

Ann Lake Internal Load Feasibility Study



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Prepared for:
Kanabec SWCD
Ann Lake Watershed Alliance
MPCA



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APPENDICES

Appendix A: UW-Stout Internal Phosphorus Loading and Management Considerations for Ann Lake, Minnesota

Appendix B: Ann Lake Non-Steady State Advection-Diffusion Sulfate Model

List of Acronyms

Al	Aluminum
BMP	Best Management Practice
Cl	Chloride
CLMP	Citizen Lake Monitoring Program
DO	Dissolved Oxygen
EDA	Environmental Data Access
La	lanthanum
m	Meters
MnDNR	Minnesota Department of Natural Resources
MPCA	Minnesota Pollution Control Agency
NCHF	North Central Hardwood Forest
O&M	Operation and Maintenance
OHW	Ordinary High Water
P	Phosphorus
PACl	poly-aluminum chloride
PhL	Phoslock ®
SWCD	Soil and Water Conservation District
TMDL	Total Maximum Daily Load
TP	Total Phosphorus
TSS	Total Suspended Solids
WRAPS	Watershed Restoration and Protection Strategy
WMA	Wildlife Management Area

1.0 Executive Summary

Ann Lake is a moderately large (653 acres), shallow, wild rice lake located six miles northwest of the City of Mora, MN. Ann Lake is located in the Ann River subwatershed which is part of the larger Snake River watershed in the St. Croix River Basin. Water quality monitoring efforts for Ann Lake show that phosphorus and chlorophyll-a concentrations have consistently exceeded state water quality standards for shallow lakes in the North Central Hardwood Forest (NCHF) ecoregion. Ann Lake was placed on the State of Minnesota's 303(d) list of impaired waters in 2004, and a Total Maximum Daily Load (TMDL) study was completed for the lake in 2013 (MPCA, 2013). The TMDL study indicated that a majority of the phosphorus reduction (approximately 86%) for the lake needed to come from reducing sediment phosphorus release.

The purpose of this study is to provide a detailed feasibility assessment of the internal load reduction alternatives for Ann Lake that include the following components: proposed treatment area(s), chemical dosing rates, costs, phosphorus removal efficiency and potential impacts to wild rice and other environmental factors. The internal load treatment options that were investigated include aluminum sulfate, Phoslock, poly-aluminum chloride, and hypolimnetic aeration.

Section 2.0 of this report provides a background of Ann Lake and the TMDL project, and Section 3.0 provides a description of the methods and results of the sediment core collection and lab analysis to support the feasibility assessment. Section 5.0 is an in-depth feasibility review of each of the four treatment alternatives.

2.0 Background

ANN LAKE DESCRIPTION

Ann Lake is a moderately large (653 acres) lake located in the Ann River subwatershed of the larger Snake River watershed. The lake is relatively shallow, with a maximum depth of 17 feet, and 91% littoral area. The major inflow to Ann Lake is the Little Ann River and lake water levels are maintained by a sheet piling dam at the lake's outlet to the Ann River on the east end of the lake (Figure 2-2). Much of the eastern arm of Ann Lake lies within the Ann Lake State Wildlife Management Area (WMA). Landuse throughout the lake's 35,826 acre watershed consists of forest land (77%), hay and pasture (11%) and open water and wetlands (10%).

Several vegetation surveys have been conducted on Ann Lake by the Minnesota Department of Natural Resources (MnDNR) dating back to the late 1940s. Results of these surveys indicate Ann Lake has, at one time or another, contained over 50 different submerged, floating leaf, and emergent plant species, including wild rice (MnDNR, 2010). Wild rice has important cultural value to Native American tribes and local communities throughout the State of Minnesota and it also provides habitat and an important food source for waterfowl. While the wild rice in Ann Lake is not intensely harvested by local residents, it is abundant throughout the shallow eastern arm of the lake at water depths less than five feet (Figure 2-2).

Intensive water quality monitoring on Ann Lake began in 2008 as part of the MPCA's 10-year assessment cycle for the Snake River Watershed. Monitoring has also been conducted since the late 1990's by the Ann Lake Watershed Alliance (ALWA) through the Citizen Lake Monitoring Program (CLMP). Results of these monitoring efforts show that phosphorus and chlorophyll-a concentrations have consistently exceeded state water quality standards for shallow lakes in the NCHF ecoregion.

ANN LAKE TMDL

Ann Lake was placed on the State of Minnesota's 303(d) list of impaired waters in 2004, and a TMDL study was completed for the lake in 2013 (MPCA, 2013). The TMDL calls for a phosphorus load reduction of 4,758 pounds per year. Approximately 86% (4,096 pounds) of the total load reduction will need to come from reducing phosphorus release from the lake's sediment. As part of the TMDL study, intact sediment cores were collected in Ann Lake to measure sediment phosphorus release rates. Results indicate phosphorus release from the sediment is very high

compared to other shallow lakes throughout the state of Minnesota and is a major source of soluble phosphorus to the lake's water column during the summer growing season. Other

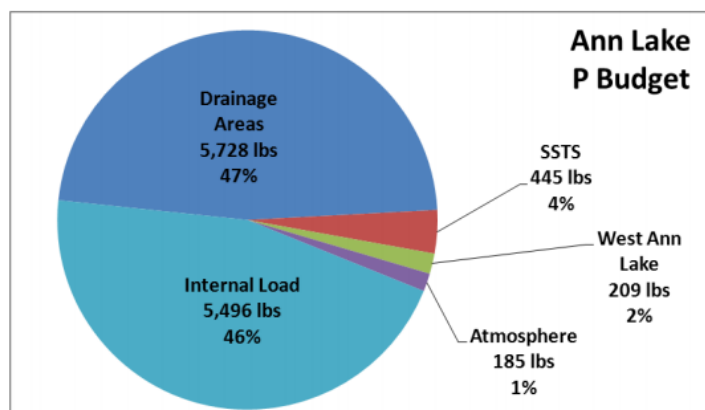


Figure 2-1. Ann Lake phosphorus budget based on the 2013 TMDL study.

lines of evidence such as elevated hypolimnetic total phosphorus (TP) and elevated surface water TP concentrations during fall turnover provide further evidence that internal loading is a major contributor to poor water quality conditions in Ann Lake (MPCA, 2013).

In addition to the internal load reduction goals, the Ann Lake TMDL study calls for a 211 pound per year TP load reduction in from the lake's watershed, and a 445 pound per year reduction from failing septics. The watershed draining to Ann Lake is mostly forest land, with smaller areas of pasture land near Ann Lake and the Little Ann River, the major surface water inflow to Ann Lake. In the Snake River Watershed Restoration and Protection Strategy (WRAPS) report (MPCA, 2014), local stakeholders and resource managers identified septic system upgrades, livestock and feedlot BMPs, and roadside erosion control projects among the key strategies in reducing watershed phosphorus loading to Ann Lake. The Kanabec SWCD and other local stakeholders are currently working on several projects in the Ann Lake watershed to reduce phosphorus loading to the lake to help achieve TMDL watershed load reductions. Some of these projects include:

- ▲ Two roadside runoff and erosion control practices
- ▲ One grassed waterway with buffer
- ▲ Two shoreline native restoration practices

GOALS OF THIS STUDY

The TMDL internal load reduction goal for Ann Lake is significantly greater than the watershed reduction goal. It will be extremely difficult, if not impossible to restore Ann Lake to meet state water quality standards without some sort of management strategy to decrease phosphorus loading from the lake's sediments. The management strategies and technology available to reduce internal loading in lakes have proven to be extremely effective, however, environmental impacts must be considered when selecting the best option. For example, the presence of wild rice in Ann Lake will need to be considered in selecting the most appropriate internal load management option for the lake. One of the most common chemicals used to treat lakes with high internal load, aluminum sulfate (alum), could potentially harm wild rice by increasing water column sulfate concentration.

The primary purpose of this study is to provide a detailed feasibility assessment of the internal load treatment alternatives for Ann Lake that includes the following components: proposed treatment area(s), chemical dosing rates, costs, phosphorus removal efficiency, and potential impacts to wild rice and other environmental factors. The internal load treatment alternatives explored in this study include alum, Phoslock®, poly-aluminum chloride, and hypolimnetic aeration.

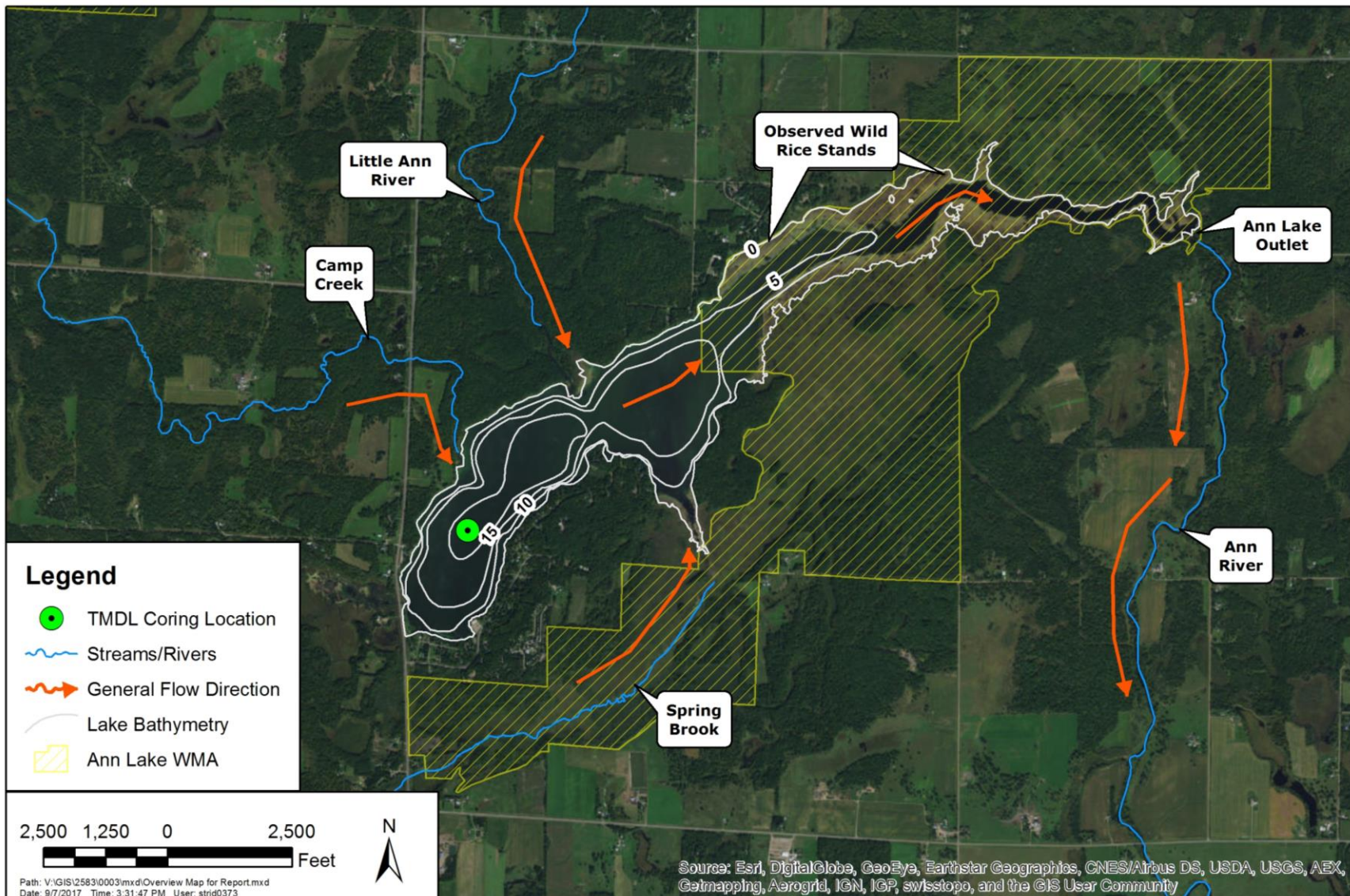


Figure 2-2. Ann Lake Overview.

3.0 Sediment Chemistry in Ann Lake

METHODS

Intact sediment cores were collected at three locations (Figure 3-3) on Ann Lake on September 11, 2016 using a gravity sediment coring device (Aquatic Research Instruments, Hope ID) equipped with an acrylic core liner (6.5-cm ID and 50-cm length). Station 10 is located in the western arm of Ann Lake within the 15-foot depth contour. Station 20 is located within the 10-foot contour in the middle basin of the lake. This station is situated near two major inflows to the lake – Spring Brook and the Little Ann River (Figure 2-2). Station 30 is located in the 5-foot contour of the eastern arm of the lake near the wild rice beds.

Sediment cores from each station were sectioned vertically at 1-cm intervals over the upper 6-cm layer, 2-cm intervals from 6-10 cm, and 2.5-cm intervals below 10 cm to evaluate variations in sediment physical-textural and chemical characteristics, including phosphorus fractionation. Phosphorus fractionation is sequential extraction analysis that characterizes the different types of phosphorus within the sediment total phosphorus pool. Understanding the total amount of each phosphorus fraction helps explain which factors are driving internal phosphorus loading within a lake. This information can be used to develop strategies and cost estimates to reduce internal phosphorus loading. Table 3-1 provides explanations of the different phosphorus fractions that were analyzed for this study.

Sediment cores from the deep location (Station 10) were also analyzed in the lab for phosphorus release under low oxygen (dissolved oxygen < 2mg/L; anoxic) conditions. Sediment phosphorus release rates under anoxic conditions are important to quantify because these are the conditions in which phosphorus release rates are highest.

Table 3-1. Definition list of phosphorus fractions measured in sediment.

Sediment Fraction	Abbreviation	Description	Mobility in Sediments	Mobile Conditions
Loosely Bound Phosphorus	Loosely-bound	This fraction includes porewater phosphorus and phosphorus that is bound to calcium carbonates.	High	All conditions
Iron Bound Phosphorus	Iron-bound P	Phosphorus that is adsorbed to oxidized iron. This fraction is highly mobile under low oxygen conditions.	High	Low Oxygen Conditions
Labile Organic Phosphorus	Labile-organic P	Phosphorus bound within organic matter that is easily broken down by bacteria. This fraction is mobile under anoxic and oxic conditions.	Moderate	All conditions
Redox Sensitive Phosphorus	Redox-P	This fraction includes loosely-bound P and iron-bound-P. Redox-P represents phosphorus in sediments that is mobile under anoxic conditions (dissolved oxygen <2 mg/L)	High	Low oxygen conditions
Aluminum Bound Phosphorus	Aluminum-bound-P	Aluminum-bound-P represents phosphorus fraction that is relatively stable in most environmental conditions	Low	High pH

SEDIMENT CHEMISTRY RESULTS

The primary factor driving internal loading in most lakes is phosphorus bound to iron in sediments (iron-bound P). Iron-bound P in benthic sediments is released during anoxic periods, which occurs when overlying water has dissolved oxygen below 2 mg/L. Therefore, lakes with a high fraction of iron-bound P have the potential to release phosphorus at a high rate. Based on our dataset of over 100 lakes in Minnesota, the approximate median concentration of iron-bound P in lakes is 0.2 mg/g. Generally, we have found that lakes with iron-bound P concentrations greater than 0.2 mg/g have higher phosphorus release rates. Furthermore, lakes that have high internal release rates typically have a large “bulge” of iron-bound and loosely-bound P near the sediment-water interface.

Sediment phosphorus fractions were analyzed at each site in Ann Lake by the University of Wisconsin - Stout Discovery Center (Appendix A). Results of these analyses indicate iron bound-P concentrations exceeded 0.2 mg/g at all three stations (Figure 3-1). Furthermore Station 10 sediments had redox-P concentrations of 1.78 mg/g in the uppermost 6 cm, which represents one of the highest concentrations of iron-bound P that we have observed in the State of Minnesota (Figure 3-1). Station 10 also demonstrated a large peak of phosphorus in the uppermost 6 cm, which is a signature for lakes with high phosphorus release from the sediment (Figure 3-2). Stations 20 and 30 both have moderately high iron-bound P concentrations (Figure 3-1 and 3-2), however, these concentrations are significantly lower than those observed at Station 10. These data suggest that the sediments in areas deeper than 15 feet likely contribute the greatest amount of phosphorus release in Ann Lake.

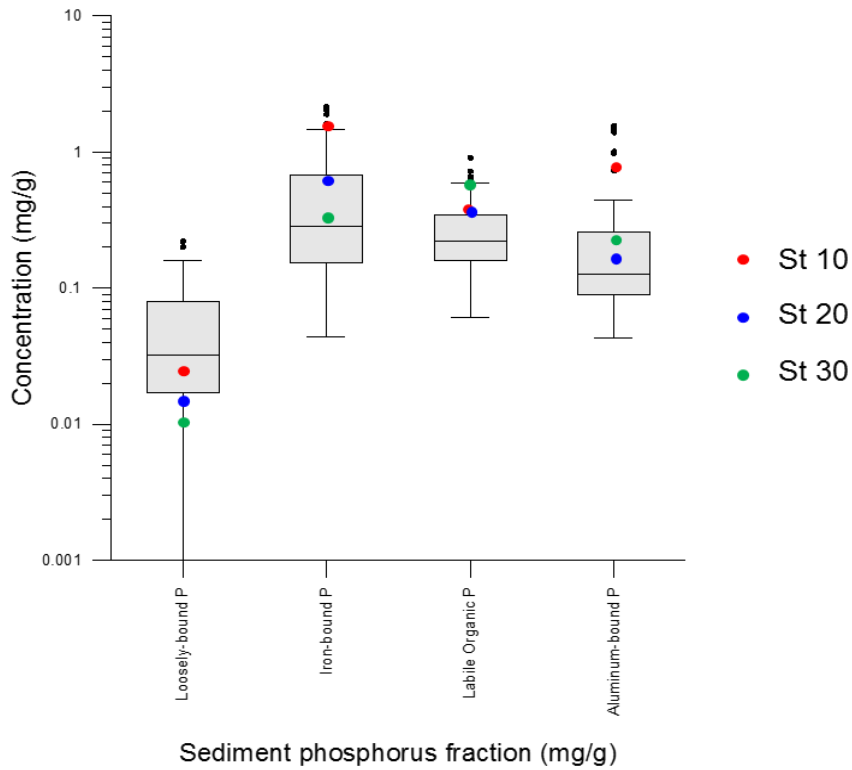


Figure 3-1. Sediment phosphorus fractionation in Ann Lake compared to other lakes in Minnesota.

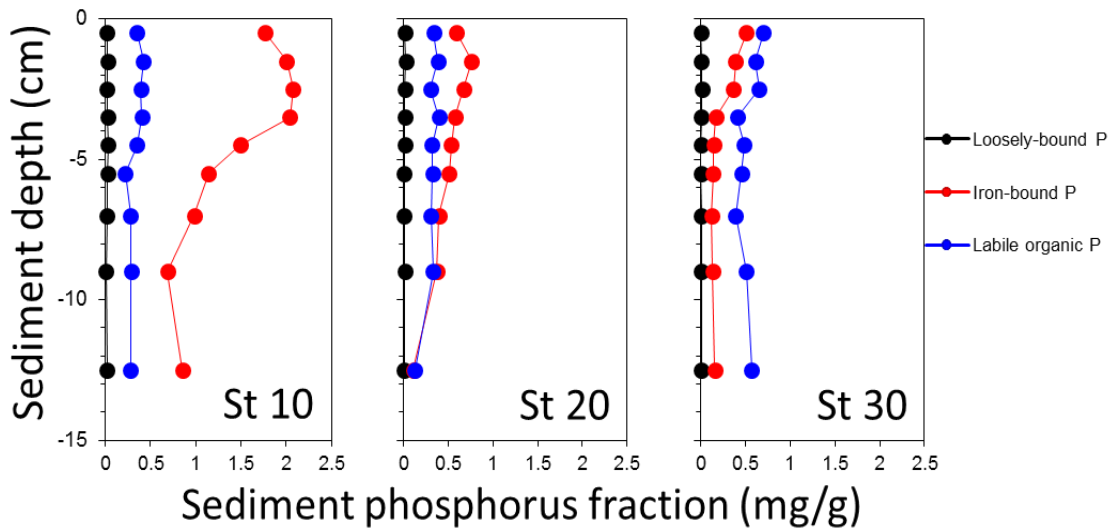


Figure 3-2. Mobile phosphorus fractions in Ann Lake sediment.

