UNIVERSITY OF MINNESOTA

ST. ANTHONY FALLS LABORATORY
Engineering, Environmental and Geophysical Fluid Dynamics

Project Report No. 582

Internal Phosphorus Load Reduction with Iron Filings

Final Project Report

by

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Prepared for
U.S. Environmental Protection Agency Section 319 Program
and
Minnesota Pollution Control Agency
520 Lafayette Road North.
St. Paul, MN 55155

September 2017
Minneapolis, Minnesota

Grant Project Summary

Project title: Internal Phosphorus Load Reduction with Iron Filings
Organization (Grantee): University of Minnesota
Project start date: 7/1/2014 Project end date: 8/30/2017 Report submittal date: 9/30/2017
Grantee contact name: John Gulliver Title: Professor
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Basin (Red, Minnesota, St. Croix, etc.) /Watershed & 8 digit HUC: Upper Mississippi River Basin/ North Fork Crow River Watershed & 07010204, and St. Croix Basin/Lower St. Croix River Watershed & 07030005 County: Wright and Chisago

Project type (check one):

☐ Clean Water Partnership
☐ Total Maximum Daily Load (TMDL)/Watershed Restoration or Protection Strategy (WRAPS) Development
☐ 319 Implementation
☒ 319 Demonstration, Education, Research
☐ TMDL/WRAPS Implementation

Grant funding

Final grant amount: $299,041.20 Final total project costs: $544,383.32
Matching funds: Final cash: $0 Final in-kind: $245,342.12 Final Loan: $0
MPCA project manager: Nick Gervino

For TMDL/WRAPS development or TMDL/WRAPS implementation projects only

Impaired reach name(s):
AUID or DNR Lake ID(s):
Listed pollutant(s):
303(d) List scheduled start date: Scheduled completion date:

AUID = Assessment Unit ID
DNR = Minnesota Department of Natural Resources

Executive summary of project

Problem

High internal loading of phosphorus occurs in many watersheds and is a difficult problem to solve in lakes. Phosphorus bound to lake sediments is released back into the lake water column, induced by changes in environmental conditions related to dissolved oxygen and pH, and this released phosphorus contributes an additional, internal load of phosphorus to the lake. Internal loading can be significant in some lakes, and both external and internal loading of phosphorus need to be addressed to reduce algal blooms and manage lake restoration efforts.

Waterbody improved

Internal phosphorus loading has been identified as important in Ann Lake and potentially important in the Rush Lake watershed. Rush Lake and Ann Lake are in the US EPA's 303(d) List of Impaired Waters due to nutrient and eutrophication problems. In this project, sediments from Rush lake and Ann lake were set up for laboratory-scale mesocosm studies. Lake sediments with overlying water were exposed to oxic and anoxic conditions, and the effects of the addition of iron filings on the release of phosphorus from the sediments were determined. The project investigated the application of iron filings as a viable option for treating lakes affected by high internal phosphorus loading and eutrophication due to excess phosphorus, and computed the quantity of iron filings required for both Ann Lake and West Rush Lake.

Project highlights

The amendment of lake sediments with iron filings to control sediment-phosphorus release was investigated in the laboratory. Sediments from two Minnesota lakes were sampled. Eightyfive lake sediment cores with an overlying water column were set up for long-term laboratory studies. The dissolved oxygen status of the water column was altered to simulate oxic and anoxic conditions. The flux of phosphate from the sediments to the overlying water was measured in sediments with and without iron filings addition under oxic and anoxic conditions. Different iron dosages were tested to determine the quantity of iron required to successfully sequester phosphorus in the sediments and the conditions under which the iron addition will be effective. The influences of temperature and high sulfate on phosphorus release and iron dosing requirements were also evaluated. Sediment analysis was performed to understand the effect of iron dosing on sediment phosphorus and mineralogy.

