentation}$) in the lake (Chapra 1975). The net deposition of P is typically reported as a net sedimentation in that it reflects the combined result of all physical, chemical, and biological processes influencing P retention and recycling within a lake. Therefore, this will underestimate the actual sedimentation rate in the lake as it includes the upward flux of sediment P. Net P sedimentation rates in the literature range from negative to more than 20 m/yr. A P settling range of 0-2 m/yr was used for Shawano Lake based on a study of Lake Okeechobee, Florida (Walker 2000). This is a smaller

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rate than reported for deeper temperate lakes, where sedimentation rates of 10-16 m/yr have been reported (Walker, 2000). This sedimentation rate seemed reasonable for Shawano Lake for because Shawano Lake is large, shallow, and wind swept. Increased mixing can lead to an upward flux of P in the water column. A sedimentation rate of 0 m/yr (0 kg) was used for the lower estimate, 1 m/yr (150 kg) for the most likely estimate, and 2 m/yr (300 kg) for the upper estimates of P sedimentation.

Table 2 summarizes the P budget for the 2006 summer (July-September). An increase in the epilimnion P mass of 1100 kg occurred from early July through September. This increase should reflect the difference between P inputs and outputs. Such was not the case and a surplus of P in the lake was calculated as a difference between the increase in P mass within the lake and the change in inputs and outputs. Assuming this surplus of P was a product of epilimnion sediment P release, a daily sediment P release rate can be calculated to explain the surplus P. Sediment P release rates of 0.49, 0.31, and 0.10 mg m^{-2} d^{-1} were calculated for the lower, most likely, and upper estimates of the P budget, respectively.

Overall, the estimated P release from the sediments would account for 81%, 71% and 46% of the net lower, most likely, and upper P inputs in the Shawano Lake summer P budget. These values are very large portions of the P budget, and that finding suggested a need to develop a detailed measurement of P release from the sediment.

Table 2. P Budget for the 2006 summer (July-September).

Source	Inputs (kg) July-September		
	lower	most likely	upper
P_{precip}[a]	19	33	94
P_{gw}[b]	13	39	150
P_{trib}[c]	90	108	126
P_{plants}[d]	142	178	214
$P_{hypo\text{-}sed}$[e]	64	190	254
$P_{input\text{-}total}$	329	548	838
	Outputs (kg) July-September		
	lower	most likely	upper
$P_{discharge}$[f]	25	0	-25
$P_{sedimentation}$[g]	300	150	0
$P_{output\text{-}total}$	325	150	-25
	lower	most likely	upper
Input – Output (kg)	3	398	863
Change P within epilimnion (kg)	1100	1100	1100
Surplus P (kg)	1097	702	237
$P_{epi\text{-}sed}$ release rate (mg m^{-2} d^{-1})	0.49	0.31	0.10
External and plant P load (%)	19%	29%	54%
Internal sediment P load (%)	81%	71%	46%

[a] based on P concentrations of 4, 7, and 12 µg L^{-1} in precipitation
[b] groundwater inflow and P concentration
[c] flow concentrated estimates using FLUX and runoff coefficients derived from monitored areas
[d] USACOE biomass and P estimate (James et al. 2006)
[e] derived from hypolimnion P concentration and volume, and Nürnberg (1995)
[f] assuming -4, 0, and 4 cfs outflow with an average P concentration of 30 µg L^{-1}
[g] derived from a settling velocity of 0-2 m yr^{-1}

4.2 Quantifying Sediment P Release Rates

The P budget suggested anoxic and oxic sediment P release was an important component to the Shawano Lake P budget. Experiments were performed to estimate the rate of P release from sediments using cores collected in Shawano Lake to confirm their likely contribution to the summer P budget. The results are presented here.