PROPOSED INTERNAL LOAD TREATMENT AREA

Selecting a treatment area is a critical component of developing an internal load management strategy. Since it is impractical to treat the entire surface area of most lakes due to cost and potential environmental impacts, the first step in determining the proper treatment area is to identify the area(s) of the lake that have the greatest contribution to internal phosphorus loading. Once these are identified, specific treatment areas can be refined by evaluating potential costs and benefits.

The two factors that have the greatest impact on internal phosphorus loading are sediment chemistry characteristics and water column dissolved oxygen. The sediment data collected for this study indicates that all three stations have higher than average iron-bound P concentrations, which is a key indicator of high potential internal load. Sediment collected from Station 10 has redox-P concentrations that are four times greater than Stations 20 and 30. Dissolved oxygen profiles from 2008 and 2009 were used to determine the maximum anoxic area within Ann Lake. These profiles suggest that low dissolved oxygen concentrations do not exist in areas shallower than 15 feet. Based on this information, the internal load treatment area for Ann Lake should focus on the 15-foot contour within the western basin (60 acres; Figure 3-3). Focusing internal load management efforts in this area should provide the greatest phosphorus reduction per dollar spent.

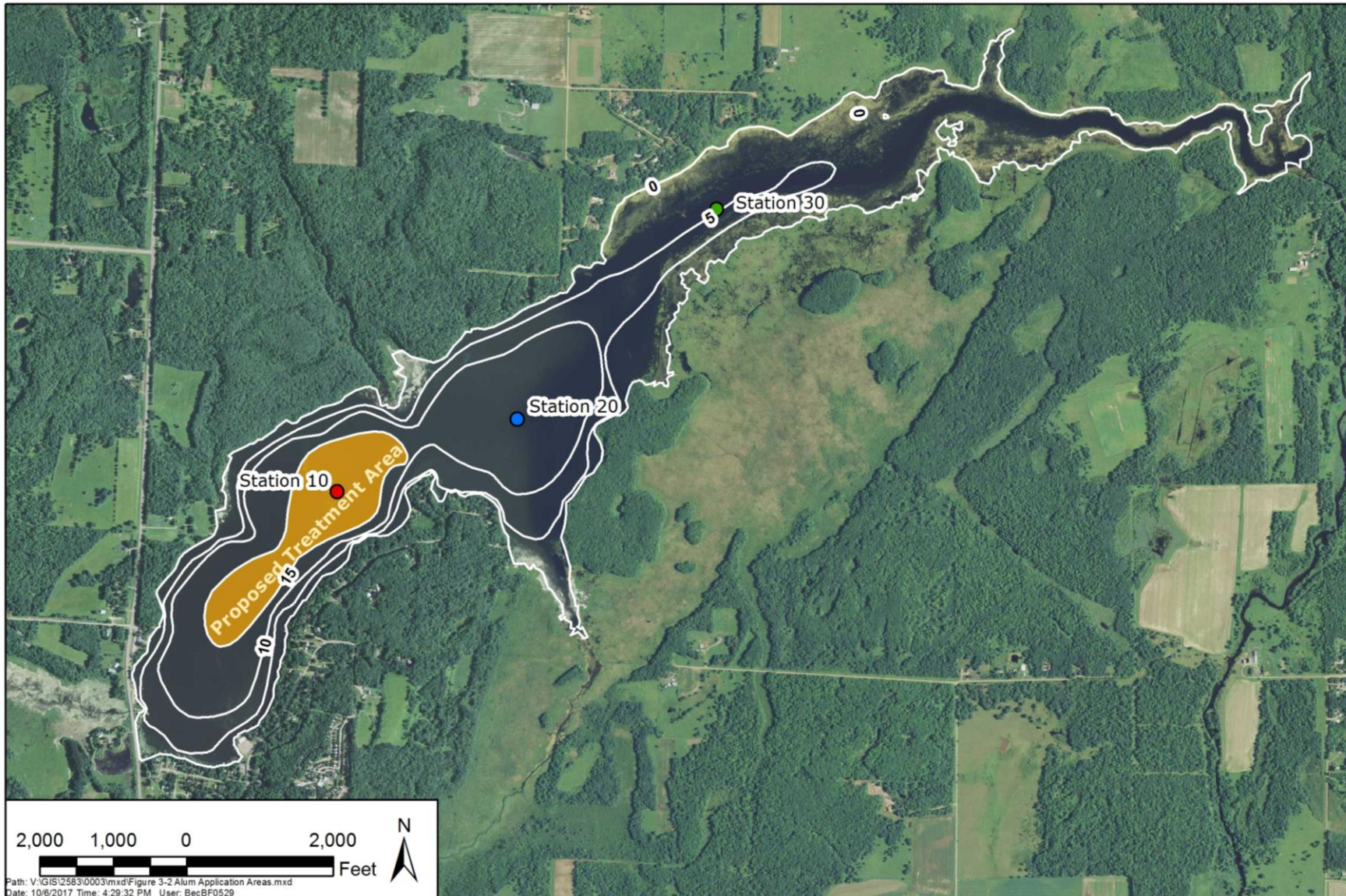


Figure 3-3. Proposed internal load treatment area for Ann Lake.

4.0 Internal Load Treatment Alternatives

ALTERNATIVE #1: ALUMINUM SULFATE (ALUM)

4.1.1 Alum Overview

Perhaps the most effective tool for controlling internal loading is sediment phosphorus inactivation, where phosphorus is permanently bound in sediments using chemical addition. One of the most common chemicals used for phosphorus inactivation is aluminum sulfate, which is also known as alum. The aluminum-phosphorus bond is very stable under environmental conditions and provides a long-term sink for phosphorus in the lake.

Alum is applied to lakes by injection of liquid alum just below the lake water surface. The alum quickly forms a floc and settles to the bottom of the lake, which converts highly mobile sediment phosphorus (redox-P) into an immobile phosphorus fraction (aluminum bound-P). This process reduces sediment phosphorus release rates, and ultimately reduces internal phosphorus loading in lakes.

4.1.2 Alum Dosing, Cost Estimate, and Application Schedule

The primary factors taken into consideration for developing alum cost estimates are the mass of elevated redox-P in the lake sediments and the total area that requires treatment. As discussed in Section 3, historic dissolved oxygen profile data for Ann Lake indicates that the depth of anoxia is approximately 15 feet and therefore the 15-foot depth contour was selected as the proposed internal load treatment area (Figure 3-3).

The sediment profiles collected in Ann Lake show that Station 10 clearly has accumulated more redox-P than the shallower sites (Stations 20 and 30) and therefore sediment profiles from Station 10 were used to determine the mass of mobile phosphorus that will be treated in Ann Lake. The primary goal of the alum treatment is to inactivate the elevated redox-P “bulge” from 0 to 6 cm (Figure 4-1).

The mass of aluminum needed to convert redox-P to aluminum bound-P was calculated using an empirically derived relationship between redox-P concentration and the ratio needed to inactivate 90% of redox-P (AL:P_{90%}) (James and Bischoff, 2015). This relationship suggests an alum application rate of 294.7 g Al/m² will be needed throughout the proposed treatment area. Based on this application rate and the size of the proposed treatment area (60 acres), the total cost of an alum treatment for Ann Lake would be approximately \$650,000 (Table 4-1). This estimated cost includes bidding, permitting, specs, application observation, and follow-up monitoring (discussed below).

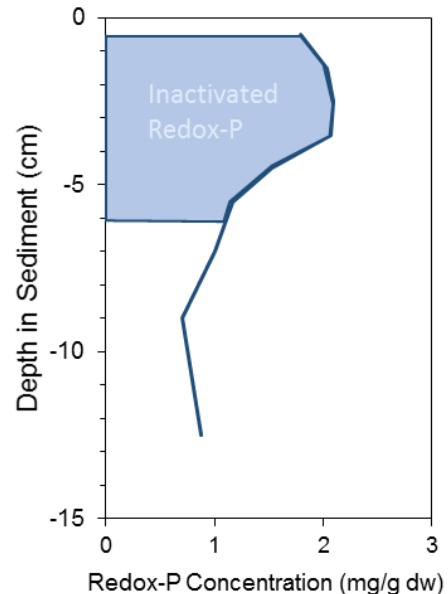


Figure 4-1. Station 10 redox-P peak used to dose sediment in the proposed treatment area.

It is important to note that Ann Lake has an unusually high concentration of redox-P within its sediments, which requires an extremely large alum application rate. Performing a one-time alum application at a rate of 294.7 g Al/m² is impractical since it would cause pH in the lake to drop below 6, which would negatively impact aquatic biota. Thus, it is recommended that the alum dose be split into 7 smaller applications of 42.1 g Al/m² (Table 4-1). This would eliminate the potential for low pH in the lake and help spread the cost of the alum application over several years. The treatment schedule is up to the stakeholder's discretion; however, it is recommended that the alum applications be spaced at least two years apart to allow the alum enough time to convert redox-P to aluminum-bound P prior to the next treatment.

It is highly recommended that follow-up sediment coring be conducted between alum applications to assess the effectiveness of the applications. For example, follow-up sediment cores after applications 1-2 may show that certain areas within the proposed treatment area have had better effectiveness than anticipated. These findings would allow for adaptive management of the alum application in certain locations, which may save money in the long term. For the purposes of this report, we recommended sediment core collection be conducted after applications 2 and 4. Follow-up monitoring after the fourth application can also help determine if all seven applications will be necessary to bind redox-P in the upper 6 cm. In summary, follow-up monitoring is a good way to understand the effectiveness of the alum treatment and potentially save money in the long run.

Table 4-1. Ann Lake alum application cost estimate.

Ann Lake Alum Application Cost Estimate				
Item	Unit	Quantity	Unit Cost	Total Cost
1st Aluminum Sulfate Dose	Gal Al ₂ (SO ₄) ₃	46,142	\$1.80	\$83,056
2nd Aluminum Sulfate Dose	Gal Al ₂ (SO ₄) ₃	46,142	\$1.80	\$83,056
3rd Aluminum Sulfate Dose	Gal Al ₂ (SO ₄) ₃	46,142	\$1.80	\$83,056
4th Aluminum Sulfate Dose	Gal Al ₂ (SO ₄) ₃	46,142	\$1.80	\$83,056
5th Aluminum Sulfate Dose	Gal Al ₂ (SO ₄) ₃	46,142	\$1.80	\$83,056
6th Aluminum Sulfate Dose	Gal Al ₂ (SO ₄) ₃	46,142	\$1.80	\$83,056
7th Aluminum Sulfate Dose	Gal Al ₂ (SO ₄) ₃	46,142	\$1.80	\$83,056
Application Total				\$581,392
Application observation and monitoring				\$15,000
Bidding, Permitting, and Specification Development				\$15,000
Follow Up Monitoring				\$40,000
Total Cost Estimate				\$651,392

Table 4-2. Proposed alum application schedule for Ann Lake.

Dose	Year									
	0	2	3	4	6	7	8	10	12	
Annual Dose [g Al/m ²]	42.1	42.1	M ¹	42.1	42.1	M ¹	42.1	42.1	42.1	
Cumulative Dose [g Al/m ²]	42.1	84.2		126.3	168.4		210.5	252.6	294.7	

¹ Denotes follow-up sediment monitoring years

4.1.3 Environmental Considerations

The primary concern with using alum in Ann Lake is its potential impact on wild rice. Elevated sulfate in lakes can produce sulfide within the rooting zone of wild rice, which may negatively impact wild rice growth (Pastor et al. 2017). Our goal was to assess if sulfate concentrations would exceed the current sulfate water quality standard (10 mg/L) after the alum application. To accomplish this, we compared the average sulfate concentration in Ann Lake after the alum treatment to the 10 mg/L sulfate standard from April 1st to September 31st (Figure 4-2). The MPCA has recently proposed an updated sulfate rule that would develop a protective sulfate standard for each wild rice water body, however, it is unclear at this time if the updated sulfate standard may change substantially from the current standard since it has yet to be finalized. Therefore, we used the current 10 mg/L sulfate standard to compare sulfate concentrations before and after the alum application. It is important to note that the current sulfate standard and the proposed standard both take into account the average concentration over a prolonged period of time (summer months and/or annual average). There is no acute sulfate standard, therefore isolated, short-term spike(s) in sulfate concentration within a lake or river system will not necessarily result in violations of state sulfate standards.

A non-steady state advection-diffusion model was built to evaluate if surface water sulfate concentrations in Ann Lake may exceed the existing 10 mg/L standard (Appendix B). This model takes into account the average annual inlet discharge rate, inlet sulfate concentration, sulfate diffusive flux into sediments, lake volume, and the alum application rate of 42.1 g Al/m² discussed in Section 4.1.2. The in-lake water quality data used to support this model was obtained from the MPCA’s Environmental Data Access database. Lake depths and morphometry information for Ann Lake were obtained through the Minnesota Geospatial Commons web page. Surface inflows from the Little Ann River were downloaded from the DNR/MPCA Cooperative Stream Gaging website ([link to website](#)).

Model results show that, under average flow conditions, peak sulfate concentration in Ann Lake would temporarily reach 12 mg/L immediately following an alum application (Figure 4-2). The sulfate concentrations quickly dissipate below 10 mg/L within 16 days due to dilution by inflow to the lake from the Little Ann River, Spring Brook, and Camp Creek. The average sulfate concentration in the lake from April to September is 6.2 mg/L, which is well below the current 10 mg/L standard.

During applications, several environmental parameters are often measured to ensure that the alum application is not causing negative environmental impacts. These parameters typically include: aluminum, pH, and alkalinity. It is highly recommended that sulfate concentrations also be measured during and after the alum application in the eastern arm of

the lake. Collecting this data should help determine if sulfate concentrations approach or exceed the sulfate standard.

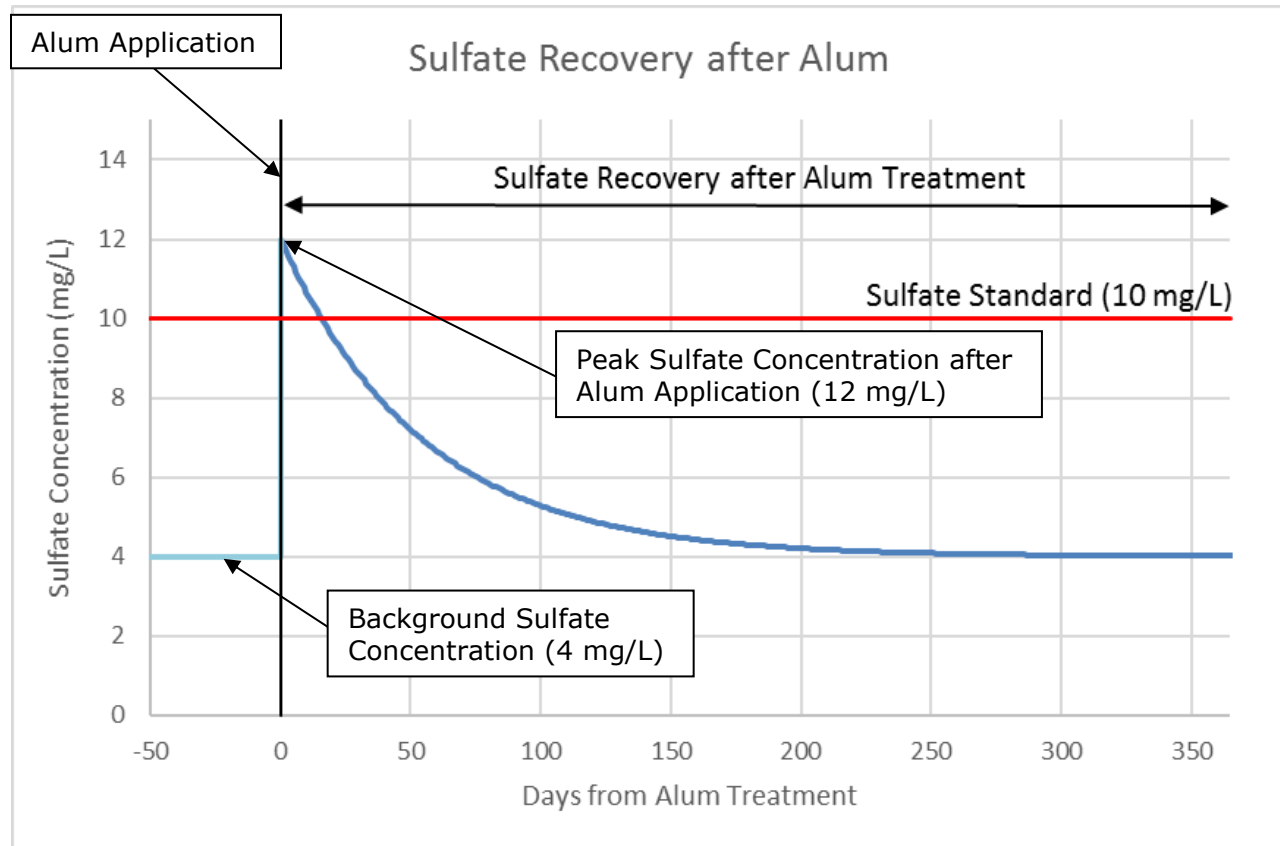


Figure 4-2. Modeled sulfate concentration in Ann Lake after aluminum sulfate treatment.

4.1.4 Permitting Requirements

No formal permits are required to conduct in-lake alum treatment. However, several agencies request that they be informed of the proposed project so they can provide comment or direction. These agencies include the MPCA and the MnDNR. When requesting comments for the MnDNR, both the MnDNR Waters division and the Fisheries and Ecological Services division typically request to provide comments.

4.1.5 Anticipated Benefits

Wenck's experience with internal load reduction using alum is that phosphorus release rates typically decrease by greater than 90%. In many cases, phosphorus release rates will decrease by 95-99%. Ann Lake sediment cores suggest that internal load is currently 5,496 pounds per year and the TMDL target load reduction is 4,096 pounds P/year, which is a 75% reduction from current conditions (MPCA, 2013). These reductions are feasible and well below the load reductions typically observed in other alum treatments. The alum longevity should be at least 30 years since the watershed phosphorus load is disproportionately small compared to the internal load from the sediment.

ALTERNATIVE #2: PHOSLOCK

4.1.6 Phoslock® Overview

Phoslock® (PhL) is a proprietary material developed by Phoslock Water Solutions that consists of bentonite clay in which the sodium or calcium ions are exchanged with lanthanum. Phoslock®, like alum, is a product that is applied to the sediment surface to control phosphorus release from sediments. The primary difference between alum and PhL is that alum actively converts redox-P to aluminum bound-P, while PhL slowly adsorbs phosphate over time through diffusion. The general concept for PhL is similar to other sediment phosphorus inactivation techniques even though the phosphate adsorption mechanisms differ.

4.1.7 Phoslock® Dosing and Cost Estimates

Similar to alum, dosing calculations for PhL are based on treating the top 6 cm of sediment within the 15-foot depth contour. One major difference between dosing alum and PhL is the sediment to P product ratio. For PhL, this ratio is typically estimated based on annual anaerobic P flux from sediment and the concentration of sediment redox-P in the upper 6-cm layer. Literature recommends that a PhL to P ratio be 105:1 (PhL:P) so that the lanthanum to P (La:P) ratio is 1:1 (Reitzel et al. 2013). We used the top 6 cm of sediment as the mass of phosphorus to inactivate using Phoslock®, which requires a dose of approximately 1,455 g PhL/m². Based on this dosing rate and the size of the proposed treatment area (60 acres), the total cost of PhL treatment for Ann Lake would be approximately \$1,325,000 (Table 4-4). This estimated cost includes bidding, 10% contingency, permitting, specs, application observation, and follow-up monitoring.

Table 4-3. Ann Lake Phoslock application cost estimate.

Ann Lake Phoslock(R) Application Cost Estimate				
Item	Unit	Quantity	Unit Cost	Total Cost
Phoslock Application	lbs Phoslock	778,866	\$1.50	\$1,168,300
Application Total				\$1,168,300
Contingency (10% of Phoslock Cost)				\$116,830
Application observation and monitoring				\$5,000
Bidding, Permitting, and Specification Development				\$15,000
Follow Up Monitoring				\$20,000
Total Cost Estimate				\$1,325,130

4.1.8 Environmental Considerations

PhL does not contain sulfate or chloride and therefore will not increase the concentration of sulfate or chloride within the water body in which it is applied. The lack of sulfate and chloride is the primary benefit of using PhL since each of these ions can have impacts on aquatic organisms. Furthermore, PhL will not cause pH shifts during the application process since aluminum hydrolysis does not occur. However, as discussed in Sections 4.1.2 and

4.1.11, the environmental impact of alum and aluminum chloride can be minimized by spreading the required dose across several applications.