Results

The sediments from Rush Lake and Ann Lake released phosphate (P) under anoxic conditions at 20°C. At 10°C, the measured P release rate was approximately one-fourth the rate at 20°C. Oxic P release was generally not observed. After the application of iron filings to the sediment surface, a clear iron dose-P release response emerged indicating that iron addition lowers the water column P level as well as prevents P release, even under anoxic conditions. Taking into consideration all simulated conditions, at least 0.05 g iron/cm^2 sediment area is recommended for phosphorus control in lake sediments. Sediment analysis indicated that the porewater phosphate concentrations are lowered because of iron filings addition, especially in the upper 4 cm of sediments, and the iron filings placed in the sediment continue to control phosphorus release through adsorption and precipitation processes under anoxic and oxic conditions. The presence of high sulfate in the water column accelerates P release from anoxic sediments and a dose > 0.1 g iron/cm^2 is required for lowering P release under such conditions. Application of iron filings is a technique with the potential ability to reduce non-point source pollution of phosphorus released by lake sediments throughout the state. With numerous lakes that experience internal phosphorus loading in Minnesota, the potential impact is substantial.

Partnerships

The Rush Lake Improvement Association, Chisago County, Ann Lake Association, and Wright County Soil and Water Conservation District (SWCD) were the project partners and provided in-kind match for this project. Monthly water quality sampling in Rush Lake was conducted as part of Chisago County's lake monitoring program. Wright SWCD conducted the water quality sampling of Ann Lake.

Pictures

Photographs are provided throughout the report.

Acknowledgements

This project was a contract between the University of Minnesota and the Minnesota Pollution Control Agency, who funded the project through the U.S. Environmental Protection Agency's Federal Clean Water Act Section 319 grant program, Award No. 44094, with Nick Gervino as Project Manager. Nick's assistance and support throughout this project is greatly appreciated. The Rush Lake Improvement Association (RLIA), Chisago County, Ann Lake Association and Wright County Soil and Water Conservation District (SWCD) provided in-kind match and assistance throughout the project.

Support from the Wright County SWCD including Joe Jacobs and Dan Nadeau, the Chisago County including Jerry Spetzmen, the Rush Lake Improvement Association including David Cartwright, Larry Steeves, Ron Rogosheke, George Harrington, Gary Reilly, and the Ann Lake Association including Frank Broghammer is greatly appreciated. Support and guidance on lake sediment coring provided by the University of Minnesota's Limnological Research Center including Kristina Brady and Ryan O'Grady is much appreciated. The St. Croix Watershed Research Station, especially Robert Dietz and Michelle Natarajan, provided guidance on the sequential phosphorus extraction procedure. Jeanette Voelz and Prof. Lee Penn from the Department of Chemistry at the University of Minnesota helped with the X-ray diffraction measurements. In addition, the assistance and support from the St. Anthony Falls Laboratory (SAFL) staff and students including Robert Gabrielson, Benjamin Erickson, Andrew Erickson, Jenni Snyder, David Liddell, Tyler Olsen, Peter Corkery, Kyle Fleming, Phi Pham is appreciated.

Participation by volunteers from the Lake Associations, County and SWCD as members of the Technical Advisory Panel, including Nick Gervino, Jerry Spetzman, Susanna Wilson, David Cartwright, Larry Steeves, Ron Rogosheske, Dan Nadeau, Alicia O'Hare, Kerry Saxton, Rhonda Rae, Frank Broghammer and Randall Smedstad, is greatly appreciated.

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Acronyms and Abbreviations

DO = Dissolved oxygen
LRC = Limnological Research Center
IL = Illinois
MI = Michigan
MN = Minnesota
MPCA = Minnesota Pollution Control Agency
NJ = New Jersey
RLIA = Rush Lake Improvement Association
SAFL = St. Anthony Falls Laboratory
SRP = Soluble reactive phosphorus or phosphate
SWCD = Soil and Water Conservation District
TAP = Technical advisory panel
TP = Total phosphorus
US EPA = United States Environmental Protection Agency
XRD = X-ray diffraction

Section I – Work Plan Review

Approved changes: There was one amendment and one change order approved to reflect changes in staff and required materials that occurred during the project. Under Amendment 1, changes were made to contract language and minor changes to grant funds allocated to each task. Under Change Order 1, the grant funds were reallocated from tasks regarding: a) collection of sediment cores; b) collection of water quality samples; c) submitting water quality data to EQuIS; and d) conducting water column studies on sediment columns from Rush Lake and Ann Lake; to: a) development of semiannual reports; and b) investigating questions regarding water column studies on sediment columns.

Objective 1. Project Administration

Task A: Semi-annual reports

Semi-annual project reports were submitted to the MPCA on February 1st and August 1st of each year during the project duration (July 2014 - August 2017). The semi-annual reports were completed as scheduled.