Figure 11 shows typical P release patterns and linear regression lines describing the anoxic and oxic P release rates. The rate of anoxic release was essentially constant from the start of incubation. The slope of linear lines shown in Figure 11 is the rate of P release over time (μg L^{-1} d^{-1}). Because the slope is constant over time, the P release rate was obtained using all the measurements. In contrast, the oxic sediment cores exhibited a two-phase P release pattern. The release was initially negative and P was removed from solution. This was followed by a positive P release through the remainder of the incubation, similar to a pattern described by Penn et al. (2000). They attributed the two-phase pattern to a formation of a microlayer at the sediment surface that initially removes P from the overlying water. Figure 11 shows this initial negative P concentration in the cores. The P release rates were calculated after the positive P release began.
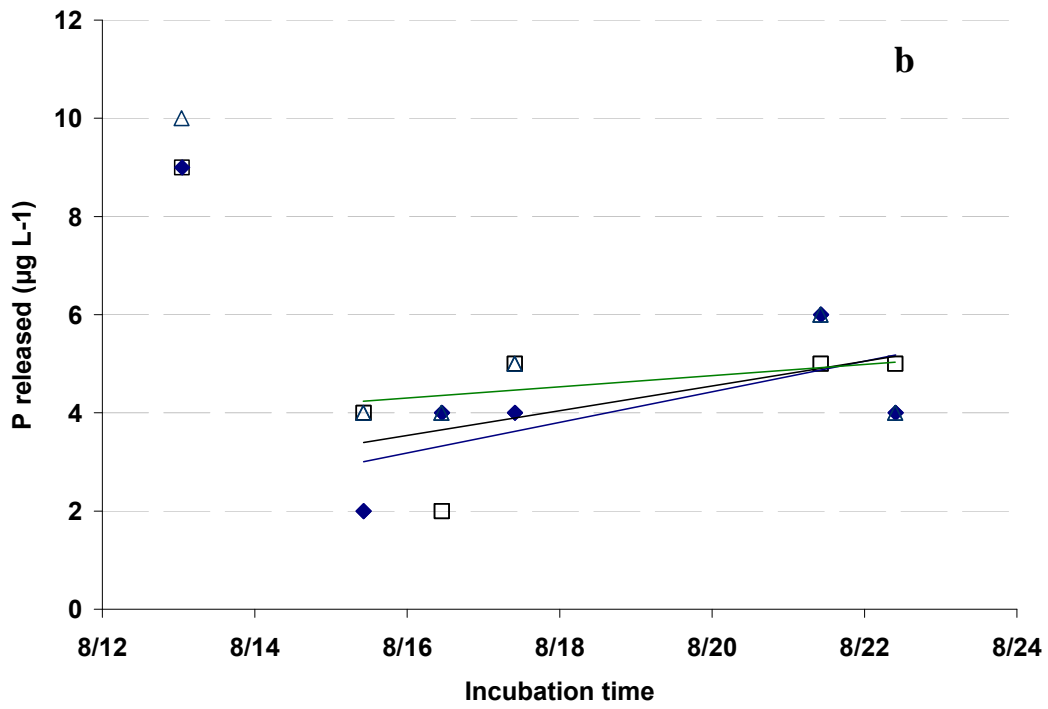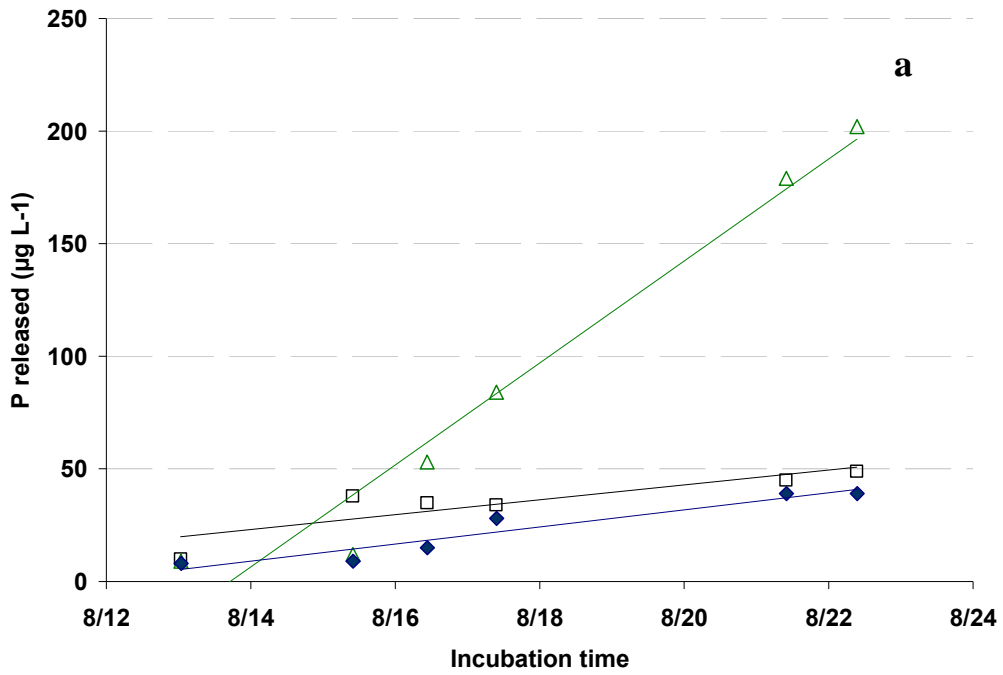
Figure 11. Typical P release pattern in anoxic (a) and oxic (b) sediment cores. Linear regression line shows time period used for calculation of release rates. Different symbols are different cores.

Laboratory sediment P release experiments resulted in a mean anoxic P release rate of 1.25 mg m^{-2} d^{-1} and a mean oxic P release rate of 0.25 mg m^{-2} d^{-1}. Table 3 summarizes the results of those experiments. A statistically significant difference (p value = .018) existed between anoxic and oxic sediment P release rates.

Table 3. P release rates for anoxic and oxic sediment cores from Shawano Lake.