PhL is relatively inert in aquatic systems which is another reason why it was selected as a possible alternative to alum. Studies of lanthanum ecotoxicity and bioaccumulation have been conducted to assess the impacts of lanthanum on aquatic biota. Studies have found that lanthanum does bioaccumulate after applications, however, observable physiological impacts have not been observed despite measurable changes in lanthanum tissue concentrations (Hickey et al. 2009). Also, lanthanum can cause acute toxicity in aquatic organisms if it applied incorrectly (Spears et al. 2013). Overall, there does not appear to be major potential environmental impacts to a PhL application if the product is applied correctly.

4.1.9 Permitting Requirements

No formal permits are required to conduct in-lake Phoslock® treatment. However, several agencies request that they be informed of the proposed project so they can provide comment or direction. These agencies include the MPCA and the MnDNR. When requesting comments for the MnDNR, both the MnDNR Waters division and the Fisheries and Ecological Services division typically request to provide comments.

4.1.10 Anticipated Benefits

The anticipated benefits from an PhL application will be similar to the benefits of an alum treatment. Internal load reductions have been well documented in Europe (Spears et al, 2013; Reitzel et al, 2013) and short-term core incubations conducted in this study (Appendix A) demonstrated that phosphorus release rates are substantially reduced after a PhL application. Therefore, it appears that a PhL application would be a scientifically sounds method for phosphorus sediment release. Since PhL is a relatively new product there are no long-term studies to assess longevity. However, there is no scientific evidence that suggests a PhL treatment would not last at least 30 years if dosed correctly.

ALTERNATIVE #3: ALUMINUM CHLORIDE

Polyaluminum chloride (PACl) is another aluminum salt that is commonly used in Europe for sediment phosphorus inactivation. The mechanisms of sediment phosphorus inactivation for PACl are similar to alum. PACl dissociates into $Al(OH)_3$, which sinks to the sediment surface. The $Al(OH)_3$ provides a reactive surface which inactivates redox-P (mobile phosphorus) within the sediments. The primary purpose of evaluating PACl as a potential alternative to alum is alum's potential environmental impacts to wild rice.

4.1.11 PACl Dosing Considerations and Cost

Dosing considerations for PACl are nearly identical to alum with the only differences being the amount of aluminum per gallon and the unit cost. The Al:P_{90%} ratio developed for the alum dose can also be used to determine the amount of PACl needed to inactivate 90% of the redox-P. The total estimated cost of a PACl treatment is approximately \$870,000. This cost assumes PACl will be applied to treat the top 6 cm of sediment within the 15-foot contour. PACl does not have the same pH drops during applications, however, we are still recommending that the application occurs over an extended period using the multiple dose methodology described in Section 4.1.2. Multiple doses will allow for interim sediment monitoring and increases the contact time between the aluminum and sediment redox-P. The total estimated cost for a PACl treatment is approximately \$868,000. This cost includes bidding, permitting, specs, application observation, and follow up monitoring (Table 4-5).

Table 4-4. Ann Lake PACl application cost estimate.

Ann Lake PACl Application Cost Estimate				
Item	Unit	Quantity	Unit Cost	Total Cost
1st PACl Dose	Gal PACl	39,336	\$ 2.90	\$114,076
2nd PACl Dose	Gal PACl	39,336	\$ 2.90	\$114,076
3rd PACl Dose	Gal PACl	39,336	\$ 2.90	\$114,076
4th PACl Dose	Gal PACl	39,336	\$ 2.90	\$114,076
5th PACl Dose	Gal PACl	39,336	\$ 2.90	\$114,076
6th PACl Dose	Gal PACl	39,336	\$ 2.90	\$114,076
7th PACl Dose	Gal PACl	39,336	\$ 2.90	\$114,076
Application Total				\$798,532
Application observation and monitoring				\$15,000
Bidding, Permitting, and Specification Development				\$15,000
Follow Up Monitoring				\$40,000
Total Cost Estimate				\$868,532

4.1.12 Environmental Considerations

PACl was selected as an alternative to alum since it contains significantly less sulfate than alum. It is important to note that the state of Minnesota has adopted chloride standards for lakes throughout the state. These standards include both chronic (230 mg/L) and acute (860 mg/L) thresholds. The non-steady state advection-diffusion model described in Section 4.1.3 was used to predict chloride concentrations in Ann Lake following the proposed PACl

treatment. Background chloride concentrations in Ann Lake are approximately 1 mg/L based on monitoring data downloaded from the MPCA EDA website. The model shows that the maximum chloride concentration after each treatment will reach a maximum concentration of 4 mg/L (Figure 4-3) based on the PACI described in Table 4-5. These results indicate that the chloride concentrations in Ann Lake should remain well below the chronic and acute chloride standards and therefore there should be no concerns of a PACI treatment from a regulatory standpoint.

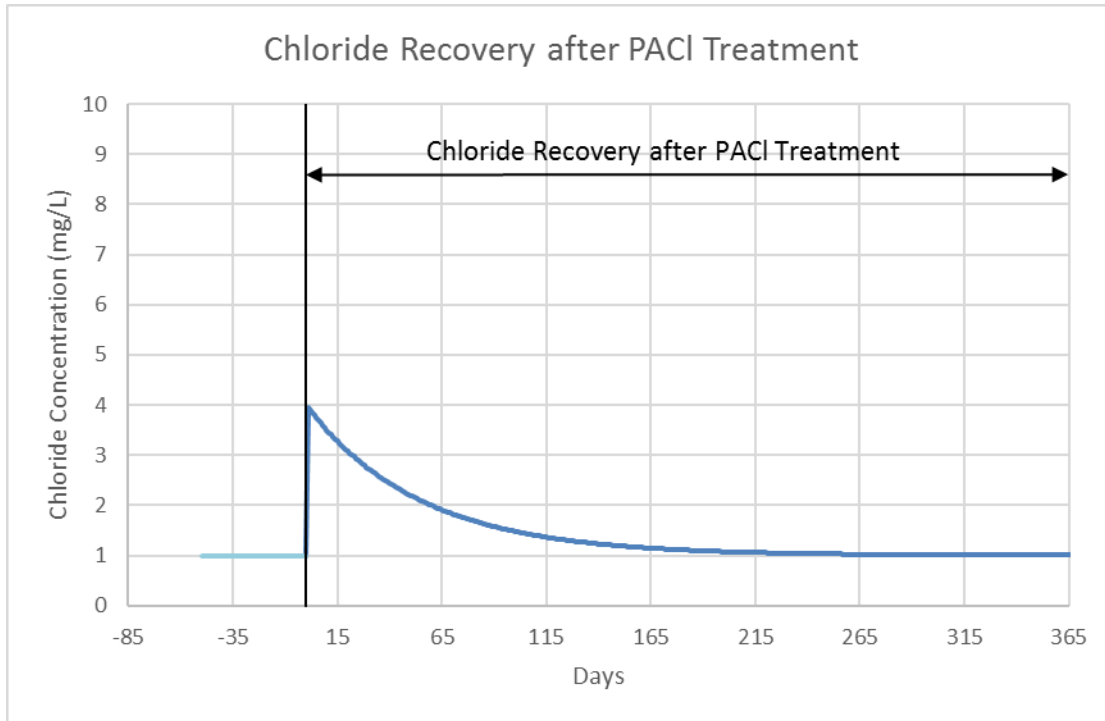


Figure 4-3. Modeled chloride concentration in Ann Lake following PACI treatments.
 Note: chronic and acute chloride standards are 230 mg/L and 860 mg/L, respectively

4.1.13 Permitting Requirements

No formal permits are required to conduct in-lake PACI treatment. However, several agencies request that they be informed of the proposed project so they can provide comment or direction. These agencies include the MPCA and the DNR. When requesting comments for the DNR, both the DNR Waters division and the Fisheries and Ecological Services division typically request to provide comments.

4.1.14 Anticipated Benefits

The anticipated benefits from an PACI application will be similar to the benefits of an alum treatment. Since the process of aluminum hydroxide settling and reaction with redox-P within the sediments are nearly identical, it is anticipated that the load reductions and treatment longevity should be very similar.

ALTERNATIVE #4: HYPOLIMNETIC AERATION

Hypolimnetic aeration controls internal loading in lakes by aerating hypolimnetic waters (cold, dense water trapped at the bottom of a lake) to maintain oxic (oxygenated) conditions in the hypolimnion and sediment surface. It is the anoxic (no dissolved oxygen) condition of the hypolimnetic sediments which contribute to the internal phosphorus load. Hypolimnetic aeration only aerates water of the hypolimnion without causing it to mix with the epilimnion. This prevents the lake from destratifying and limits the amount of water to be aerated.

4.1.15 Hypolimnetic Aeration Design Considerations and Cost Estimate

Under this option, two hypolimnetic aeration units would be placed in the proposed treatment area of Ann Lake. Hypolimnetic aerators, also referred to as air-lift units, work by introducing diffused air at the bottom of the aerator in the hypolimnion, and the buoyancy of the air-water mixture lifts the water through the central pipe to the top of the aerator. The air bubbles leave the water and are vented to the water surface, while the water returns to the hypolimnion by sinking through the external tube.

Hypolimnetic aeration is the only alternative in this study that requires an initial investment and annual operation and maintenance (O&M). The initial installation would cost approximately \$1,250,000 and the annual O&M cost would be \$29,000. The annual operating costs cover energy and estimated operation and maintenance of aeration equipment. Therefore, the 30-year life cycle cost including installation, O&M, and overhaul would be approximately \$2,016,000.

TIBEAN-Technology

Atmospheric air is inserted by an ejector. A mixture of water and oxygen is forced upwards in the upstream pipe. At the end of the upstream pipe the mixture flows into the degassing chamber. Residual gases are separated from the oxygenated water. The gas escapes into the atmosphere, the oxygenated water flows through the downstream pipe. The outlet provides a laminary flow and a horizontal outflow into the hypolimnion.

Technical data

Oxygen Input: from 1,5 kg h⁻¹
Application Depth: from 5 m
Flow Rate: from 100 m³ h⁻¹

Individual Parts

- 1 Floating Tanks
- 2 Upstream Pipe (Telescope)
- 3 Degazing Head
- 4 Mixing Device
- 5 Suction Fence
- 6 Covering Fence
- 7 Downstream Pipe
- 8 Oxygen Input
- 9 Submersible Pump with ejector
- 10 Main Ballast Tanks

Material

TIBEAN can be made of PE/PP (Polyethylene /Polypropylene), stainless steel, and an Al/Mn-alloy.

Options

device for precipitation of nutrients,
device for phosphate elimination



Figure 4-4. Hypolimnetic aeration unit proposed for Ann Lake. Image provided by Canadian pond (Source: www.canadianpond.ca).

Table 4-5. Ann Lake hypolimnetic aeration annual cost and life cycle cost.

Alternative:		Hypolimnetic Aeration: Air-lift Units		
Item	Quantity	Unit	Unit Cost	Cost
Investment Cost Estimate				
Air-lift units	2	ea.	300,000	\$ 600,000
Install and anchor units	2	ea.	7,000	\$ 14,000
Blower and housing	2	ea.	45,000	\$ 90,000
Air supply hose	3,650	l.f.	12	\$ 43,800
Electric service	1	ea.	10,000	\$ 10,000
Mobilization, Demobilization	1	ea.	10,000	\$ 15,000
Contingencies	1	ea.	20%	\$ 154,560
Subtotal, Construction	--	--	--	\$ 927,360
Engineering, Legal, Permits, Admin.	1	ea.	35%	\$ 324,576
Total Investment Cost				\$ 1,250,000
Annual Operating Cost				
Electric demand price	30	kW	\$ 90.00	\$ 2,700
Electric energy requirements	250,000	kWh	\$ 0.07	\$ 16,250
Annual operation & maintenance	1	ea.	10,000	\$ 10,000
Annual operation costs				\$ 29,000
Overhaul Cost at 10 years				
Air-lift unit maintenance and replacement	1	ea.	18,000	\$ 18,000
Blower, motor replacement	1	ea.	35,000	\$ 35,000
Hose replacement	3,650	l.f.	12	\$ 43,800
Replacement occurs at:	10	yr.		
Replacement occurs at:	20	yr.		
Total replacement costs				\$ 194,000
Project Present Value				
Investment Cost				\$ 1,250,000
Economic life	30	yr.		
Present Value of 10 Year Overhaul				\$ 137,000
Present Value of 20 Year Overhaul				\$ 97,300
Present Value of Annual Operating Costs over Lifetime				\$ 532,000
Total Present Value				\$ 2,016,300
Project Annual Cost				
Annual cost (annuity)				\$ 110,000
Interest rate assumed for present value =	3.50%			

4.1.16 Environmental Considerations

Based on literature review conducted as part of this study, there are no clear negative environmental impacts to hypolimnetic aeration. Construction and installation of the hypolimnetic aeration units, compressor, pipes, and anchors may cause erosion during the construction process. However, these environmental impacts could easily be mitigated using construction best management practices

If the aeration system is used through the winter, it has the potential to limit ice cover and cause open water, which could pose a safety hazard to winter lake users. Therefore, strict safety measures would need to be observed during winter operation.

4.1.17 Permitting Requirements

Two permits are required from the MnDNR. The first is from the Division of Fisheries. The second is the General Work in Public Waters Permit due to work being conducted below the ordinary high water (OHW) elevation, such as the placement of the pipes, anchors and aeration units. The MnDNR Area Hydrologist recommends notifying the MnDNR early in the project, prior to permit application submittal regardless of the type of project. This is suggested so that the MnDNR can work through any potential issues prior to the permitting process. The typical period to acquire a General Work in Public Waters permit is 60 days. However, depending on the complexity of the project and the potential for controversy with the lake shore residents and/or general public the permitting process could take considerably longer. The MPCA would also need to review the project in conjunction with the MnDNR permits.

4.1.18 Anticipated Benefits

Hypolimnetic aeration is unique when compared to other internal load management options in this feasibility assessment. The other feasibility options rely on inactivating mobile phosphorus within sediments, while hypolimnetic aeration relies on controlling oxidation-reduction conditions within the water column to limit the amount of phosphorus release from sediments. Hypolimnetic aeration has demonstrated that it can effectively reduce internal phosphorus loading (Beutel and Horn, 1999)

5.0 Conclusions

Ann Lake is a shallow, nutrient impaired lake containing wild rice located in the Snake River Watershed in east-central Minnesota. A TMDL study for Ann Lake completed in 2013 suggests internal loading from the sediment is a major source of phosphorus to the lake and will require a TP load reduction of approximately 4,000 lbs/year to meet state water quality standards.

The primary purpose of this study was to provide a detailed feasibility assessment of the alum and non-alum internal load treatment alternatives for Ann Lake that includes the following components: proposed treatment area(s), chemical dosing rates, costs, phosphorus removal efficiency and potential impacts to wild rice and other environmental factors. The internal load treatment alternatives that were investigated include alum, Phoslock, aluminum-chloride, and hypolimnetic aeration. Table 5-1 below provides a general summary of the major findings from the feasibility assessments of the four treatment alternatives.

Table 5-1. Summary of internal load treatment options for Ann Lake.

Alternative	Cost Estimate	Proposed Treatment Schedule/Area	Environmental Concerns	Benefits/Limitations
Alum	\$651,000	7 separate applications in the >15-foot contour	MN state sulfate standard should not be exceeded if product is applied across 7 different treatments	<ul style="list-style-type: none"> Known effectiveness Readily available in USA Most Cost-Effective alternative
Phoslock ®	\$1,325,000	1 application in the >15-foot contour	None if applied correctly	<ul style="list-style-type: none"> No apparent environmental concerns Less commonly used
Polyaluminum chloride	\$870,000	7 separate applications in the >15-foot contour	MN state chloride standard should not be exceeded if product is applied across 7 different treatments	<ul style="list-style-type: none"> Rarely used in US for internal load reduction
Hypolimnetic Aeration	\$1,250,000 Investment Cost \$29,000 Annual Operating Cost	two units deployed in >15-foot contour	None	<ul style="list-style-type: none"> Must be operated in perpetuity to meet water quality goals May not be effective for internal phosphorus load control

6.0 References

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Appendix A:
UW-Stout Internal Phosphorus Loading and Management
Considerations for Ann Lake, Minnesota



Internal Phosphorus Loading and Management Considerations for Ann Lake, Minnesota



Ann Lake, MN (Google Maps, TerraMetrics)

1 March, 2017



Responsive partner.
Exceptional outcomes.

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OBJECTIVES

The objectives of these investigations were to examine rates of phosphorus (P) release, sediment chemistry, and internal P loading management strategies in Ann Lake, Minnesota. The specific outcomes and deliverables of this research were to,

1. determine rates of P release from intact sediment cores under anaerobic conditions,
2. examine spatial and vertical variations in biologically-labile (i.e., subject to recycling via Eh, pH, and bacterially-mediated reactions in the sediment; loosely-bound, iron-bound, and labile organic P) P fractions that are potentially active in sediment internal P loading,
3. evaluate the potential for Phoslock® application and costs to control internal P loading,
4. evaluate aluminum chloride treatment and costs to control internal P loading.

APPROACH

Sediment coring stations and gravity coring methodology

Sediment coring stations and numbers of cores collected for analytical purposes are identified Figure 1 and Table 1. Three intact sediment cores were collected from deeper station 10 for determination of rates of P release under anaerobic conditions and the Phoslock® experiments. Additional sediment cores collected at all stations were sectioned vertically over the upper 15-cm to evaluate variations in sediment physical-textural and chemical characteristics for Phoslock® and Al dosage estimation. Cores were sectioned at 1-cm intervals over the first 6 cm, at 2-cm intervals between 6 and 10 cm, and at 5-cm intervals below the 10-cm depth.

A gravity sediment coring device (Aquatic Research Instruments, Hope ID) equipped with an acrylic core liner (6.5-cm ID and 50-cm length) was used to collect sediment in September, 2016, by Wenck Associates, Inc. The core liners, containing both sediment and overlying water, were immediately sealed using rubber stoppers and stored in a covered container in a cool location until analysis. Additional lake water was collected for incubation with the collected sediment. Sediment cores were sectioned within 24 hours of collection. Fresh sediment sections were stored in glass jars and refrigerated until analysis.

Rates of phosphorus release from sediment

In the laboratory, sediment were carefully drained of overlying water and the upper 10 cm of sediment transferred intact to a smaller acrylic core liner (6.5-cm dia and 20-cm ht) using a core remover tool. Surface water collected from the lake was filtered through a glass fiber filter (Gelman A-E), with 300 mL then siphoned onto the sediment contained in the small acrylic core liner without causing sediment resuspension. Sediment incubation systems consisted of the upper 10-cm of sediment and filtered overlying water contained in acrylic core liners that were sealed with rubber stoppers. They were placed in a darkened environmental chamber and incubated at a constant temperature (20 °C). The oxidation-reduction environment in the overlying water was controlled by gently bubbling nitrogen (anaerobic) through an air stone placed just above the sediment surface in each system. Bubbling action insured complete mixing of the water column but did not disrupt the sediment. Triplicate sediment incubation systems were prepared for rate determination under anaerobic conditions.

Water samples for soluble reactive P (SRP) were collected from the center of each system using an acid-washed syringe and filtered through a 0.45 µm membrane syringe filter (Nalge). The water volume removed from each system during sampling was replaced by addition of filtered lake water preadjusted to the proper oxidation-reduction condition. These volumes were accurately measured for determination of dilution effects. Soluble reactive P was measured colorimetrically using the ascorbic acid method (APHA

2005). Rates of P release from the sediment ($\text{mg}/\text{m}^2 \text{ d}$) were calculated as the linear change in mass in the overlying water divided by time (days) and the area (m^2) of the incubation core liner. Regression analysis was used to estimate rates over the linear portion of the data.

Sediment chemistry

A known volume of sediment was dried at $105\text{ }^\circ\text{C}$ for determination of moisture content, wet and dry bulk density, and burned at $500\text{ }^\circ\text{C}$ for determination of loss-on-ignition organic matter content (Avnimelech et al. 2001, Håkanson and Jansson 2002; Table 2). Phosphorus fractionation was conducted according to Hieltjes and Lijklema (1980), Psenner and Puckso (1988), and Nürnberg (1988) for the determination of ammonium-chloride-extractable P (loosely-bound P), bicarbonate-dithionite-extractable P (i.e., iron-bound P), and sodium hydroxide-extractable P (i.e., aluminum-bound P). A subsample of the sodium hydroxide extract was digested with potassium persulfate to determine nonreactive sodium hydroxide-extractable P (Psenner and Puckso 1988). Labile organic P was calculated as the difference between reactive and nonreactive sodium hydroxide-extractable P. Additional sediment was sent to Pace Analytical for analysis of total Al and Fe (EPA 3050 and 6020A).