Task B: Project Meetings

The Technical Advisory Panel (TAP) was established as scheduled. TAP meetings were held on August 20, 2014 (field meeting), August 31, 2015, April 7, 2016, December 12, 2016, and August 9, 2017, at the St. Anthony Falls Laboratory. Data and results from the project were presented during these meetings, which included questions and discussions between the TAP members and project staff. The meeting presentation notes (PowerPoint slides) were distributed to the TAP members.

Objective 2. Rush Lake and Ann Lake field studies

Task A: Collect Sediment Column Samples

Task B: Collect Water Quality Samples

Task C: QAPP Development

Task D: Submit Water Quality Data to EQuIS

After site reconnaissance, fifty intact sediment cores were collected from Rush Lake in January 2015. Dredged sediment and lake water were collected from Ann Lake in November 2015. The Ann Lake sediments were homogenized at the laboratory and then sediment cores were prepared for the column studies.

The Rush Lake water sampling was performed by the Chisago County staff. Samples were taken from East and West Rush Lake on an approximately monthly basis from May through September for chlorophyll-A, total phosphorus, Secchi disk depth, ammonia nitrogen and surface temperature. Sulfate and iron were added to these measurements in the 2015 season. Dissolved oxygen level and temperature measurements, and water samples for total and soluble reactive phosphorus were collected from the sampling station in Ann Lake by the Wright SWCD staff.

The Quality Assurance Project Plan (QAPP) for this project was developed and submitted in 2015 and approved by the MPCA in February 2016.

Rush Lake monitoring sites have been established in EQuIS. Chisago County has been collecting and submitting lake monitoring data from East and West Rush Lake (13006900-01 and 13006900-02) into the EQuIS system. The water quality data for Ann lake sampling location (86-0190-00-201) have been submitted to the EQuIS database.

Objective 3. Laboratory Analysis of iron dosing, and its effect on lake sediments and water quality

Task A: Year 1

Task B: Year 2

Task C: Year 3

The sediment mesocosms consisted of lake sediments with filtered overlying lake water contained in polycarbonate liner tubes with sealed endcaps. In Year 1, laboratory column studies on Rush Lake sediment were conducted. The water column conditions were altered to simulate oxic and anoxic conditions at 20 °C and 10 °C. Three dosages of zero-valent iron filings, 0.01 g iron/cm^2, 0.1 g iron/cm^2 and 1 g iron/cm^2, were applied to the sediment surface and the effectiveness of the dosages in controlling phosphorus release from the sediments was determined under oxic and anoxic conditions. Influences of temperature, iron filings quantity, and timing of iron application on the sediments and water quality were determined. In Year 2, homogenized sediment cores from Ann Lake were exposed to lake water in laboratory columns. Sediment-phosphorus flux from sediments amended with three iron filings dosages, 0.01 g/cm^2, 0.05 g/cm^2 and 0.1 g/cm^2, was measured under oxic and anoxic conditions. Temperature, high sulfate in the water column, amount of iron filings, and timing of iron application were evaluated. The results from Year 1 and Year 2 studies were investigated further during Year 3 of the project. The lake sediments were extruded from the columns and analyzed to understand the impact of iron filings addition on the sediment phosphorus and the release potential. Sediment pore water phosphate concentrations, sediment mineralogy, and sediment phosphorus pools were analyzed to interpret the observed phosphorus release from iron-amended sediments. Batch studies were also conducted on various iron samples sourced from the upper Midwest region to determine their potential application for phosphorus treatment. The laboratory analysis and studies were completed as scheduled.

Objective 4. Project Report

Task A. Draft Final Project Report

Task B. Final Project Report

The draft final report was prepared and shared with the MPCA Project Manager and TAP members for review and comment. The draft version was revised and the final report submitted. The research study results will be disseminated through journal publications and conference presentations.

Section II – Grant Results

Introduction

Lake sediments can act as a source or sink of phosphorus (Bostrom et al. 1982). Release of phosphorus from sediments into the overlying lake water is called internal loading and can cause eutrophication of the lake. Combined with external phosphorus input from surrounding watershed, internal phosphorus loading plays an important role in the deterioration of water quality and trophic status of lakes. Internal loading can be significant in some lakes, and when not addressed after reducing external load, the internal loading delays the lake recovery process due to phosphorus recycling from sediments (Smolders et al. 2006; Søndergaard et al. 2013).