	Anoxic mg m^{-2} d^{-1}	Oxic mg m^{-2} d^{-1}
Mean	1.25*	0.25*
Standard deviation	1.49	0.31
Minimum value	-0.02	-0.04
Max value	5.12	1.07
Samples (n)	14	17

* significantly different at the 95% confidence interval

Sediment P release rates under anoxic conditions fell within a range of values found for other lakes of similar trophic classification (Nürnberg 1986; Nürnberg,1987), and were consistent with previous work preformed in Shawano Lake by James et al. (2006). James et al. (2006) observed anoxic sediment P release rates from less than 0.1 to 6.1 mg m^{-2} d^{-1} throughout the lake. Many of the shallow littoral stations they sampled had the lowest P release while the deeper central area had the greatest P release rates. James et al. (2006) believed a weak relationship did exist between depth and rate of release as the higher rates of release generally occurred a stations greater than 6 m and lower release rates were observed in shallower stations. The average

anoxic P release rate for this research (1.25 mg m^{-2} d^{-1}) is similar to the anoxic P release rates from sediment cores collected at similar depths reported by James et al. (2006).

Nürnberg et al. (1986) observed a positive relationship between internal sediment P release rates and lake trophic classification. They showed lakes with greater P release rates usually had a higher trophic classification. P release rates were consistent with trophic classification for a mesotrophic to moderately eutrophic lake.

Shawano Lake exhibits an anoxic P load associated with its anoxic hypolimnion. As previously covered in the P budget portion of this thesis, two methods were used to evaluate sediment P release under anoxic conditions. The first method used the anoxic factor approach from Nürnberg (1995) and a measured P release rate to estimate an anoxic P load of 190 kg. The second method used the known volume of water in the hypolimnion (0.9 hm^{-3}) and the maximum measured P concentration (223 μg L^{-1}) to estimate the anoxic P load of 200 kg. Both methods lead to similar estimates, demonstrating that P concentrations measured in the hypolimnion were consistent with anoxic P release rates measured in the laboratory with sediment cores by James et al. (2006). James et al. (2006) collected their cores from anoxic portions of the lake. In contrast, the anoxic sediment release measured from sediment cores in this research were collected in shallow littoral areas. Using the mean anoxic P release rate (1.25 mg m^{-2} d^{-1}) of this research, only 55 kg of P would be expected to accumulate in the hypolimnion. This shows how the rate of sediment P release could vary in different parts of the lake.

It is difficult to estimate the importance of anoxic sediment P release in the hypolimnion over the long term in Shawano Lake because stratification patterns are variable from year to year. Stratification was first documented in the lake in 2005. The lake became strongly stratified in the summer of 2006. This stratification led to anoxia above the sediment and high concentrations of P in the hypolimnion. In contrast, monitoring during previous years did not show stratification. The long term record going back to 1988 never showed the lake stratified (Wisconsin DNR – Self Help Monitoring, 1988-2007). This year-to-year variability makes it difficult to determine the long term P contribution from an anoxic hypolimnion.

It is also difficult to estimate anoxic P release in shallow littoral regions of the lake. Daily and seasonal fluctuations of dissolved oxygen are known to exist in many lakes, particularity in areas of dense aquatic plant and algal growth. Anoxia in these regions can occur for short periods. These fluctuations have been shown to enhance sediment P release. James et al. (1996) observed anoxia in dense aquatic plant beds in Delavan Lake, Wisconsin that led to enhanced P release. Because my laboratory results showed a range of P release rates under which anoxic conditions lead to an almost immediate release of P from the sediment, even these short-term fluctuations could lead to the increased sediment P release.

Changes to the redox status at the sediment water interface following aquatic macrophyte senescence can also occur. Decomposing plant material can be in direct contact with the sediment. An example of this in Shawano Lake is curly-leaf pondweed beds following senescence. As decomposition persists, the sediment surface

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may exhibit localized reductions in oxygen and pH. These changes could increase sediment P release rates due to anoxia in addition to release from the decomposing plant material.

Monitoring for dissolved oxygen and pH and was performed in Shawano Lake in 2006 to evaluate these fluctuations. Data was collected by the USACOE at a single monitoring location and by UWSP in the early morning at 14 aquatic plant beds. Anoxia and low pH were never measured but a relatively high pH was observed using both methods. Dissolved oxygen concentrations never fell below 5 mg L^{-1} (min. = 5.48 mg L^{-1}) and pH ranged from 7.3 to 9.5 at the location monitored by the USACOE (James et al. 2006). Daily fluctuations monitored at 14 aquatic macrophyte beds showed dissolved oxygen concentrations fell below 5 mg L^{-1} only once (site 5 = 3.8 mg L^{-1}) and pH ranged between 7.6 and 10.0. Because anoxia was not observed in the shallow aquatic macrophyte beds, a P load attributed to an anoxic epilmnion was assumed to be zero. This is an area that could be investigated in more detail in the future.