The loosely-bound and iron-bound P fractions are readily mobilized at the sediment-water interface as a result of anaerobic conditions that lead to desorption of P from sediment and diffusion into the overlying water column (Mortimer 1971, Boström et al. 1982, Boström 1984, Nürnberg 1988; Table 3). The sum of the loosely-bound and iron-bound P fraction represents redox-sensitive P (i.e., the P fraction that is active in P release under anaerobic and reducing conditions; redox-P). In addition, labile organic P can be converted to soluble P via bacterial mineralization (Jensen and Andersen 1992) or hydrolysis of bacterial polyphosphates to soluble phosphate under anaerobic conditions (Gächter et al. 1988, Gächter and Meyer 1993, Hupfer et al. 1995). The sum of redox-P and labile organic P collectively represent biologically-labile P. This fraction is active in recycling pathways that result in exchanges of phosphate from the sediment to the

overlying water column and potential assimilation by algae. In contrast, aluminum-bound P is more chemically inert and subject to burial rather than recycling (Table 3).

Al dosage determination

The upper 5-cm section of sediment collected at station 10 (Figure 1) was subjected to a range of aluminum chloride (as Al) concentrations to determine the Al dosage required to inactivate the redox-P fraction (Rydin and Welch 1999). A concentration of 1.25 g Al/L was combined with DI water to form an aluminum hydroxide (Al(OH)₃) floc. Aliquots of this solution, diluted to a final volume of 10 mL with distilled water, were added to centrifuge tubes containing the equivalent of 0.025 g dry weight (DW) of fresh sediment to obtain Al concentrations ranging from 0 (i.e., control) to ~ 50 mg Al/g DW sediment. The assay tubes were shaken for a minimum of 2 hours at 20 °C in a darkened environmental chamber, centrifuged at 500 g to concentrate the sediment, and decanted for redox-P determination (see method description above).

Vertical profiles of sediment redox and biologically-labile P were evaluated and mean integrated concentrations were estimated over the upper 5 to 10 cm layer. The aluminum sulfate dosage (expressed as Al) required to bind sediment P in the upper layer was determined as described in James and Bischoff (2015). In general, the dry mass concentration of redox-P (mg/g) was converted to an area-weighted concentration (g/m²) as,

$$\text{Redox-P (g/m}^2\text{)} = \text{Redox-P (mg/g)} \cdot \rho \text{ (g/cm}^3\text{)} \cdot \theta \cdot h \text{ (m)} \cdot 1,000,000 \text{ (cm}^3\text{/m}^3\text{)} \cdot 0.001 \text{ (g/mg)} \quad 1)$$

where, ρ is sediment bulk density (g/cm³), θ is the percentage of sediment solids (100 – percent moisture content; dimensionless), and h is sediment thickness (m). A stoichiometric Al:P binding ratio (i.e., the mass of Al required to bind redox-P) was estimated from regression equations between redox-P and the Al:P binding ratio developed in James and Bischoff (2015). The Al concentration (g/m²) required to bind P in the upper sediment layer was estimated as,

$$\text{Al (g/m}^2\text{)} = \text{Redox-P (g/m}^2\text{)} \cdot \text{Al:P} \quad 2).$$

The Al dosage calculated in this manner does not take into account decreased binding efficiency of the Al floc over time. Berkowitz et al. (2006) and De Vicente et al. (2008) found that Al binding efficiency can decrease by > 50% within months in the absence of P adsorption due to crystallization and polymerization. Since the Al floc usually layers on top of the original sediment surface rather than instantaneously mixing or sinking into the sediment, P sequestration proceeds as a result of slower upward diffusion. This scenario leads to a decrease in binding efficiency over time and a potential need for future (and lower dose) maintenance Al applications (see below).

Maximum allowable Al dosage based on alkalinity and pH

Addition of aluminum sulfate to a lake leads to hydrolysis and the liberation of hydrogen ions which lowers the pH of the water column. Since Al toxicity to the biota can occur if the pH falls below ~4, maintaining a pH ≥ 6.0 as a margin of safety should also be considered in dose determination (Cooke et al. 2005). For situations where alkalinity is low or the required dosage exceeds the maximum allowable dosage to maintain pH ≥ 6.0 , a buffered aluminum sulfate-sodium aluminate treatment will be needed to maintain pH near neutrality. Surface water collected from each lake was analyzed for total alkalinity and pH according to APHA (2005). A titration procedure was used to determine the maximum allowable dosage of aluminum sulfate that can be added and yet maintain pH above 6.0 (Cooke et al. 2005). A 1.25 g Al/L solution of $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{ H}_2\text{O}$ was used as the titrant: 1.0 mL additions to 500 mL of lake water were each equivalent to 2.5 mg Al/L. Lake water was titrated with the Al solution until an endpoint of pH 6 was reached. The total volume (mL) of Al solution needed to titrate lake water to pH 6 was multiplied by 2.5 mg Al/L to estimate the maximum allowable concentration. This calculation was then compared with estimates based on sediment redox-P to ensure that the latter was at or below the maximum allowable dosage. Caution needs to be used

because a vertical alkalinity and pH profile over the entire vertical water column needs to be estimated in order to more accurately evaluate the maximum allowable dosage.

Phoslock® experiments

Additional replicate sediment cores collected at station 10 in Ann Lake were experimentally subjected to a range of Phoslock® concentrations to examine impacts on anaerobic P release control. Phoslock® is a lanthanum modified bentonite clay product from Australia that is very effective in binding orthophosphate or SRP . Recent research (Meis et al. 2012, Reitzel et al. 2013, Dithmer et al. 2015, 2016,) has suggested that a Phoslock®:mobile P binding ratio of at least 100:1 (i.e., 100 parts Phoslock® to 1 part mobile P) or greater is needed to sequester mobile P in sediments. In addition, binding effectiveness of Phoslock® diminishes at higher pH (i.e., > 9, Ross et al. 2008, Haghseresht et al. 2009).

Phosphorus release under anaerobic conditions from intact sediment cores collected from station 10 were subjected to Phoslock®:redox-P ratios between 100:1 and 200:1 (Table 4). The ratios were based on the redox-P concentration (g/m^2) in the upper 5-cm sediment layer. Overall, Phoslock® concentrations ranged from 1,200 to 2,400 g/m^2 and were much higher than reported field applications (Liu et al 2012, Spears et al. 2016). A slurry with known mass was created using granular Phoslock® obtained from SePro Corp. and Ann Lake water (Figure 2). An aliquot of the slurry equivalent to the Phoslock® mass required for the various ratios presented in Table 3 was carefully added to the overlying water column of individual incubation systems and allowed to settle for 12 hours (Figure 3). Three replicate sediment core incubation systems were set up per Phoslock® treatment for a total of 15 experimental units including 3 controls (i.e., no Phoslock® addition).

Each incubation system was carefully bubbled with nitrogen gas containing 300 ppm CO_2 to induce anaerobic conditions and maintain pH at ~ 8.0 units. Water samples for soluble reactive P (SRP) were collected from the center of each system using an acid-

washed syringe and filtered through a 0.45 μm membrane syringe filter (Nalge) as described above. Soluble reactive P was measured colorimetrically using the ascorbic acid method (APHA 2005). Rates of P release from the sediment ($\text{mg}/\text{m}^2 \text{ d}$) were calculated as the linear change in mass in the overlying water divided by time (days) and the area (m^2) of the incubation core liner. Regression analysis was used to estimate rates over the linear portion of the data.

RESULTS AND INTERPRETATION

Sediment phosphorus release rates

Under anaerobic conditions, P mass and concentration increased rapidly and approximately linearly in the overlying water column of Ann Lake station 5 sediment incubation systems (Figure 4). The mean anaerobic P release rate measured in 2016 was relatively high at $4.79 \text{ mg}/\text{m}^2 \text{ d}$ ($\pm 0.97 \text{ SE}$). By comparison, the mean anaerobic P release rate determined in 2011 was much higher for Susan Lake sediment was much higher at $15.0 \text{ mg}/\text{m}^2 \text{ d}$ ($\pm 2.5 \text{ SE}$, Figure 5). Differences suggested potential variability as a function of collection time (winter in 2011 versus summer in 2016) and location. Nevertheless, anaerobic P flux determined in 2016 was near the median compared to other Minnesota Lakes in the region and fell within ranges compared to other eutrophic systems (Nürnberg 1988).

Sediment characteristics

Ann Lake sediment exhibited moderate moisture contents (88 to 92%), organic matter content (19 to 39%), and wet and dry bulk density ranges in the upper 5-cm sediment layer (Figure 6 and Table 5). In addition, there was a spatial gradient in physical-textural characteristics; moisture content, organic matter content, and porosity (i.e., interstitial spaces for porewater) were lower, while wet and dry bulk densities and solids content were higher, at station 10 and 20 versus station 30. Thus, the station 30 region was

characterized by finer-grained, more flocculent surface sediments versus the deeper basin area. Compared to other lake sediments in the region, station 10 and 20 surface sediments generally fell below the median, but within the lower 25% quartile, for moisture content, porosity, and organic matter content (Figure 7). Solids content and dry and wet bulk densities fell above the median and within the upper 25% quartile for Ann Lake station 10 and 20 surface sediments. Shallower station 30 sediments exhibited the opposite pattern (Figure 7). Newly precipitated Al floc is usually very fluid with low density during the first year of application. Thus, exposure to and binding of redox-P in the upper sediment layer will depend on density differences between the Al floc and surface sediment (James 2017).

Vertically in the sediment column, moisture content decreased while dry and wet bulk densities increased as a function of increasing sediment depth (Figure 8). Station 20 and 30 sediment cores exhibited a sharp change in these variables below 10 cm. Part of this pattern may be due to consolidation of the 5-cm section between 10 and 15 cm for analysis. Changes at this sediment depth may also be due to historical increases in watershed inputs. Organic matter content also tended to decrease sharply below 10-cm. In contrast, changes in sediment physical-textural characteristics were much more gradual as a function of sediment depth at station 10.

Surface sediments collected from the various stations also contrasted with respect to mobile P concentrations in the upper 5-cm layer (Figure 9 and Tables 6 and 7). Station 10 surface sediments exhibited very high iron-bound, redox-P, and biologically-labile P concentrations compared to the other stations. In contrast, the labile organic P concentration was greatest at station 30 (Figure 9). Aluminum-bound P, more inert to sediment P recycling pathways, was also very high in station 10 sediments. Overall, biologically-labile P, subject to recycling pathways resulting in internal P loading, exceeded 2 mg/g in the upper 5-cm sediment layer at station 10 (Figure 10). While lower by 50% at the other stations, biologically-labile P was still moderately high at ~ 1 mg/g (Figure 10).

Compared to other lakes in the region, iron-bound P concentrations in the upper 5-cm sediment layer fell above the upper 25% quartile at station 10, and within the upper 25% quartile for station 20 and 30 sediments (Figure 11). Labile organic P concentrations fell above the upper 25% quartile for all stations and was very high in station 30 sediments. These patterns suggested that mineralization and breakdown of organic P and polyphosphates from the labile organic P fraction could be an additional source contributing to internal P loading in Ann Lake and may need to be considered internal P loading management.

Vertically in the sediment column, loosely-bound P concentrations were relatively homogeneous with sediment depth and accounted for a minor portion of the biologically-labile P at all stations in Ann Lake (Figure 12). At station 10, where iron-bound P dominated the biologically-labile P fraction, a concentration maximum was observed between 0 and 4 cm and iron-bound P exceeded 2 mg/g. Vertical concentration patterns were lower and less pronounced at station 20 and 30. Nevertheless, a modest surface concentration maximum was observed between 0 and 3 cm at these stations as well. Other research has linked surface concentration peaks in iron-bound P and total P to internal P loading in eutrophic aquatic systems (Carey and Rydin 2011, Rydin et al. 2012).

Aluminum-bound P was relatively constant with sediment depth at station 20 and 30, but exhibited a concentration peak between 0 and 5 cm in the station 10 sediment column (Figure 12). The aluminum-bound P concentration in the upper 5-cm layer was also high and fell within or above the upper 25% quartile compared to other lakes in the region. Since the aluminum-bound P fraction also reflects P that is bound to added alum, these pre-treatment vertical profiles will be used to evaluate future sediment P binding efficiency and effectiveness of the precipitated Al floc, if an alum treatment is conducted in Ann Lake.

Overall, total iron concentrations were moderately high in Ann Lake sediment and exhibited a trend of decreasing concentration as a function of increasing sediment depth

(Figure 13 and 14). Sediment total aluminum patterns and concentration ranges will be used as a pretreatment benchmark for evaluation of future alum floc location and concentration in relation to sediment P. Total aluminum concentrations in the upper 5 cm were similar among stations (Figure 13).

Aluminum dosage

For station 10 sediment assay tubes subjected to a range of Al concentrations, the redox-sensitive P concentration declined exponentially as a function of increasing Al concentration, due to binding onto the $\text{Al}(\text{OH})_3$ floc (Figure 15). Exposure of a relatively low concentration of Al (~ 15 mg/g sediment dry mass) resulted in binding of > 70% of the redox-sensitive P. However, much more Al was needed to bind and sequester at least 90% or more of the redox-sensitive P because other constituents in the sediment (organic compounds and other anions) were also competing with PO_4^{3-} for the same binding sites. Overall, the Al:P binding ratio of ~ 13:1 (i.e., 13 parts Al to 1 part redox-P) was close to the predicted ratio of 20:1 (James and Bischoff 2015) determined from various lake sediments throughout the region (Figure 16).

Al dosage for various sediment thicknesses is shown in Table 8. We considered sequestration of redox-P in the upper 3, 4, 5, and 6 cm sediment layer (Figure 17). Because redox P concentrations were moderately high, particularly at stations 10 and 20, and sediment densities were moderate, the mass of sediment P per square meter of sediment surface was relatively high. For station 10, Al dosage increased from ~ 140 g/m^2 to nearly 300 g/m^2 , depending on sediment thickness. Since peak redox-P concentrations were located between 0 and 5 cm, a theoretical Al dose of ~ 250 g/m^2 is needed within the 15-ft depth contour of the lake. Because redox-P concentrations were lower at station 20, Al dosage requirements were lower for the sediment area between 10 and 15 ft at ~ 160 g/m^2 (Table 8). They were lowest at station 30 at ~ 80 g/m^2 to inactivate redox-P within the upper 5-cm layer. Estimated ranges for Ann Lake fell within ranges for other recently treated lakes (Table 9).

Total alkalinity in Ann Lake at the time of sediment core sampling was moderately low at ~ 40 mg CaCO₃/L, suggesting low buffering capacity for regulating pH during alum application if aluminum sulfate is used. Al binding of P is most efficient within a pH range of 6 to 8. As pH declines below 6, Al becomes increasingly soluble (as Al³⁺) and toxic to biota. The maximum allowable Al dosage that could be applied and yet maintain pH at or above 6, determined via jar tests (Cooke et al. 2005), was low at 6.25 mg Al/L as aluminum sulfate. Splitting aluminum sulfate applications into smaller doses spread out over several years will minimize low pH issues during application. Alternatively, a buffered aluminum sulfate-sodium aluminate treatment can be chosen to maintain neutral pH during application.

Phoslock® experiments and dosage estimation

Phoslock® binding efficiency for redox-P in sediment (i.e., PO₄ adsorbed to iron oxyhydroxides) was relatively low compared the alum (Figure 18). Overall, Phoslock® sequestered some redox-P over the range of introduced concentrations, but binding efficiency was < 40% at very high introduced Phoslock® concentrations. The Phoslock®:redox-P ratio was > 200:1 for all treatments. These findings indicated that, unlike alum, Phoslock® was most effective at binding SRP and had very poor affinity for PO₄ adsorbed to iron oxyhydroxides in sediment.

However, when experimentally added to anaerobic sediment incubation systems, Phoslock® entirely controlled SRP release from Ann Lake sediment at all dosage and Phoslock®:P ratios (Figure 19). Lower Phoslock®:P ratios would have probably also controlled diffusive P flux during the incubation period. Phoslock® essentially covered the sediment surface throughout the experiment (Figure 20). However, some minor sediment disturbance and redistribution occurred because of tubificid worm and invertebrate burrowing activities to escape anoxia. The thickness of the Phoslock® layer on top the sediment also increased with increasing dosage and was ~2 mm thick at the highest dosage.

Phoslock® dosage was estimated based on annual anaerobic P flux as SRP from sediment and the concentration of sediment redox-P in the upper 5-cm layer. For instance, 82 g Phoslock®/m² would be needed to control an anaerobic P release rate of 15 mg/m² d below the 12-ft depth for 52 days in the summer for 1 year at a Phoslock®:P ratio of ~ 105:1 (Reitzel et al. 2013, Table 10). Control of internal P loading for 15 years would require a Phoslock® dose of 1,230 g/m² (Table 10). This latter dose was equivalent to the dose needed to sequester mobile P in the upper 5-cm sediment layer at station 10 (Table 11).

ACKNOWLEDGMENTS

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Wauer G, Gonsiorczyk T, Hupfer M, Koschel R. 2009. Phosphorus balance of Lake Tiefwareensee during and after restoration by hypolimnetic treatment with aluminum and calcium salts. *Lake Reserv Manage* 25:377-388.

Table 1. Sediment sampling locations and numbers of sediment cores collected for determination of rates of phosphorus (P) flux and sediment chemistry in Ann Lake, Minnesota.

Station	Sediment P flux ¹	Chemistry	Phoslok
10	3	1	12
20		1	
30		1	

Table 2. Sediment physical-textural characteristics, phosphorus species, and metals variable list.

Category	Variable
Physical-textural	Moisture content Wet and dry sediment bulk density organic matter content
Phosphorus species	Loosely-bound P Iron-bound P Labile organic P Aluminum-bound P
Metals	Total Al Total Fe

Table 3. Sediment sequential phosphorus (P) fractionation scheme, extractants used, and definitions of recycling potential.		
Variable	Extractant	Recycling Potential
Loosely-bound P	1 M Ammonium Chloride	Biologically labile; Soluble P in interstitial water and adsorbed to CaCO ₃ ; Recycled via direct diffusion, eH and pH reactions, and equilibrium processes
Iron-bound P	0.11 M Sodium Bicarbonate-dithionate	Biologically labile; P adsorbed to iron oxyhydroxides (Fe(OOH)); Recycled via eH and pH reactions and equilibrium processes
Labile organic P	Persulfate digestion of the NaOH extraction	Biologically labile; Recycled via bacterial mineralization of organic P and mobilization of polyphosphates stored in cells
Aluminum-bound P	0.1 N Sodium Hydroxide	Biologically refractory; Al-P minerals with a low solubility product

Table 4. Experimental Phoslock® concentrations added to replicate sediment incubation systems for examination of impacts on anaerobic diffusive phosphorus flux.			
Phoslock®:redox P	g/m2	mg P/g Phoslock®	g Phoslock®/incubat
100	1212.4	10	4
125	1515.5	8	5
150	1818.6	6.7	6
200	2404.8	5	8

Table 5. Physical-textural characteristics in the upper 5-cm sediment layer for sediment cores collected at various stations in Ann Lake, MN.

Station	Moisture Content (%)	Solids content (%)	Wet Bulk Density (g/cm ³)	Dry Bulk Density (g/cm ³)	Organic Matter (%)
10	88.0	12.0	1.064	0.129	19.2
20	88.1	11.9	1.060	0.127	22.3
30	92.2	7.8	1.031	0.082	38.8

Table 6. Concentrations of redox-sensitive P (Redox P; the sum of the loosely-bound and iron-bound P fraction) and biologically-labile P (Bio-labile P; the sum of redox-P and labile organic P), in the upper 5-cm sediment layer for various stations in Ann Lake, MN. DW = dry mass.

Station	Redox P (mg/g DW)	Bio-labile P (mg/g DW)
10	1.901	2.286
20	0.643	0.991
30	0.328	0.901

Table 7. Concentrations of biologically labile and refractory P in the upper 5-cm sediment layer for various stations in Ann Lake, MN. DW = dry mass.