P release rates under oxic conditions were lower than those under anoxic conditions. Oxic P release rates were generally low and at times, negative. Negative P release suggests the sediment was adsorbing P. The oxic release rates were relatively small compared to other lakes of similar trophic classification but are similar to those measured in Shawano Lake by James et al. (2006). James et al. (2006) observed oxic sediment P release rates within a range of less than 0.1 mg m^{-2} d^{-1} to 2.9 mg m^{-2} d^{-1}, where most were less than 0.1 mg m^{-2} d^{-1}. The relatively low oxic P release rates

observed in this study and James et al. (2006) are similar to what would be needed to account for an epilimnion sediment P contribution as presented in the July-September P budget. Although the oxic P release rate is relatively low per area, the basin area of Shawano Lake is large relative to the water volume. Large shallow lakes have large areas where oxic sediment P release can occur. The research described here demonstrates that for shallow lakes, oxic P release can be very important. Because oxic P release can be so important to the P budget, it is useful to examine the factors that control this release.

4.3 Role of pH in Sediment P Release

Both high and low pH could influence sediment P release rates in Shawano Lake. At high pH, ligand exchange of P by hydroxyl ions can occur on iron oxides, particularly in lakes where a large fraction of P is bound to iron (Jensen et al. 1992, Boers 1991, Drake and Haney 1987). High pH also favors the formation of $CaCO_3$ and calcium-P minerals that can increase the sorption of P. The dissolution of $CaCO_3$ and calcium-P minerals and their subsequent release of adsorbed P occur at low pH (Driscoll et al. 1993, Penn et al. 2000). As a result, the effect of pH on sediment P release may be complex.

Comparing the pH to sediment P release rates shows they do vary with pH, but statistically significant trends are not apparent. This was observed when comparing mean sediment P release rates for oxic cores (0.25 mg m^{-2} d^{-1}) and the mean release rate for the oxic, low pH cores (0.80 mg m^{-2} d^{-1}) from this research (Table 4). These means are not statistically different (p = 0.09) due to high variability and a low sample size. Overall, the mean sediment P release rates measured under oxic, low pH (pH = 7.2) conditions were about 30% higher than those measured at the higher pH (pH = 7.8 – 8.5) but variations between sites may also be complicating this trend.

Table 4. P release rates for oxic and oxic, low pH sediment cores from Shawano Lake.

	Oxic mg m^{-2} d^{-1}	Oxic, low pH mg m^{-2} d^{-1}
Mean	0.25	0.80
Standard deviation	0.31	1.26
Minimum value	-0.04	0.08
Max value	1.07	3.80
Samples (n)	17	8

The laboratory oxic P release rates were combined with those of James et al. (2006) to further examine the role of pH. Figure 12 shows a weak overall relationship between oxic P release rate and pH, but it may also reflect the spatial variations in release in different parts of the lake. The results in Figure 12 do show the low sediment oxic P release rates in Shawano Lake, particularly when pH values of 9 or greater are reached. The majority of oxic P release rates were less than 1.0 mg m^{-2} d^{-1} and many were less than 0.1 mg m^{-2} d^{-1}. Figure 12 shows these are much lower than measured release rates from other lakes
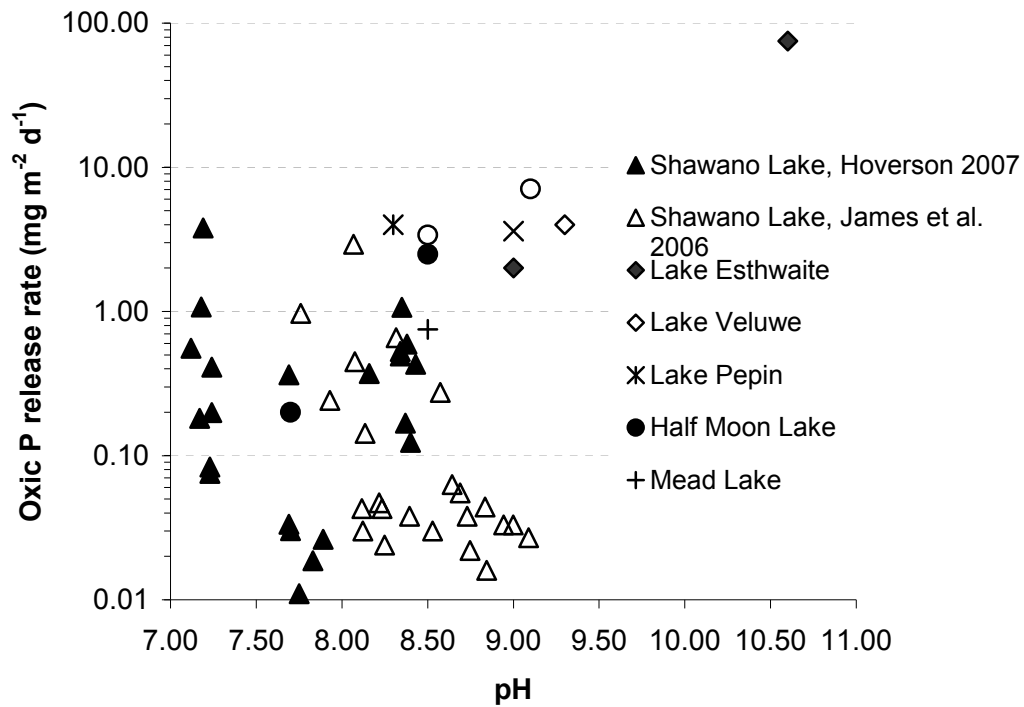
Figure 12. Relationship between pH and P release rate under oxic conditions for Shawano Lake and compared to other lakes where oxic P release rates were measured.