Station	Loosely-bound P (mg/g DW)	Iron-bound P (mg/g DW)	Labile organic P (mg/g DW)	Al-bound P (mg/g DW)
10	0.024	1.877	0.385	0.811
20	0.016	0.627	0.348	0.181
30	0.010	0.318	0.573	0.232

Table 8. The redox-sensitive phosphorus (P) concentration integrated over the 3-, 4-, 5-, and 6-cm sediment thickness and Al dosage to treat various sediment thicknesses in Lake Ann, MN.						
Sediment thickness (cm)	Station 10		Station 20		Station 30	
	Redox-sensitive P (mg/g)	Alum Dosage (g/m ²)	Redox-sensitive P (mg/g)	Alum Dosage (g/m ²)	Redox-sensitive P (mg/g)	Alum Dosage (g/m ²)
3	1.978	140	0.692	96	0.431	47
4	2.002	193	0.665	129	0.345	66
5	1.897	242	0.639	162	0.304	80
6	1.758	291	0.618	195	0.273	95

Table 9. Recent alum (as Al) dosages for various lakes.		
Lake	Al Dose (g Al m ⁻²)	Reference
Lake Ann ¹	80 - 250	Present study
Lake Riley	100	Present study
Bald Eagle, MN	100	(unpubl. data)
Black Hawk, MN	145	(unpubl. data)
Tiefwareensee, Germany	137	Wauer et al. (2009)
East Alaska, WI	132	Hoyman (2012)
Half Moon, WI ³	115	James (2011)
Susser See, Germany	100	Lewandowski et al. (2003)
Green, WA	94	Dugopolski et al. (2008)

¹Over the upper 4-cm sediment layer

²Over the upper 10 to 12.5-cm sediment layer

³West and east arm dosages were 150 and 75 g/m², respectively

Table 10. Phoslock® concentration needed to control summer internal P loading (15 mg/m² d) for various years. A Phoslock®:P ratio of 105:1 was used in the calculations.

Internal P load control (y)	Phoslock® (g/m ²)
1	82
5	410
10	819
15	1,229

Table 11. Equivalent Phoslock® concentration needed to bind redox-P in the upper 5-cm sediment layer assuming a Phoslock®:P ratio of 105:1.

Station	Redox-P (g/m ²)	Phoslock (g/m ²)
10	12.124	1273
20	4.020	422
30	1.225	129

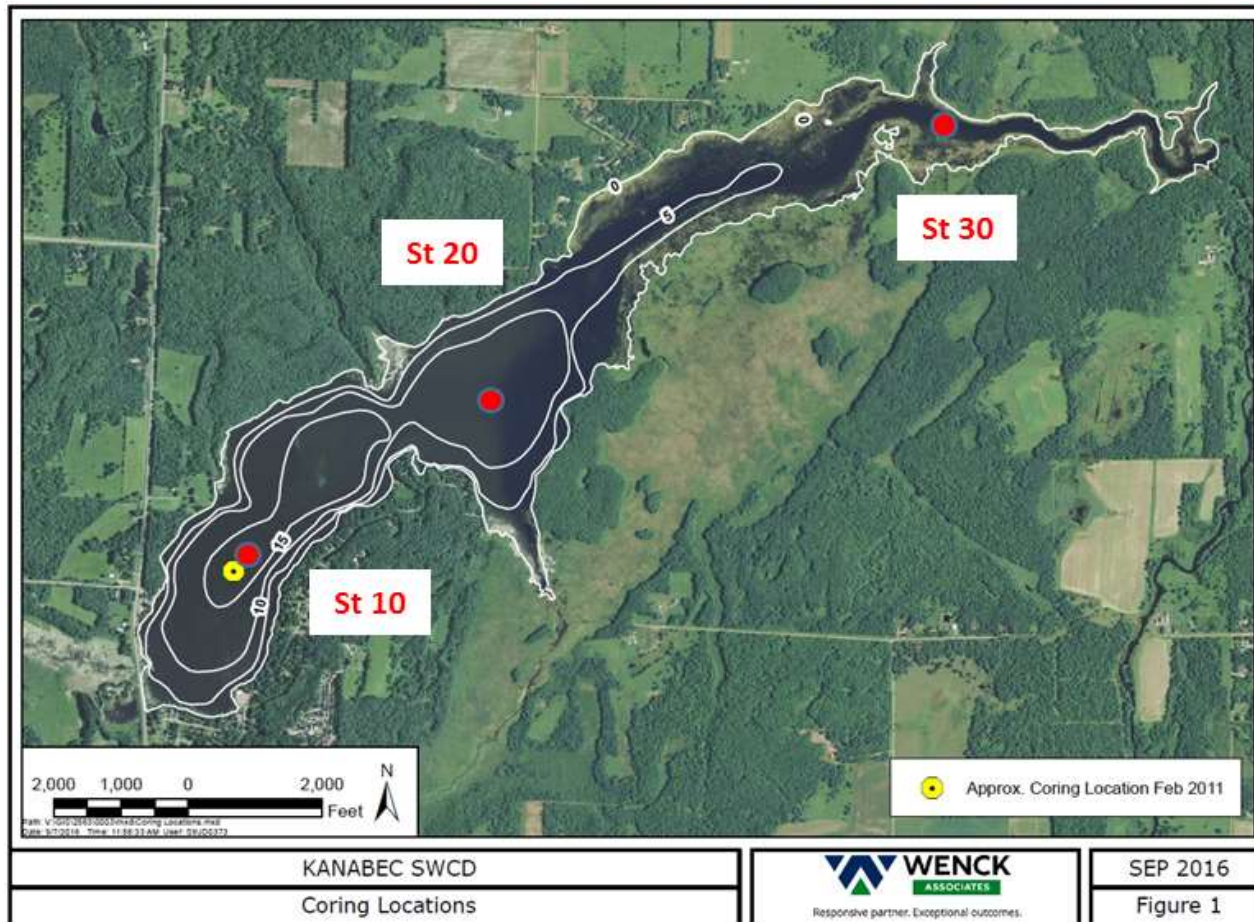


Figure 1. Sediment core sampling stations in Ann Lake, MN.



Figure 2. Picture showing the settled Phoslock® slurry.

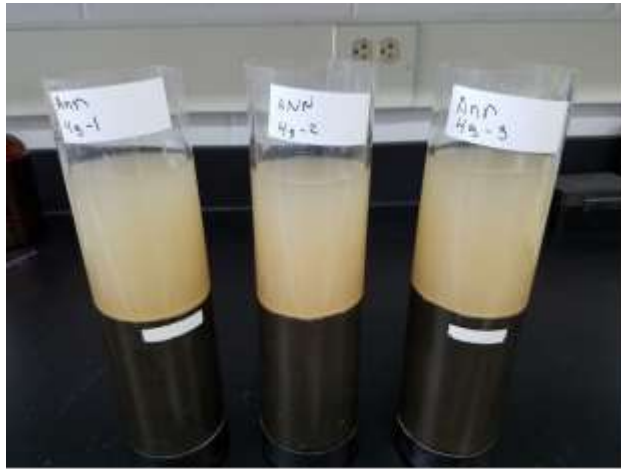


Figure 3. Addition of Phoslock® to sediment incubation systems.

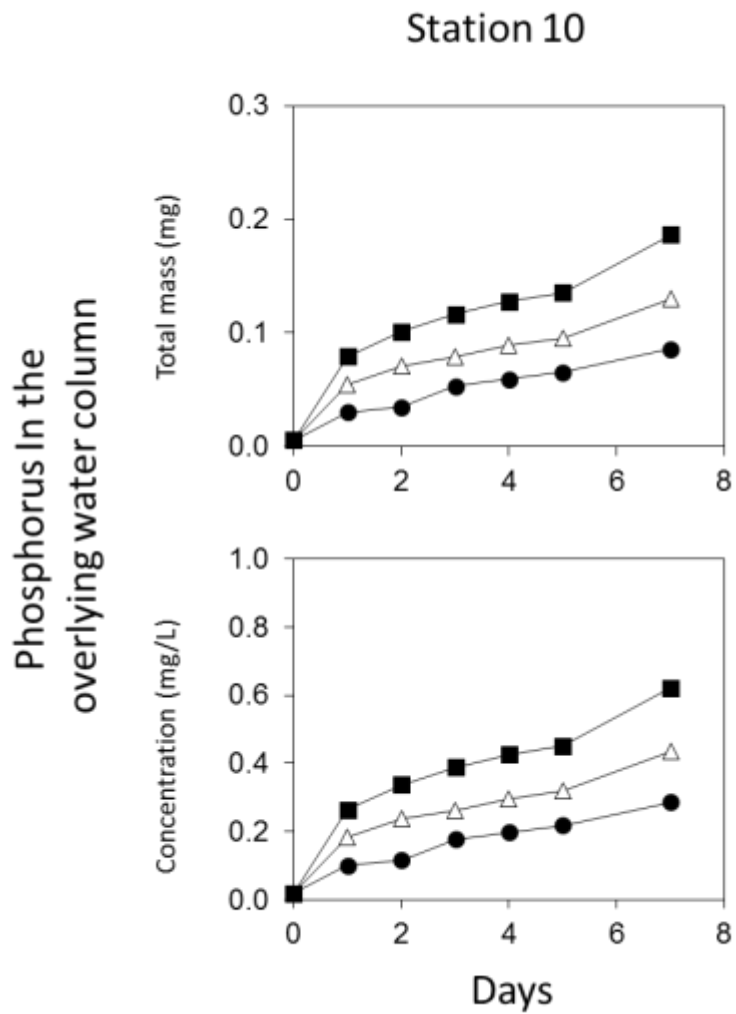


Figure 4. Changes in soluble reactive phosphorus mass and concentration in the overlying water column under anaerobic conditions versus time for sediment cores collected from station 10 in Ann Lake, MN.

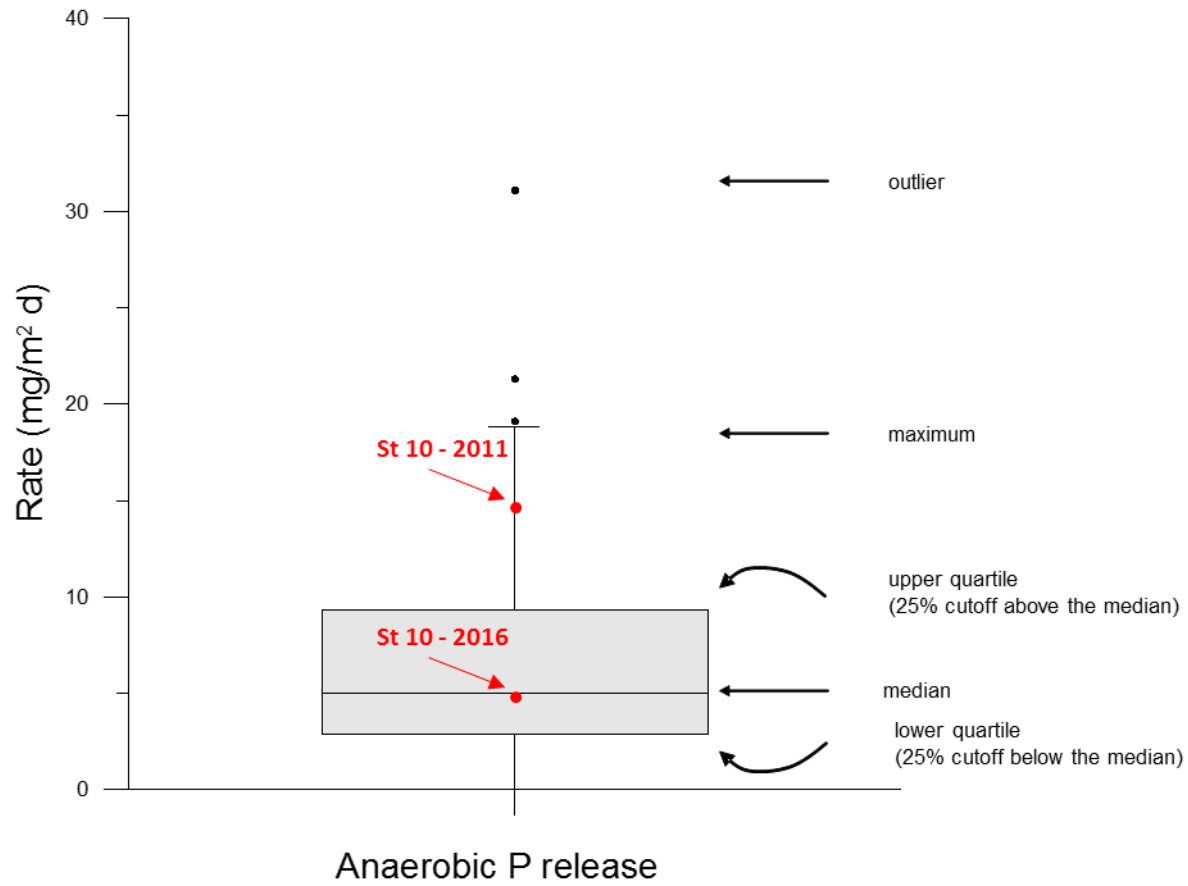


Figure 5. Box and whisker plot comparing the anaerobic phosphorus (P) release rate measured at station 10 (red circle) with statistical ranges for other lakes in Minnesota.

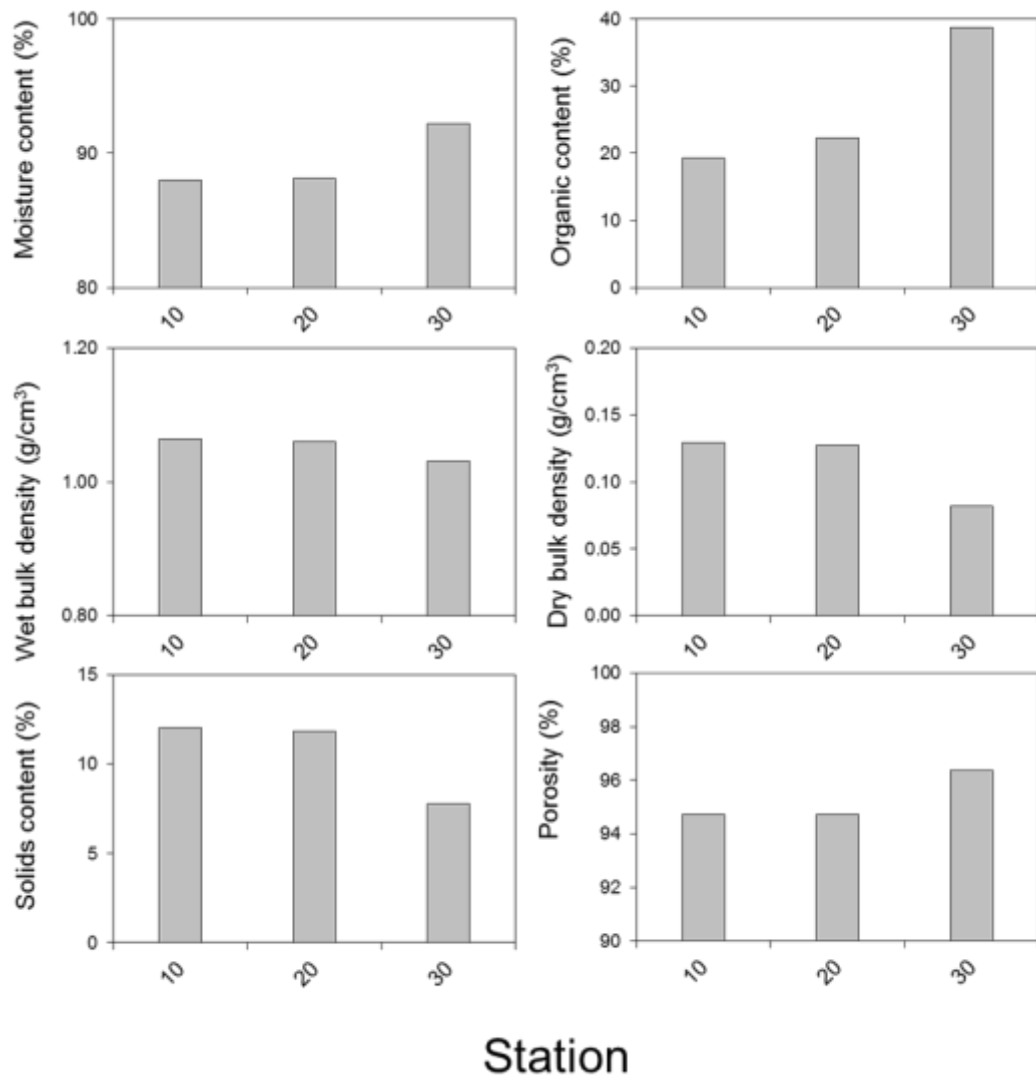


Figure 6. Sediment textural-physical characteristics in the upper 5-cm layer for various stations in Ann Lake, MN.

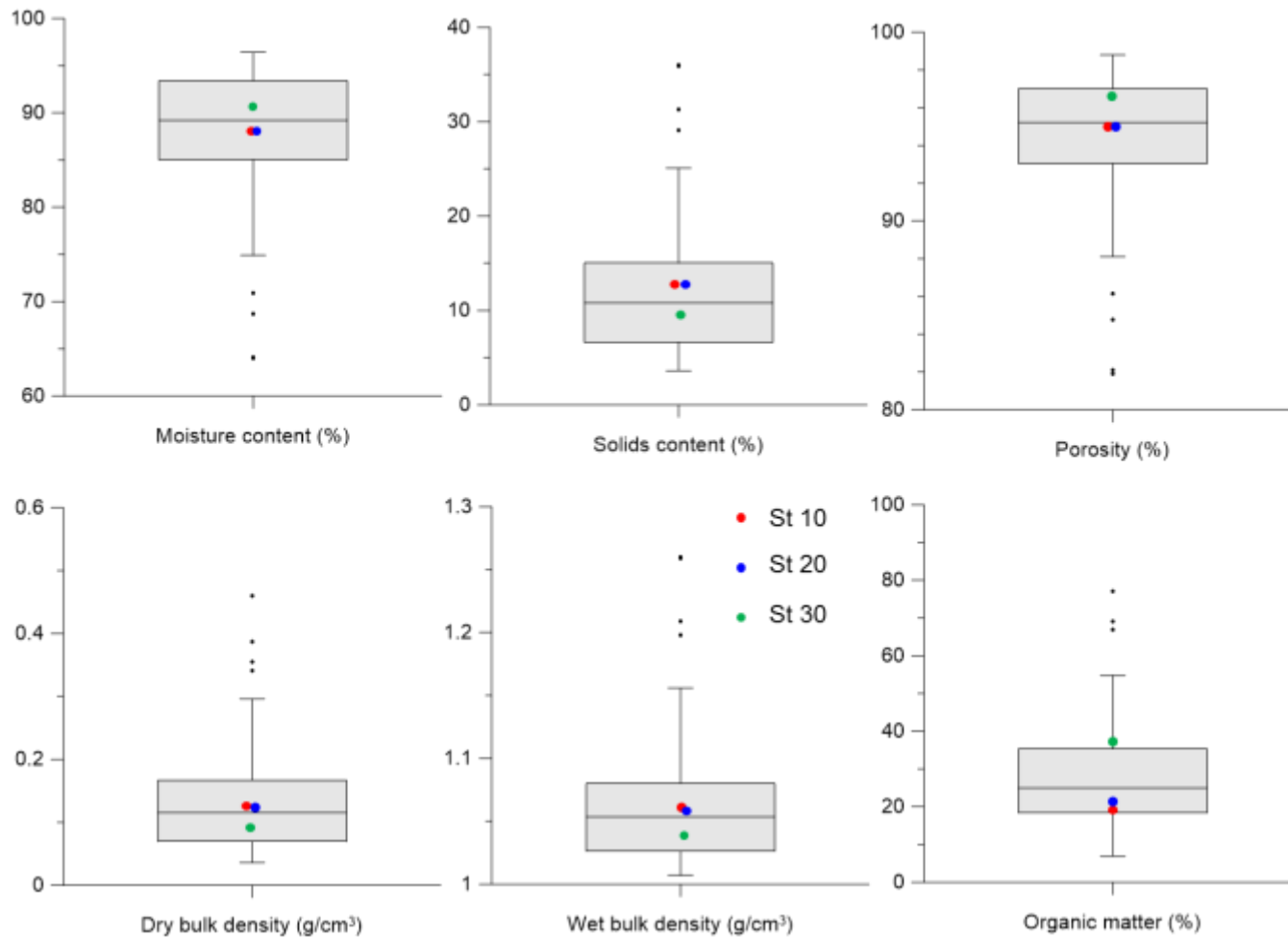


Figure 7. Box and whisker plot comparing textural-physical characteristics of the upper 5-cm sediment layer in Ann Lake, MN with statistical ranges for other lakes in Minnesota.