Fluctuations in pH that occur over short time frames may be important to P release. Laboratory results showed that oxic P release rates and pH showed a weak relationship between high pH and a decreased oxic P release. Photosynthesis and respiration from aquatic plant and algae communities are responsible for pH fluctuations. These pH fluctuations, sometimes occurring for only a short period have been suggested by James et al. (1996) to enhance sediment P release in a lake where P release occurs by ligand exchange. Similarly, Frodge (1991) found high pH and enhanced P release under large mats of algae. In Shawano Lake, these short-term pH fluctuations may actually reduce oxic P release.

4.4 Sediment Characteristics

To better understand what controls sediment P release in Shawano Lake, P fractions in the sediment were measured. The P fractions are operationally defined forms of P in the sediment. The sediment is extracted with a sequence of solutions and the P that is removed with each solution is considered a different form of P. The sequential P extraction approach used was developed by Hieltjes and Lijklema (1980). The fractionation extracted P-NH$_4$Cl (loosely bound, interstitial P, and CaCO$_3$ adsorbed P), P-NaOH (iron and aluminum bound P), and P-HCl (calcium bound P). A final P acid digestion was performed to determine any residual P (organic bound P).

The results of the P fraction analysis are shown in Table 5 and Figure 13. The organic bound P (56.7%) was the largest fraction of P in the sediment. Calcium bound P was the second largest fraction (40.3%) and made up the majority of the inorganic P, followed by iron and aluminum bound P (2.9%). The loosely bound, interstitial, and CaCO$_3$ adsorbed P made up only a small fraction of the P (0.2%). This indicates that the dominant P fractions were organic bound P and calcium bound P. Over half of the P was organic bound and the most of the inorganic P was associated with calcium. The inorganic portion included only 8.0% of the iron and aluminum bound P and 4.0% of the loosely bound, interstitial, and CaCO$_3$ adsorbed P. In general, the total organic fraction made up about 56.7% of the total sediment P and the total inorganic P made up the remaining 43.3%.

Table 5. Sediment P fractions determined by sequential extraction.

Sediment P fraction	n	Mean mg/g dry weight	Stand dev	Min value	Max value	Mean % Total P	Mean % Inorganic P
P-NH$_4$Cl	24	< 0.01	< 0.01	< 0.01	< 0.01	< 0.1%	4.0%
P-NaOH	24	0.02	< 0.01	< 0.01	0.03	2.9%	8.0%
P-HCl	24	0.22	0.04	0.16	0.33	40.3%	88.0%
P-residual	24	0.31	0.08	0.16	0.52	56.7%	--
Total P	24	0.55	0.11	0.39	0.78	100.0%	--
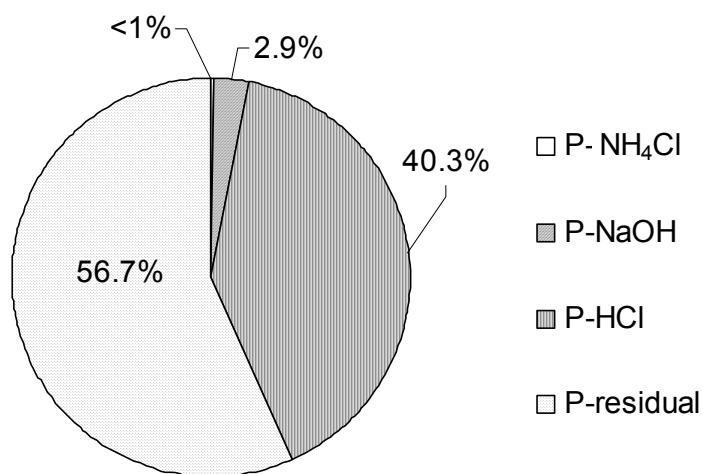
Figure 13. P fractions of surficial sediment sampled at Site 5.

The elemental composition of some of the sediments was also measured. The sediment composition consisted of approximately 2.0 % dry weight as calcium, 1.3% as iron, 0.8% as magnesium, and 0.04% as P. Carbonate consisted of roughly 1.7% dry weight on average, and assuming all the carbonate was bound to calcium, CaCO$_3$ consisted of roughly 2.8% dry weight. A summary of sediment characteristics and elemental composition is shown in Table 6.

Table 6. Elemental composition and other characteristics of sediment.

Sediment P fraction	n	Mean dry weight mg/g	Stand dev	Min value	Max value	Mean % dry weight
Total Fe	6	13.4	2.4	11.2	17.6	1.3%
Total Ca	6	19.5	6.2	12.1	29.8	2.0%
Total Mg	6	8.3	1.3	6.9	10.5	0.8%
Total P	6	0.45	0.1	0.4	0.6	0.04%
CaCO$_3$	6	28.0	8.8	17.7	42.3	2.8%
Total organic matter	6	--	--	--	--	18.3%

Significant correlations between oxic P release rates and sediment characteristics did not exist in the six sediment samples. P-NH$_4$Cl, P-NaOH, and P-org were negatively correlated to oxic P release, but P-HCl was positively correlated. This suggests that P-HCl may be enhancing oxic P release while P-NH$_4$Cl, P-NaOH, and P-organic are not. Because of the low correlations, these P fractions may not be important to oxic P release and suggests other variables are controlling P release.

Significant correlations did exist between P fractions, P-total, calcium, and iron. P-total was positively correlated with all the P fractions, calcium, and iron. These correlations were high and suggest that an increase in P-total reflects an increase in P, calcium, and iron. This is consistent with the complex picture of sediment P interactions with both calcium and iron.

Table 7. Pearson correlation coefficients (r) for oxic P release rates (mg m^{-2} d^{-1}), sediment P fractions (mg/g dry weight), and calcium, iron, and P (mg/g dry weight). Asterisks indicate significant correlations at the 0.05 level or less.

	P-NH$_4$Cl	P-NaOH	P-HCl	P-Org	P-Total	Ca	Fe
Oxic P release	-0.479	-0.244	0.261	-0.600	-0.322	-0.555	-0.107
P-NH$_4$Cl		* 0.826	0.675	* 0.957	* 0.836	* 0.881	0.555
P-NaOH			* 0.832	* 0.889	* 0.978	0.611	0.804
P-HCl				0.607	0.788	0.461	0.732
P-Org					* 0.911	0.807	0.633
P-Total						0.597	* 0.849
Ca							0.430

Unfortunately, the correlations obtained with this small set of samples do not allow definite conclusions to be made regarding controls over oxic sediment P release in Shawano Lake. The results seem to indicate a role of iron, calcium, and perhaps organic matter in oxic P release.

It has been suggested that Fe:P ratios can aid in evaluating oxic P release. Jensen et al. (1992) determined that Fe:P ratios in the surface sediment could be used to indicate P release from oxic sediments. Their results showed that oxic P release was negatively correlated with the surface sediment at a high Fe:P ratio. They indicated high Fe:P ratios provided more free sorption sites for P on iron oxides. Fe:P ratios above 15 were indicative of lakes in which it was possible to control P release from these sediments by keeping them oxidized. Fe:P ratios less than 15 usually indicated that most sorption surfaces were saturated and may have lead to P release, particularly at high pH. The sediment sampled in Shawano Lake had a Fe:P ratio in the range of 26 to 38. According to Jensen et al. (1992) these ratios are high and indicative of lakes that would be expected to exhibit a low oxic internal P release. In Shawano Lake,

where iron is bound to a small fraction of P (2.9%) but is relatively abundant in the sediment, the mechanism controlling low P release rates may be the many sorption sites on the iron oxides.

Interestingly, the P-NH_4Cl extraction, which included the fraction of P that would be associated with $CaCO_3$ adsorbed P, was the smallest P fraction. Prior to experimentation, it was assumed a large portion of the P would be removed during this process, but this was not so. About 55% of the calcium in the sediment could be attributed to $CaCO_3$ and the remaining 45% is assumed to be bound to calcium minerals such as apatite ($Ca_5(PO_4)_3(OH,F,Cl)$). The largest fraction of inorganic P was associated with these calcium minerals (P-HCl) and suggests that with the relatively small oxic P release rates in Shawano Lake, P may over time become buried and removed from interactions with the overlying water.

Results indicate that ligand exchange processes so important to many lakes with oxic internal P loading may not be as important in Shawano Lake. The relatively high Fe:P ratio suggests an increased sorption of P as more sites are available for P sorption on the iron oxides. Calcium is more apt to bind P and inhibit exchange at high pH, and may also be reducing P release in Shawano Lake. Calcium bound P is relatively inert at high pH and over time may ultimately remove P from interactions with the overlying water as it becomes buried. Iron and calcium are likely controlling P release in oxic sediments at high pH and enhancing P release at low pH.

4.5 Summary

Laboratory experiments demonstrated that P contained in the sediments of Shawano Lake can be released to the water column and act as an important source of P. The relatively small oxic sediment P release rate calculated for the $P_{epi\text{-}sed}$ was shown to play an important role in the Shawano Lake P budget. When combined with anoxic P sediment release from the hypolimnion, the internal sediment P contribution accounted for 71% (46% to 81% range) of the July-September P budget. This P release could be explained with an oxic P release rate of 0.31 mg m^{-2} d^{-1} (0.10 to 0.49 mg m^{-2} d^{-1}).