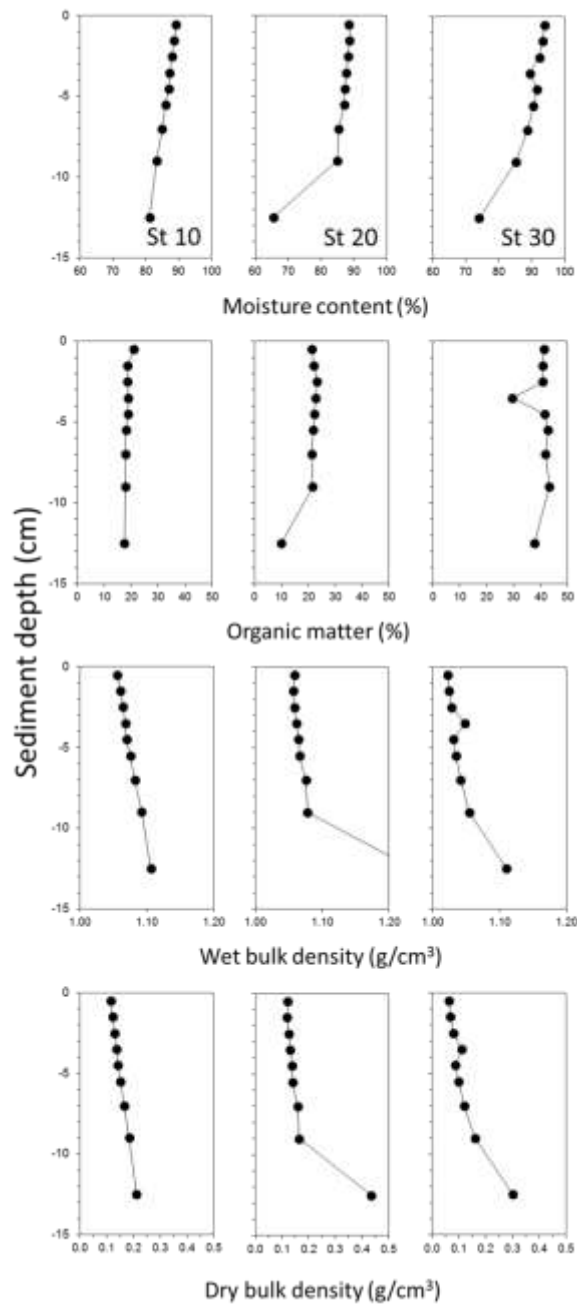


Figure 8. Vertical variations in moisture content, organic matter content, and wet and dry bulk density for sediment cores collected from various stations in Ann Lake, MN.

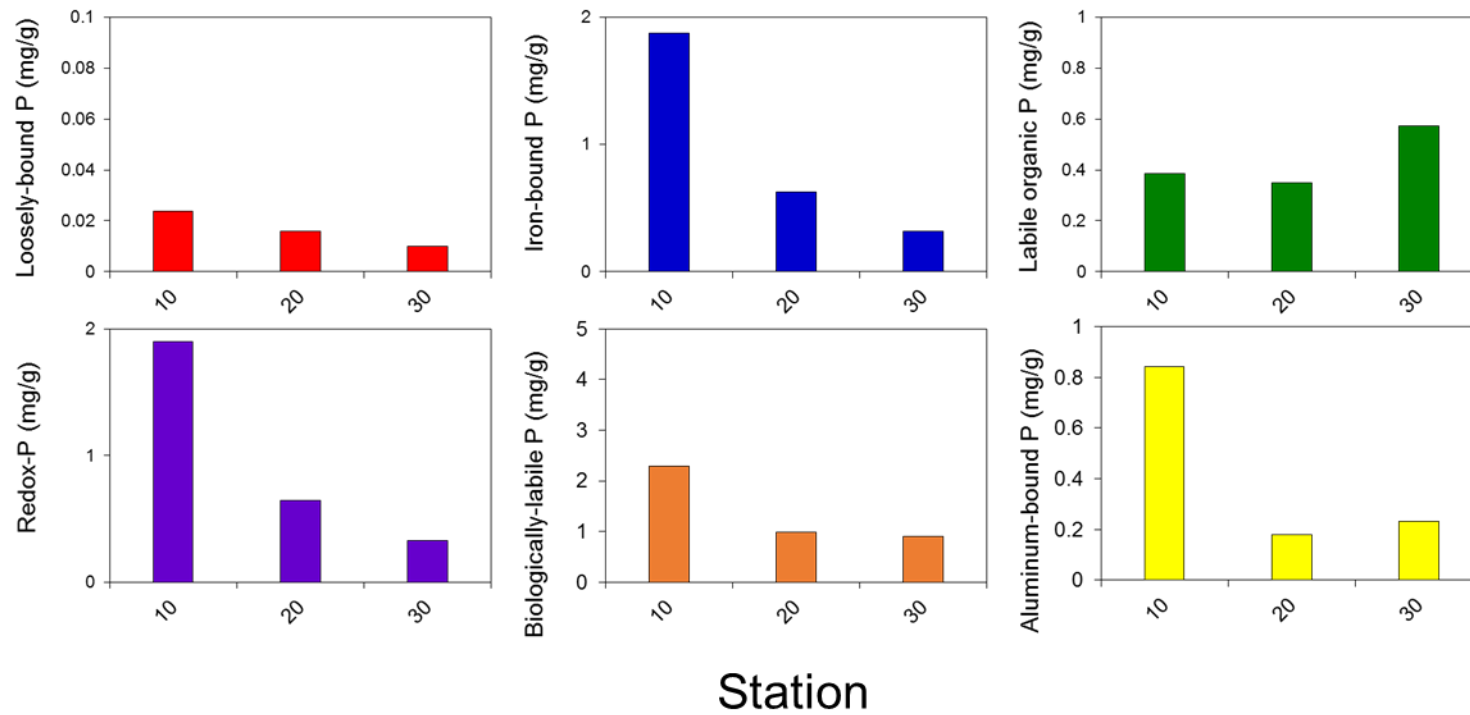


Figure 9. Concentration of various phosphorus (P) fractions in the upper 5-cm sediment layer.

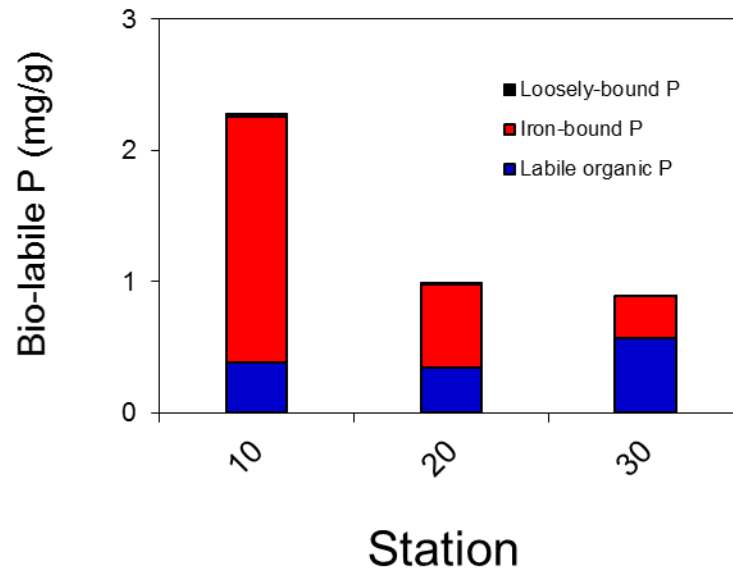


Figure 10. Composition of biologically labile phosphorus (P; i.e., subject to internal P loading) in the upper 5-cm sediment layer.

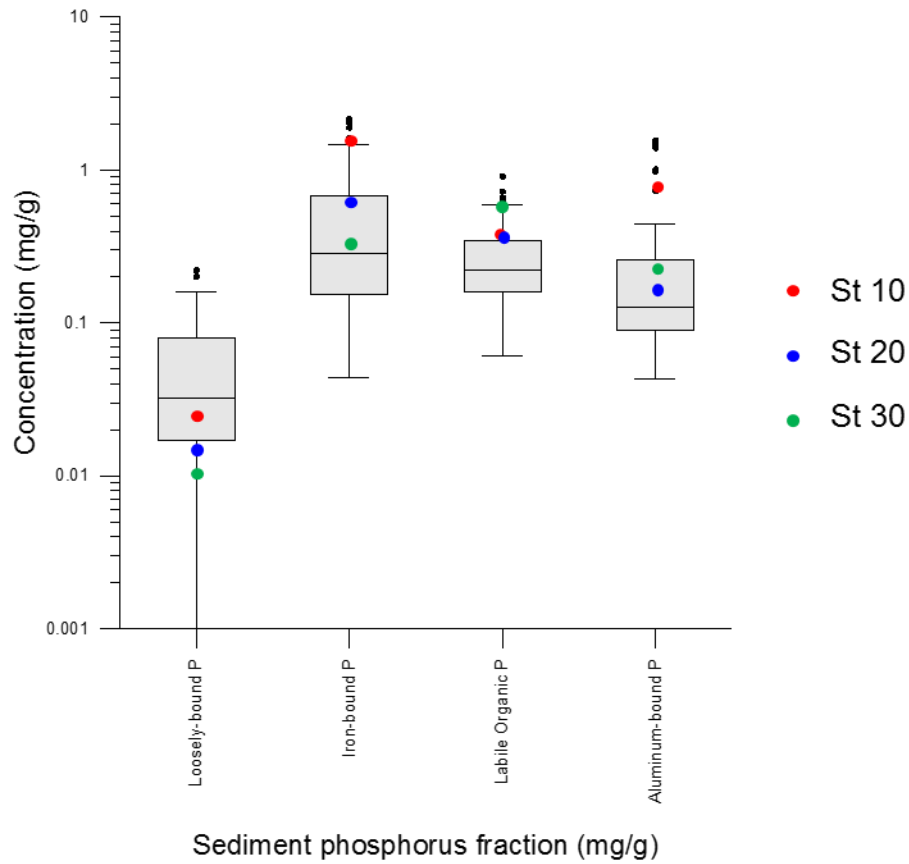


Figure 11. Box and whisker plots comparing various sediment phosphorus (P) fractions measured for sediment collected Ann Lake, MN, with statistical ranges for other lakes in Minnesota. Loosely-bound, iron-bound, and labile organic P are biologically-labile (i.e., subject to recycling) and aluminum-bound, calcium-bound, and refractory organic P are more inert to transformation (i.e., subject to burial). Please note the logarithmic scale.

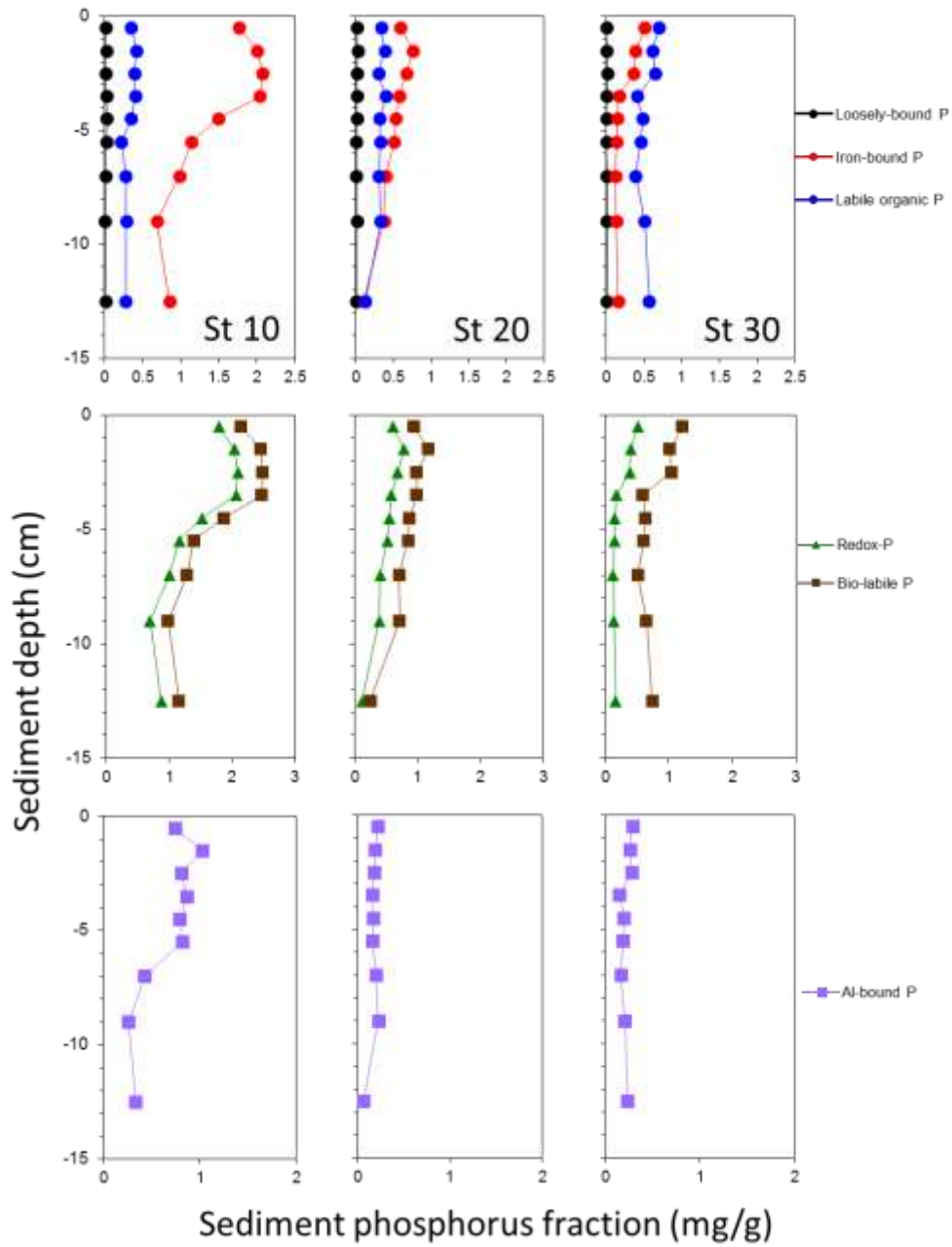


Figure 12. Vertical variations in loosely-bound phosphorus (P), iron-bound P, labile organic P, redox-P, biologically-labile P, and aluminum-bound P concentrations.

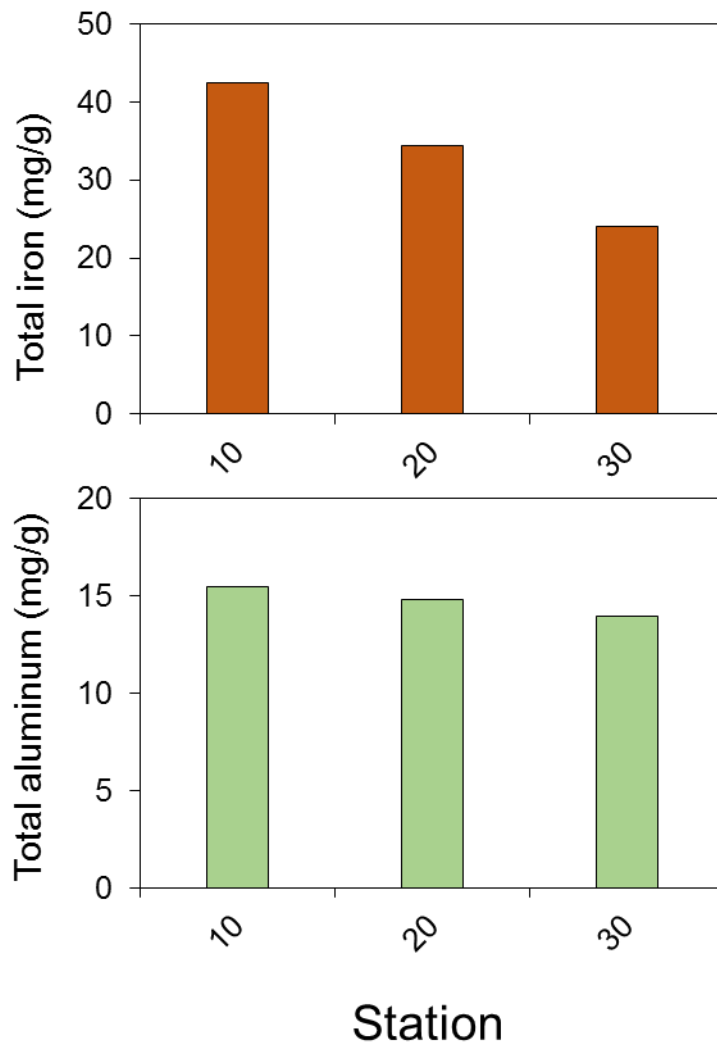


Figure 13. Concentrations of total iron and aluminum in the upper 5-cm sediment layer.

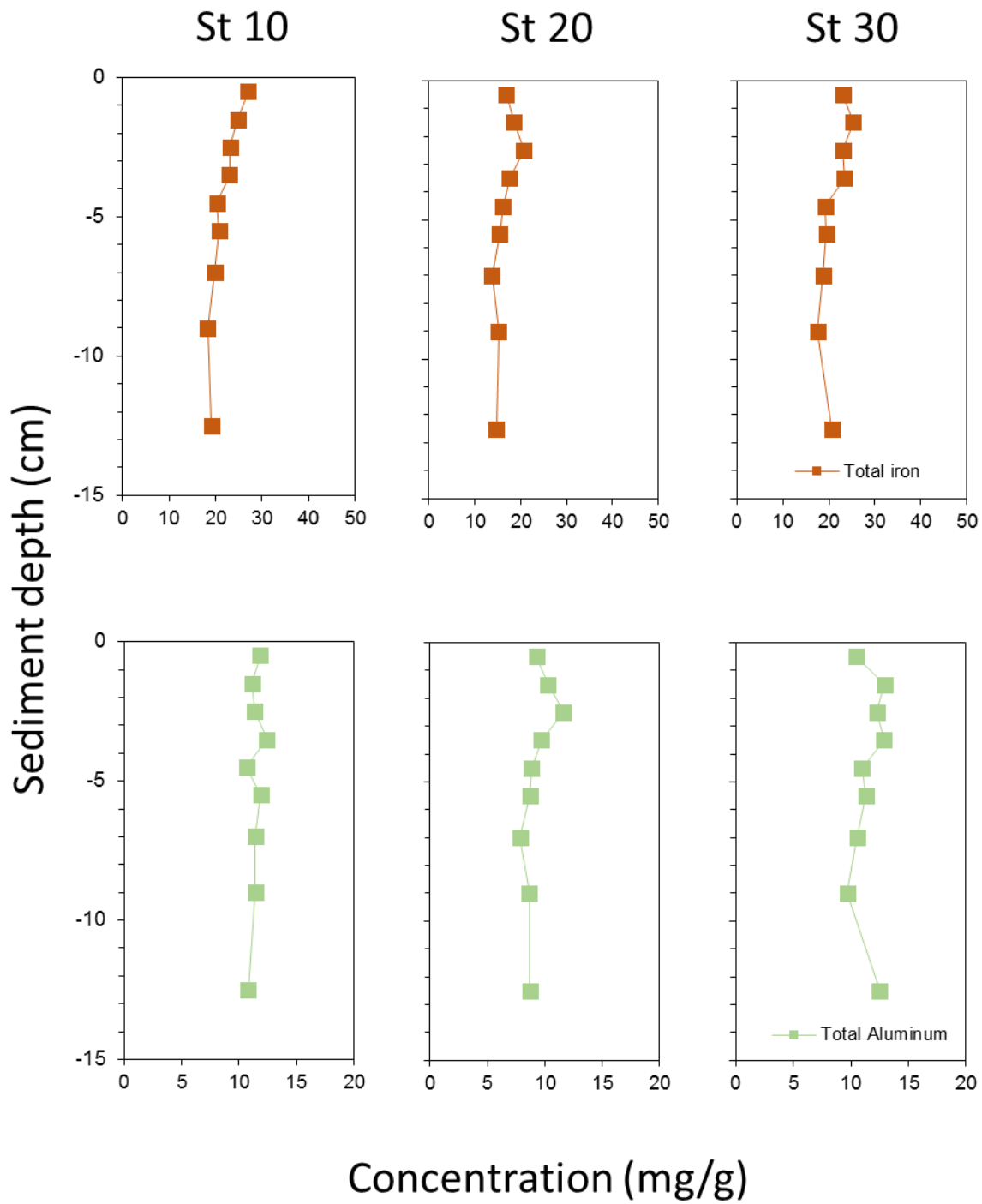


Figure 14. Vertical variations in total iron and aluminum concentrations.

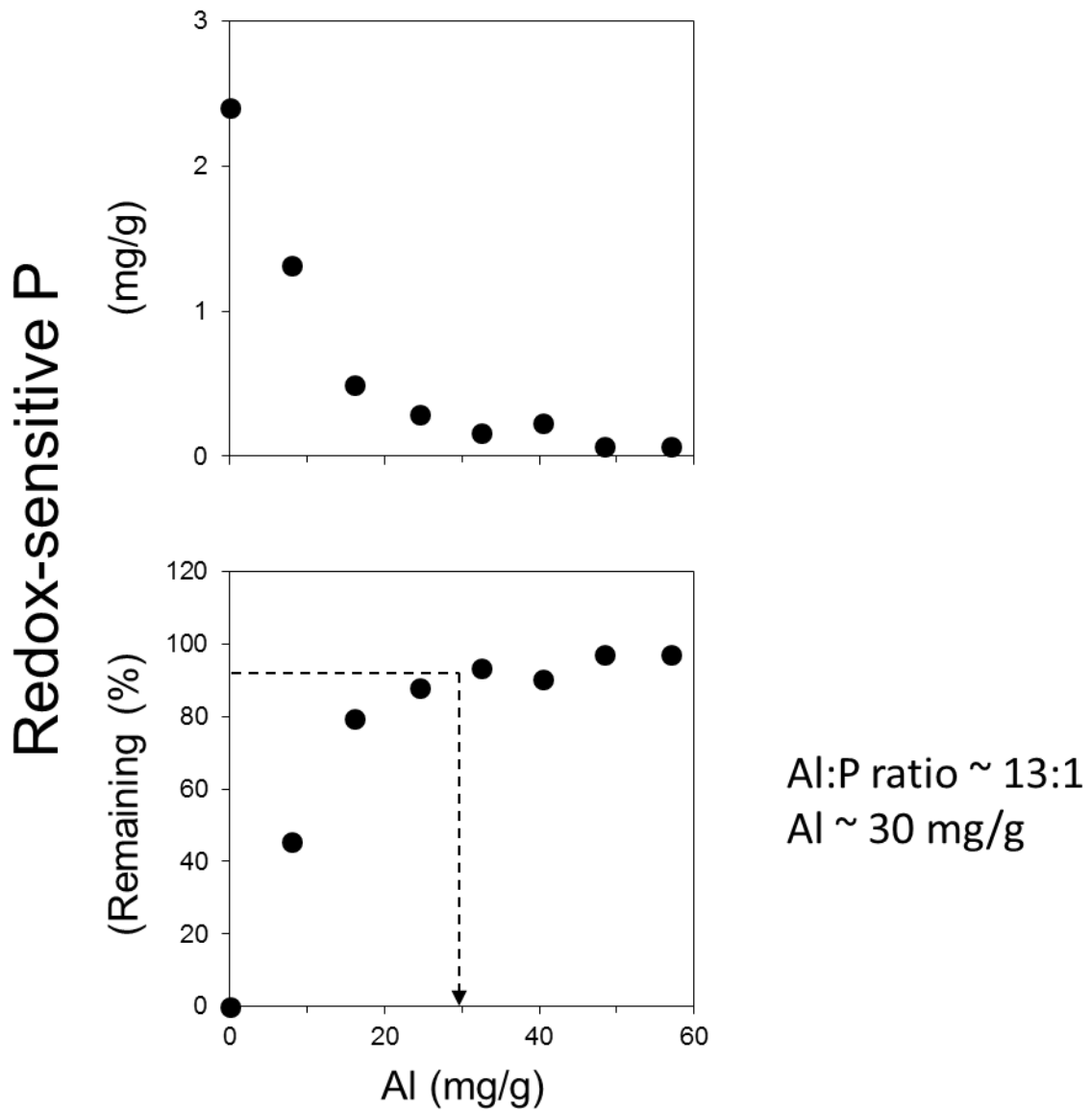


Figure 15. Variations in the concentration of redox-sensitive phosphorus (P; upper panel) and percent removed or adsorbed to the aluminum (Al) floc (lower panel) as a function of increasing Al concentration.

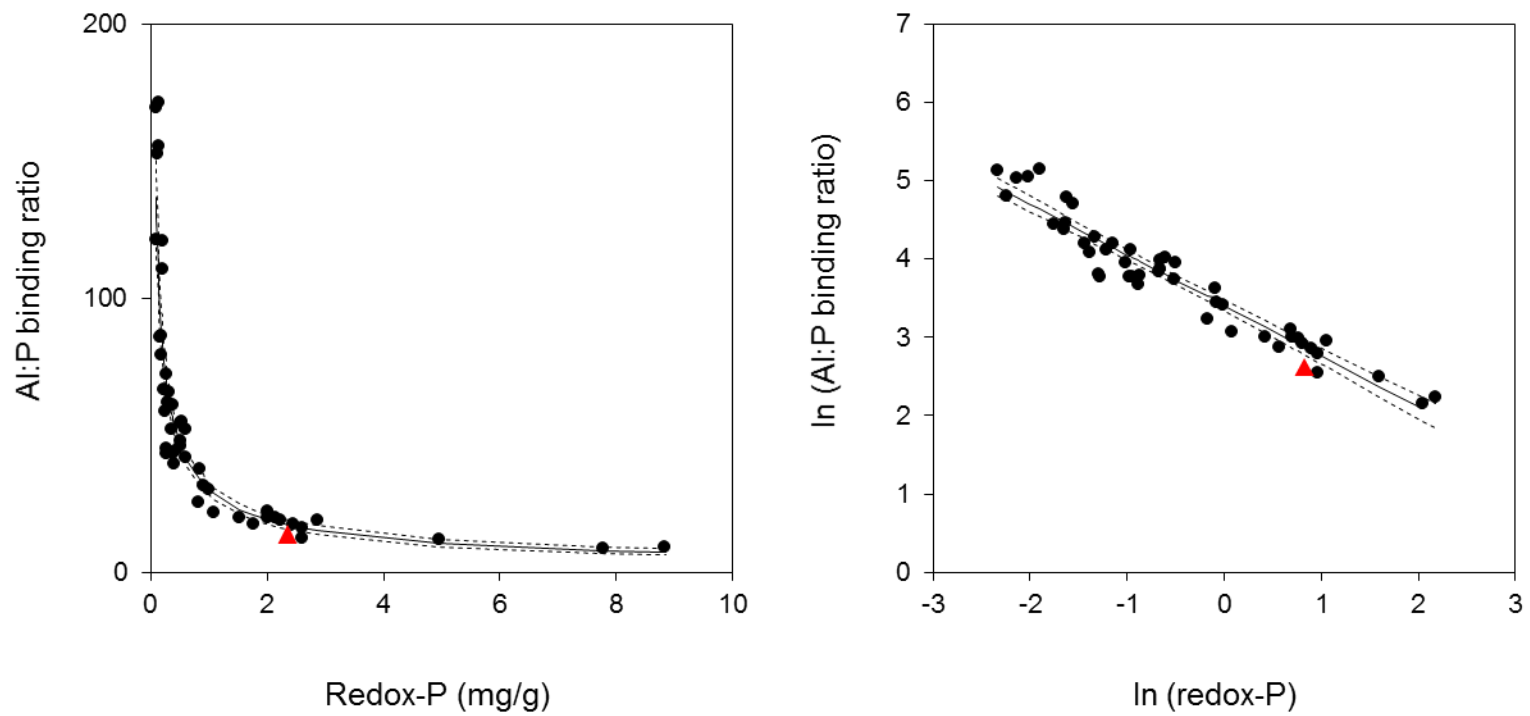


Figure 16. Relationship between the redox-sensitive P (redox-P) concentration and the aluminum:phosphorus ratio (Al:P binding ratio; upper panels). The red triangle represents Ann Lake sediment from station 10.

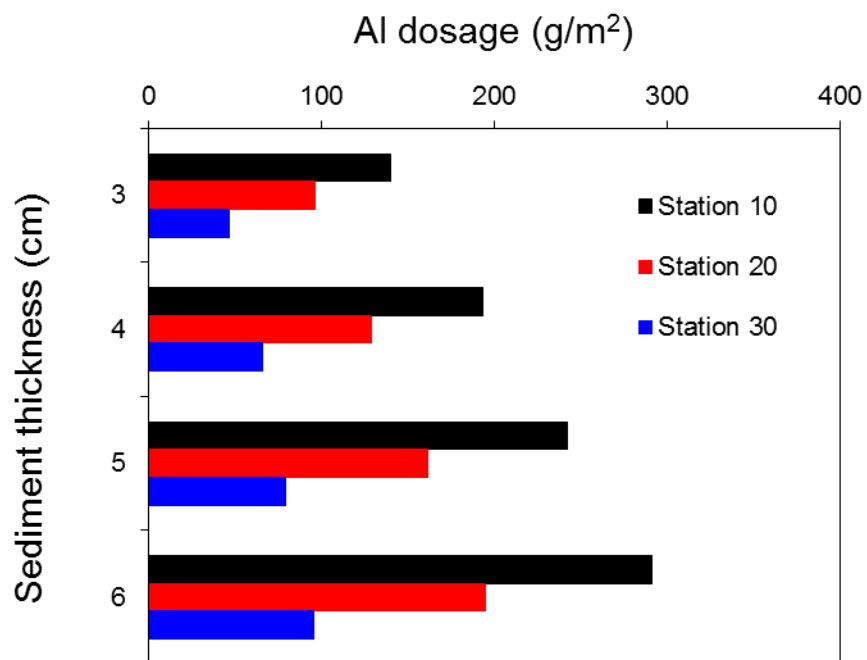


Figure 17. Al dosage estimated from the redox-P concentration (g/m^2) in the upper 3-, 4-, 5-, and 6-cm sediment layers at various stations in Ann Lake, MN.

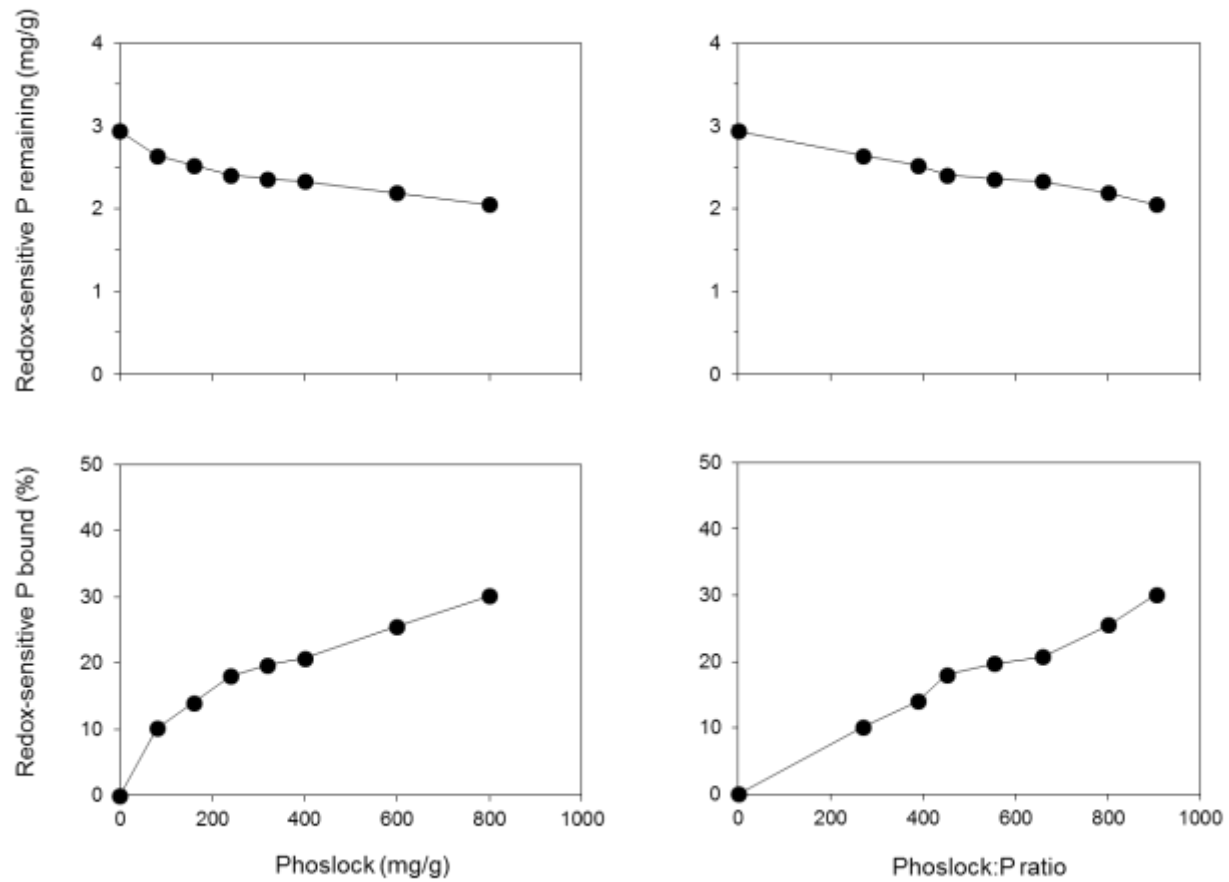


Figure 18. Variations in Phoslock® concentration and Phoslock®:P ratio versus redox-sensitive P concentration and percent removed or adsorbed by Phoslock®.

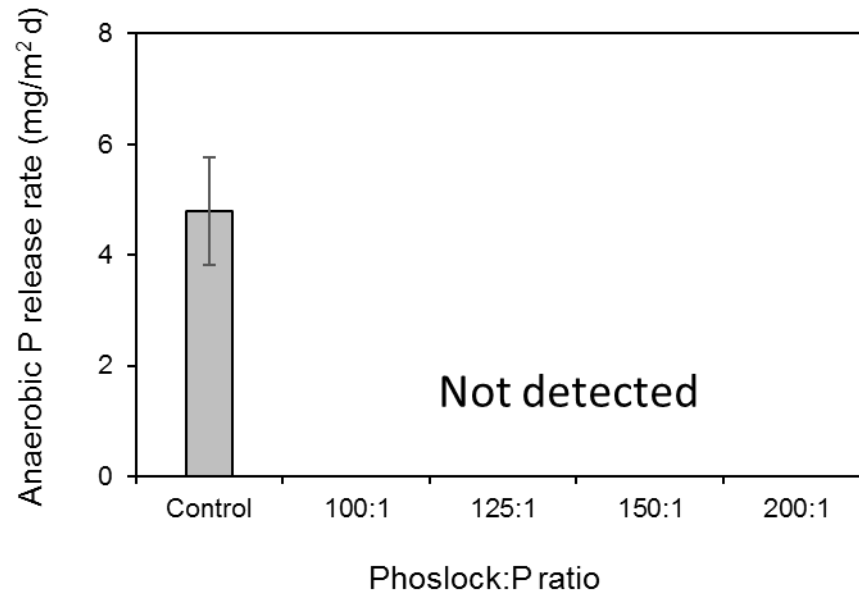


Figure 19. Mean (n = 3) anaerobic phosphorus (P) release rate in control (no Phoslock® addition) and experimentally-treated sediment core systems (see Table 4).

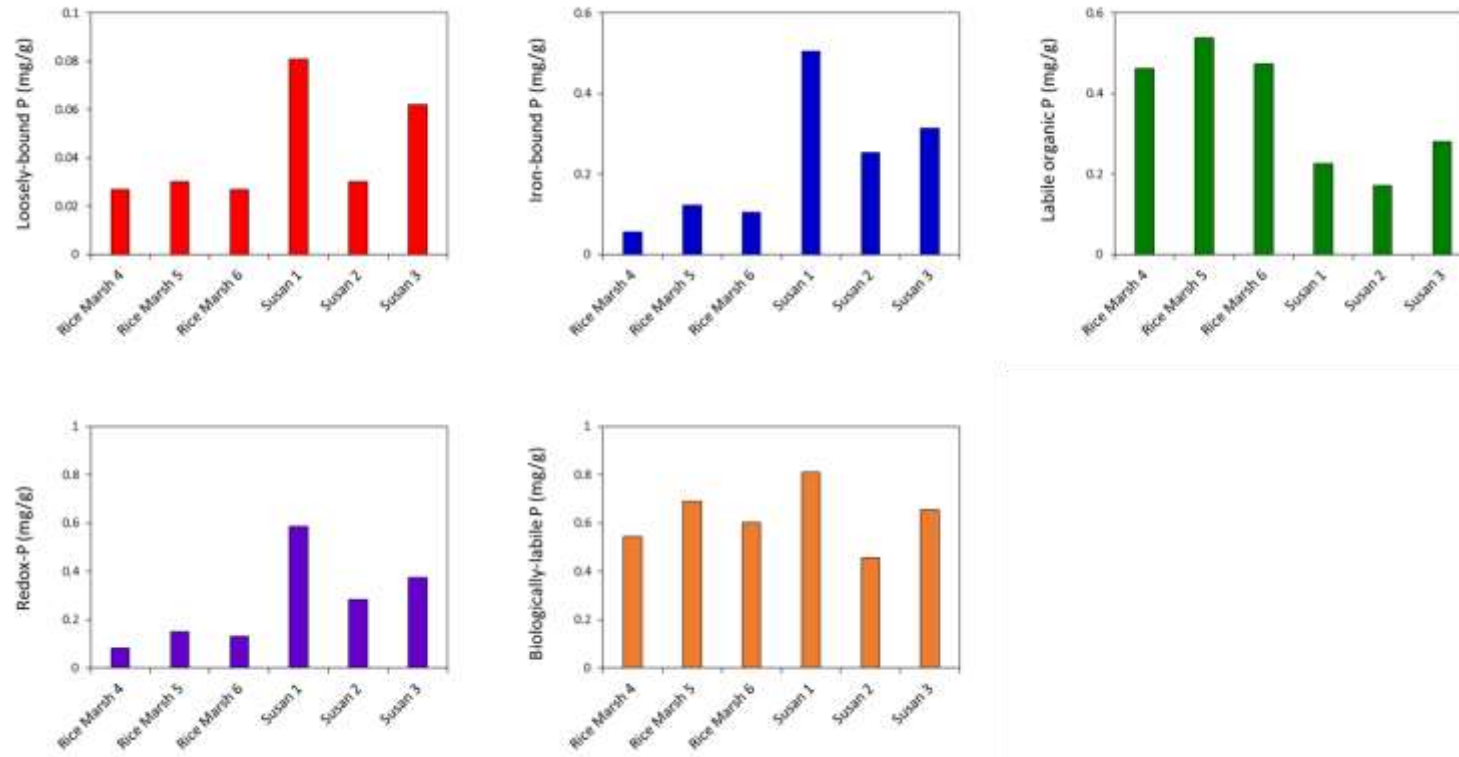


Figure 5. Variations in the composition of biologically-labile phosphorus (i.e., loosely-bound, iron-bound, and labile organic P) and redox-sensitive phosphorus (i.e., loosely-bound and iron-bound P) in the upper 5-cm sediment layer for various stations in Rice Marsh and Susan Lakes, MN.