Laboratory sediment P release experiments resulted in an average anoxic P release rate of 1.25 mg m^{-2} d^{-1} and an average oxic P release rate of 0.25 mg m^{-2} d^{-1}. The measured oxic P release rates were relatively small, but when placed within the context of the lake P budgets were able to account for the observed increase in P mass. Previous studies and preliminary results here suggest that both iron and calcium play roles in controlling oxic P release in Shawano Lake, but the mechanisms controlling release are still incompletely understood.

Sediment P release was clearly important to P dynamics in Shawano Lake. The sediment P load accounted for the largest P source for the summer P budget. This internal P source is a vital P pathway to the lake and should always be considered when attempting to manage P cycling in Shawano Lake and other shallow lakes.

5.0 Recommendations and further research

The research demonstrated the importance of oxic sediment release in the growing season phosphorus budget of a large, shallow lake, but also generated ideas for future research. One important aspect of this release may be the effect of pH. Although this has been studied by others, a detailed evaluation of sediment release at a wide range of pH values in sediment cores sampled at singular locations may help in understanding pH mechanisms contributing to sediment P release. The range would have to be greater than what was undertaken in this research, and should include very low and very high pH values.

Further evaluation of sediment characteristics and compositions would likely also help develop lake-wide budgets for oxic P release. Low release rates observed at locations where sediment analysis was preformed make it difficult to determine significance correlations between sediment compositions and P release rates. Variability within sites was high for sediments sampled within close proximity of one another and an evaluation of P release rates and sediment characteristics at multiple locations throughout the lake would help in determining locations and sediment characteristics most susceptible to sediment P release in Shawano Lake.

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Appendix 1 - Laboratory derived P release rates, pH, and upper and lower bounds 95% confidence interval, site 3 and 4

Site	Treatment	Final pH	Sediment P release mg m^{-2} d^{-1}	lower 95 CI mg m^{-2} d^{-1}	upper 95 CI mg m^{-2} d^{-1}
3	Oxic (2)	8.35	1.07	0.45	1.68
3	Oxic (2)	8.43	0.43	-0.03	0.89
3	Oxic (2)	8.38	0.59	0.28	0.91
3	Oxic (2)	8.16	0.37	0.11	0.64
3	Oxic low pH (3)	7.18	1.08	0.58	1.57
3	Oxic low pH (3)	7.17	0.18	0.09	0.27
3	Oxic low pH (3)	7.19	3.80	-10.27	17.87
3	Oxic low pH (3)	7.12	0.56	0.35	0.76
3	Anoxic (1)	8.34	3.03	1.83	4.22
3	Anoxic (1)	8.4	0.90	-0.01	1.87
3	Anoxic (1)	8.34	0.41	0.01	0.82
3	Anoxic (1)	8.37	0.29	0.24	0.34
4	Oxic (2)	8.34	0.53	0.36	0.70
4	Oxic (2)	8.4	0.12	0.06	0.18
4	Oxic (2)	8.34	0.49	-0.40	1.38
4	Oxic (2)	8.37	0.17	0.05	0.29
4	Oxic low pH (3)	7.24	0.41	-0.12	0.94
4	Oxic low pH (3)	7.23	0.08	0.04	0.13
4	Oxic low pH (3)	7.24	0.20	0.11	0.28
4	Oxic low pH (3)	7.23	0.08	0.02	0.13
4	Anoxic (1)	8.35	4.79	4.05	5.53
4	Anoxic (1)	8.43	1.26	0.56	1.95
4	Anoxic (1)	8.38	0.74	0.16	1.31
4	Anoxic (1)	8.16	0.26	-0.23	0.76

Appendix 1 (continued) - Laboratory derived P release rates, pH, and upper and lower bounds 95% confidence interval, site 5

Site	Treatment	Final pH	Sediment P release mg m^{-2} d^{-1}	lower 95 CI mg m^{-2} d^{-1}	upper 95 CI mg m^{-2} d^{-1}
5	Anoxic (1)	8.15	0.32	0.07	0.57
5	Anoxic (1)	8.35	0.35	0.16	0.54
5	Anoxic (1)	7.98	2.19	1.56	2.82
5	Anoxic (1)	8.24	0.37	0.21	0.53
5	Anoxic (1)	8.09	-0.02	-0.06	0.25
5	Anoxic (1)	8.3	0.35	0.09	0.61
5	Oxic (2)	7.75	0.01	-0.04	0.58
5	Oxic (2)	7.69	0.36	0.15	0.58
5	Oxic (2)	7.69	0.03	-0.08	0.14
5	Oxic (2)	7.7	0.03	-0.03	0.09
5	Oxic (2)	7.77	-0.04	-0.43	0.35
5	Oxic (2)	7.83	0.02	-0.04	0.78
5	Oxic (2)	7.89	0.03	-0.03	0.80
5	Oxic (2)	7.82	0.00	0.00	0.00
5	Oxic (2)	7.81	-0.02	-0.07	0.02

Appendix 2 - Sediment characteristics at site 5

mg g dry weight

Core ID	As	Ca	Cu	Fe	K	Mg	Mn	Na	P	Pb	SO4	Zn
10	0.008	12.103	0.011	11.161	0.609	6.901	0.355	0.229	0.363	0.021	7.409	0.043
11	0.013	16.885	0.013	13.886	0.893	10.478	0.416	0.392	0.365	0.011	15.847	0.033
12	0.010	20.983	0.020	17.640	1.161	8.469	0.568	0.467	0.619	0.034	15.846	0.063
15	0.010	29.764	0.016	14.382	0.665	7.609	0.491	1.516	0.534	0.029	13.352	0.052
16	0.009	21.973	0.010	11.459	0.597	9.024	0.358	1.023	0.402	0.019	10.137	0.039
17	0.010	15.252	0.011	12.060	0.625	7.376	0.382	0.947	0.429	0.022	9.901	0.044
mean	0.010	19.494	0.014	13.431	0.758	8.309	0.428	0.762	0.452	0.023	12.082	0.046
stan dev	0.002	6.217	0.004	2.439	0.226	1.310	0.085	0.486	0.103	0.008	3.474	0.011
min	0.008	12.103	0.010	11.161	0.597	6.901	0.355	0.229	0.363	0.011	7.409	0.033
max	0.013	29.764	0.020	17.640	1.161	10.478	0.568	1.516	0.619	0.034	15.847	0.063

% dry weight

Core ID	As	Ca	Cu	Fe	K	Mg	Mn	Na	P	Pb	SO4	Zn
10	0.00%	5.07%	0.00%	4.68%	0.26%	2.89%	0.15%	0.10%	0.15%	0.01%	3.10%	0.02%
11	0.01%	7.45%	0.01%	6.13%	0.39%	4.62%	0.18%	0.17%	0.16%	0.00%	6.99%	0.01%
12	0.00%	9.18%	0.01%	7.72%	0.51%	3.71%	0.25%	0.20%	0.27%	0.01%	6.93%	0.03%
15	0.00%	12.75%	0.01%	6.16%	0.29%	3.26%	0.21%	0.65%	0.23%	0.01%	5.72%	0.02%
16	0.00%	9.96%	0.00%	5.19%	0.27%	4.09%	0.16%	0.46%	0.18%	0.01%	4.60%	0.02%
17	0.00%	6.81%	0.00%	5.38%	0.28%	3.29%	0.17%	0.42%	0.19%	0.01%	4.42%	0.02%
mean	0.00%	8.54%	0.01%	5.88%	0.33%	3.64%	0.19%	0.33%	0.20%	0.01%	5.29%	0.02%
stan dev	0.00%	2.70%	0.00%	1.07%	0.10%	0.63%	0.04%	0.21%	0.04%	0.00%	1.54%	0.00%
min	0.00%	5.07%	0.00%	4.68%	0.26%	2.89%	0.15%	0.10%	0.15%	0.00%	3.10%	0.01%
max	0.01%	12.75%	0.01%	7.72%	0.51%	4.62%	0.25%	0.65%	0.27%	0.01%	6.99%	0.03%

Appendix 3 - P fractions as mg P g^{-1} sediment

24 sediment cores sampled in at site 5, fractions determined by sequential extraction (Hieltjes and Lijklema, 1980)

Core ID	% Moisture	Loosely- Bound P	Fe- and Al- Bound P	Ca- Bound P	Total Organic P	Total P
1	85	0.000	0.015	0.214	0.271	0.500
2	83	0.000	0.018	0.221	0.267	0.506
3	88	0.000	0.018	0.240	0.307	0.566
4	84	0.000	0.011	0.233	0.239	0.484
5	84	0.000	0.014	0.155	0.265	0.434
6	86	0.000	0.014	0.196	0.293	0.503
7	84	0.000	0.011	0.187	0.294	0.493
8	76	0.000	0.004	0.226	0.158	0.387
9	86	0.000	0.013	0.181	0.338	0.532
10	83	0.000	0.008	0.167	0.261	0.436
11	83	0.000	0.010	0.216	0.219	0.445
12	90	0.001	0.031	0.267	0.440	0.738
13	87	0.000	0.017	0.204	0.349	0.570
14	89	0.001	0.026	0.332	0.303	0.662
15	84	0.000	0.009	0.218	0.271	0.498
16	85	0.000	0.018	0.222	0.302	0.542
17	89	0.000	0.024	0.234	0.524	0.782
18	87	0.000	0.014	0.230	0.333	0.577
19	86	0.000	0.022	0.233	0.326	0.581
20	91	0.001	0.023	0.244	0.457	0.724
21	85	0.000	0.016	0.200	0.358	0.574
22	88	0.000	0.017	0.253	0.331	0.601
23	87	0.000	0.023	0.238	0.399	0.660
24	77	0.000	0.005	0.206	0.175	0.386