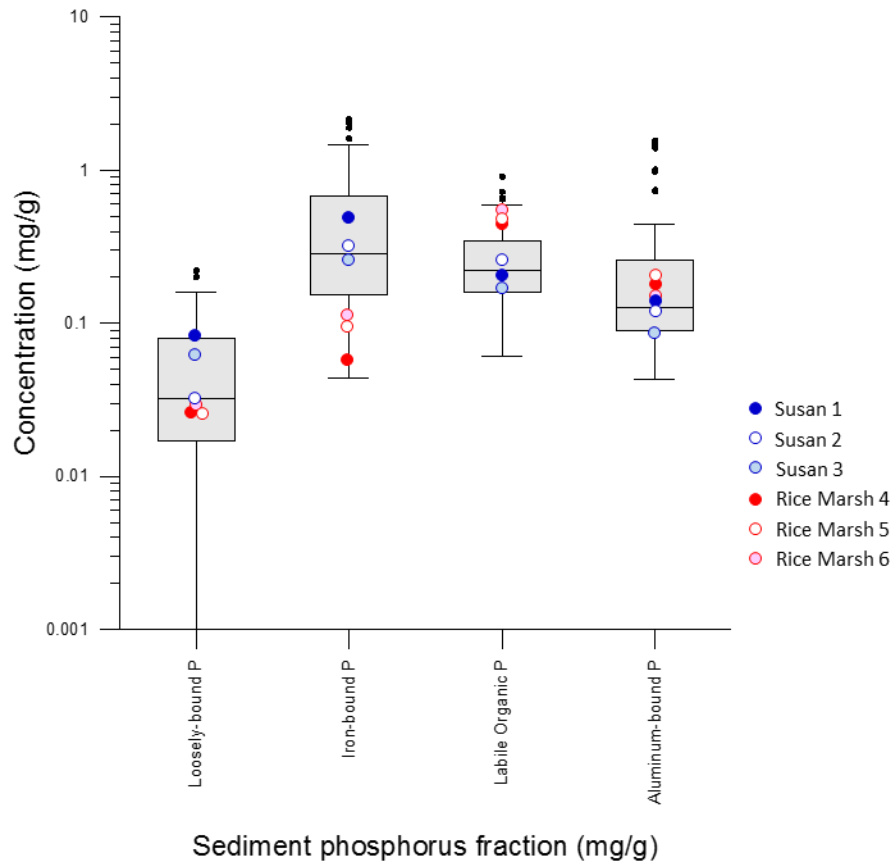


Figure 6. Box and whisker plots comparing various sediment phosphorus fractions measured in Rice Marsh and Susan Lakes with statistical ranges for other lakes in the region. Loosely-bound, iron-bound, and labile organic P are biologically-labile (i.e., subject to recycling) and aluminum-bound P is more inert to transformation (i.e., subject to burial). Please note the logarithmic scale.



Figure 7. Pie charts showing the composition of biologically-labile phosphorus in the upper 5-cm sediment layer for sediment cores collected in Rice Marsh and Susan Lakes, MN.

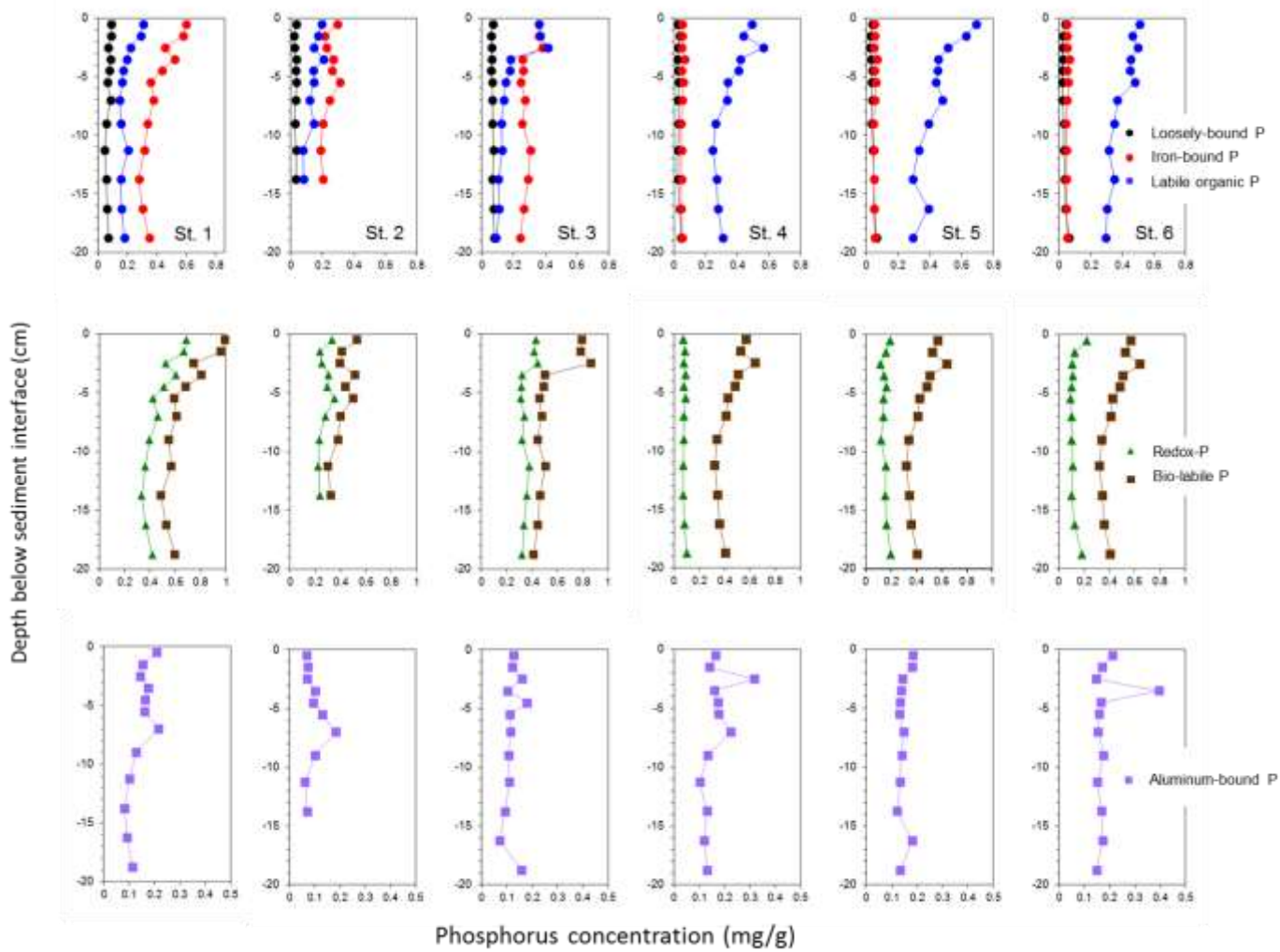
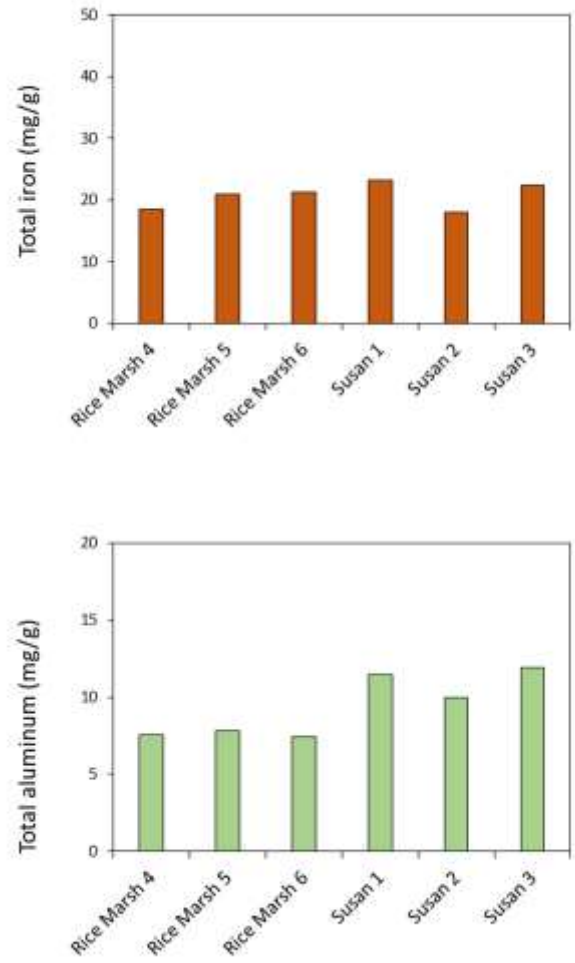


Figure 8. Vertical variations in loosely-bound phosphorus (P), iron-bound P, labile organic P, and aluminum-bound P concentrations for sediment cores collected from various stations in Susan and Rice Marsh Lakes, MN.

Figure 9. Variations in total iron (Fe) and aluminum (Al) in the upper 5-cm sediment layer for various stations in Rice Marsh and Susan Lakes, MN.



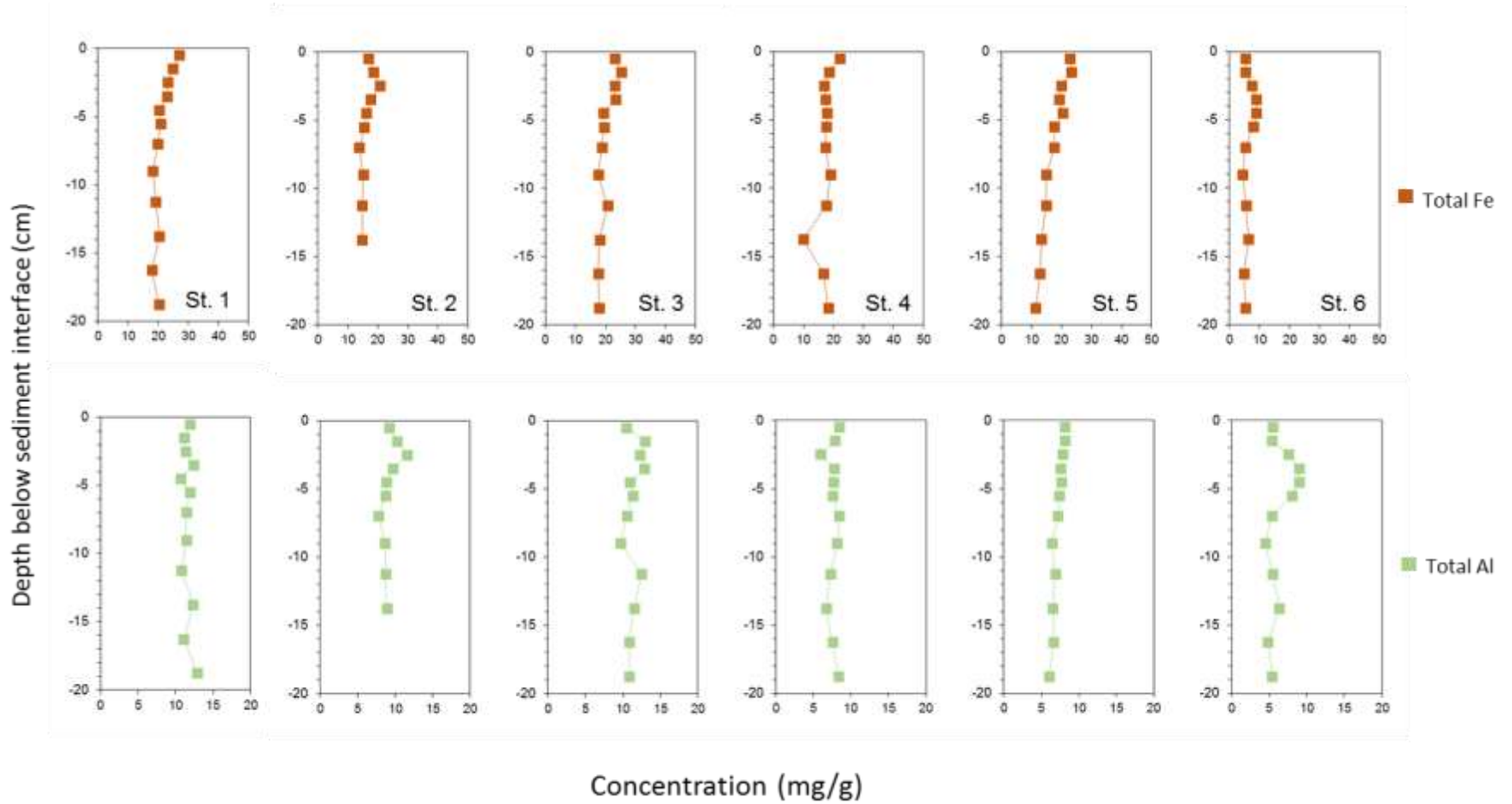


Figure 10. Vertical variations in total iron (Fe) and aluminum (Al) concentrations for sediment cores collected from various stations in Susan and Rice Marsh Lakes, MN.

Susan Lake

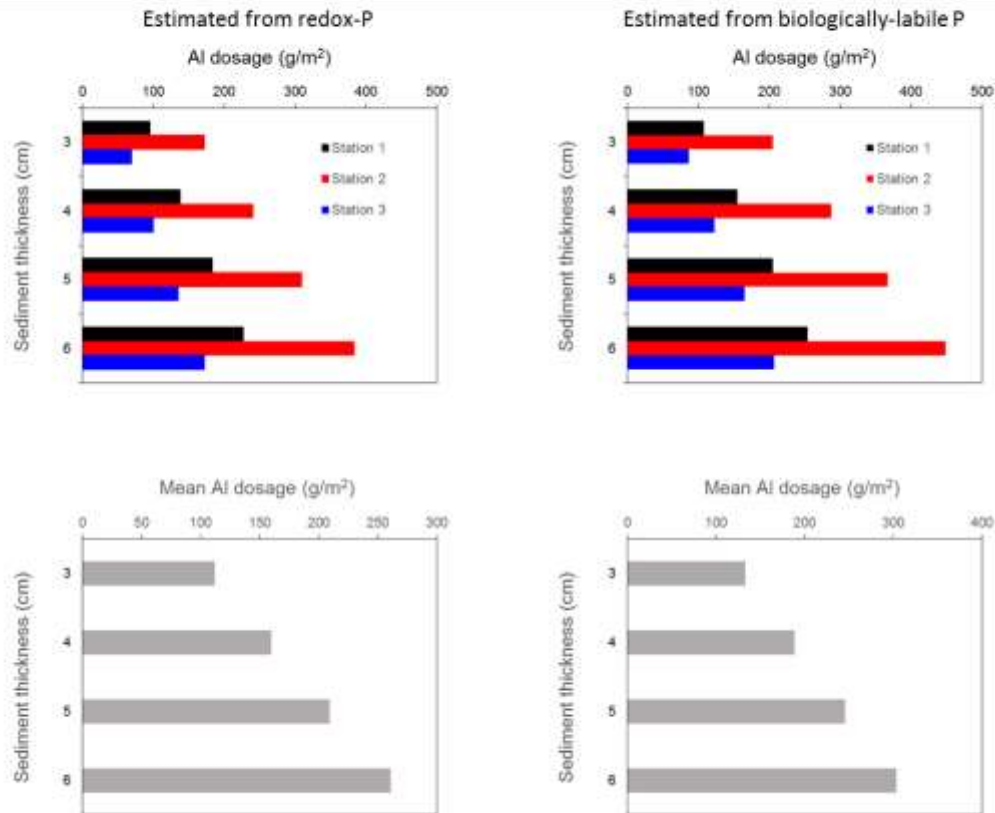


Figure 11. Estimated Susan Lake Al dosage based on the mean redox-P (left panels; i.e., average of stations 1, 2, and 3) and mean biologically-labile P (right panels) concentration in the 0-3, 0-4, 0-5, and 0-6 cm sediment layers.

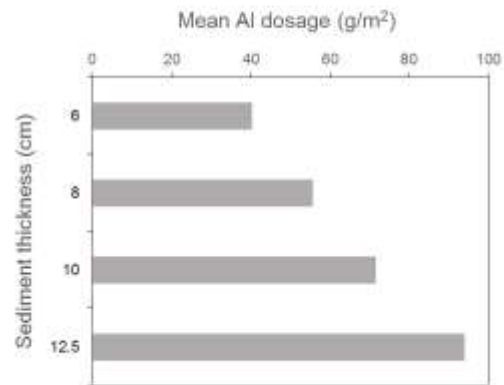
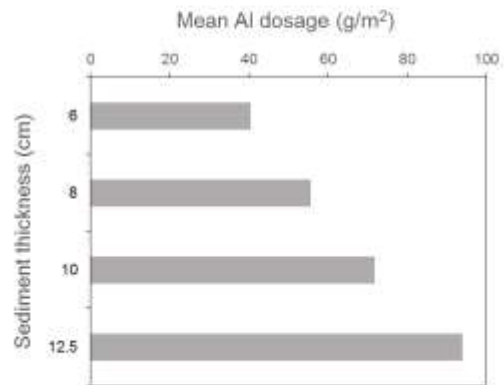
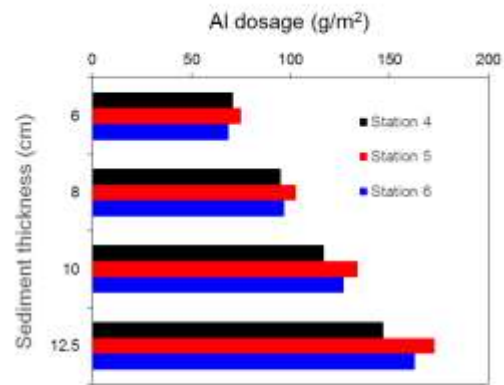
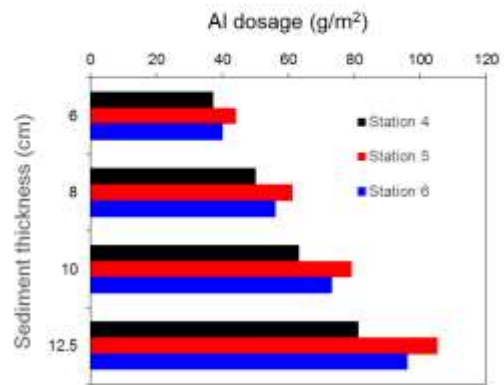


Figure 12. Estimated Rice Marsh Lake Al dosage based on the mean redox-P (left panels; i.e., average of stations 4, 5, and 6) and mean biologically-labile P (right panels) concentration in the 0-6, 0-8, 0-10, and 0-12.5 cm sediment layers.

Appendix B:
Ann Lake Non-Steady State Advection-Diffusion Sulfate
Model

The goal of this analysis is to estimate sulfate concentrations in Ann Lake after an aluminum sulfate application. This differential equation model for Ann Lake estimates sulfate dilution from lake inflow and sulfate flux into sediments. This modeling effort required several assumptions which include:

1. The inflow in Ann Lake is equal to the annual average estimated in the Ann Lake TMDL.
2. Sulfate is distributed evenly throughout the lake immediately after the aluminum sulfate application
3. Evaporation is ignored so that inflow and outflow are equal
4. Sulfate flux (F) into sediments assumes that:
 - a. Sulfate concentrations in porewaters are near 0 g/m³ approximately 7 cm below the sediment water interface (Beck 2013). This means that the surface water concentration is equal to the sulfate gradient between the sediment porewater and overlying water.
5. Tortuosity is estimated as $\frac{1}{\phi^2}$ (Boudreau 1996)

Original Differential Equation

$$V \frac{dC}{dt} = -(Q + FA)C + QC_{in}$$

F=Flux which is defined as the mass per unit area that is diffusing into the sediment, which is d

Steady State Solution

$$C_{ss} = \frac{\frac{QC_{in}}{V}}{\left(\frac{Q}{V} + \frac{FA}{V}\right)}$$

Using “integrating factor” to solve original differential equation

$$\frac{dC}{dt} + \left(\frac{Q}{V} + \frac{FA}{V}\right)C = \frac{Q}{V}C_{in}$$

$$p = \left(\frac{Q}{V} + \frac{FA}{V}\right)$$

$$q = \left(\frac{Q}{V}C_{in}\right)$$

$$C(t) = \frac{\int (e^{\int p dt} q) dt + R}{e^{\int p dt}}$$

Integrate using “integrating factor”

$$C(t) = \frac{q \frac{e^{pt}}{p} + R}{e^{pt}}$$

Simplified solution

$$C(t) = \frac{q}{p} + R e^{-pt}$$

Solution with Variables

$$C(t = 0) = C_0 = \frac{q}{p} + R \rightarrow R = C_0 - \frac{q}{p}$$

$$C(t) = \frac{\left(\frac{Q}{V} C_{in}\right)}{\left(\frac{Q}{V} + \frac{FA}{V}\right)} + \left(C_0 - \frac{\left(\frac{Q}{V} C_{in}\right)}{\left(\frac{Q}{V} + \frac{FA}{V}\right)}\right) e^{-\left(\frac{Q}{V} + \frac{FA}{V}\right)t}$$

Where:

F=Flux of Sulfate into sediments $\frac{\varphi D}{\theta^2} * \frac{1}{d_m}$

V= Volume (m³)

C₀ = Sulfate concentration immediately after the aluminum sulfate application (g/m³)

C_{ss} = Stead state sulfate concentration in Ann Lake (g/m³)

D=diffusion coefficient (m²/day)

d_m = Sulfate diffusion gradient length (m)

C = Lake Sulfate Concentration (g/m³)

Q = Average Annual Flow Inflow/Outflow (m³/d)

C_{in} = Inlet flow sulfate concentration (g/m³)

A= Area of sediment in which sulfate can diffuse (m²)

Θ² = Tortuosity (dimensionless)

φ = Porosity (cm³/cm³)