Mobilization of phosphorus from sediments is a complex process involving physical, chemical, and biochemical mechanisms such as desorption, ligand exchange, dissolution of precipitates, mineralization, release from living cells, and autolysis (Bostrom et al. 1982). These occur in conjunction with environmental factors such as redox potential, temperature, pH, biological activity, alkalinity, and concentrations of metals (Fe, Ca, Mg, Mn), sulfate and nitrate that also affect phosphorus cycling (Bostrom et al. 1982; Gächter and Müller 2003; Christophoridus and Fytianos 2006; Smolders et al. 2006). Although influenced by several mechanisms described above, phosphorus release under anaerobic or anoxic conditions is strongly correlated to the mass of iron-bound and loosely-bound phosphates (also referred to as redox-P) in the sediments (Bostrom et al. 1982; Nürnberg 1988; Pilgrim et al. 2007; James 2011). Because the liberated phosphorus is bioavailable, its presence in the water column makes it available for algal uptake and cyanobacteria growth (Nürnberg 1988; Søndergaard et al. 2013; James and Bischoff 2015).

Iron (Fe) plays an important role in lake sediments because the abundance of iron directly impacts the cycling and burial of phosphate through the Fe-P cycle or Fe-P-S cycle in sulfate-sensitive systems. Shallow lakes with sediments rich in iron (total Fe:P >15; by weight) have shown low sediment phosphorus release and low total phosphorus in the lake water (Jensen et al. 1992). However, application of iron for lake treatment has been less common when compared to alum application (Smolders et al. 2006). This is mainly because of the belief that low redox will induce re-mobilization of ferrous-phosphates [Fe(II)-P] and therefore maintenance of oxygenated conditions by artificial aeration is required, and that long-term success is rare with iron treatment (Cooke et al. 1993; Engstrom 2005). For example, treatment of a shallow lake with ferric chloride ($FeCl_3$) lasted only three months, although a high concomitant external P loading was noted (Boers et al. 1994). When supplemented with hypolimnetic aerators iron chloride ($FeCl_3$) injections in four lakes namely, chain of lakes that supply water to St Paul, MN, Vadnais Lake, MN, and two lakes in Berlin, Germany, reduced the water column phosphorus and prevented re-release of phosphorus from the iron-enriched sediments over 10 to 20 years (Walker et al. 1989; Engstrom 2005; Kleeberg et al. 2012). More recent and successful whole-lake and in-lake mesocosm applications of iron salts ($FeCl_2$, $FeCl_3$, $FeClSO_4$, $Fe_2(SO_4)_3$), with and without artificial aeration, have been effective in treating phosphorus in hypereutrophic lakes (Deppe and Benndorf 2002; Kleeberg et al. 2013; Orihel et al. 2016), reducing growth of macrophytes (Immers et al. 2014), and decreasing cyanobacterial toxicity (Orihel et al. 2016). With proper iron dosage accounting for sulfate/sulfide and sediment organic matter, the phosphorus binding capacity of the lake sediments is improved and a long-term effect on the phosphorus water quality is achievable (Gächter and Müller 2003; Kleeberg et al. 2013). These dosing studies highlight the suitability of iron for lake phosphorus treatment despite its perceived sensitivity to oxygen supply.

The primary objective of this project is to investigate the addition of zero-valent iron filings on the surface of lake sediments as a measure for solving the internal phosphorus loading problem in lakes. The hypothesis is that iron filings placed in lake sediments will provide dissolved iron and form iron oxide corrosion products that will precipitate and adsorb phosphorus and thus substantially reduce or eliminate the release of phosphorus from the sediments to the overlying lake water. The surface application of solid iron filings to amend lake sediments is conceivably easier to implement, considering most of the applications have used liquid iron containing chloride that is injected into the hypolimnion or sediment.

The effectiveness of iron filings amendment on sediment phosphorus was investigated in the laboratory using lake sediment-water columns (or mesocosms) from two eutrophic Minnesota lakes, Rush Lake (Chisago County) and Ann Lake (Wright County). The laboratory mesocosm system provided the advantage of altering experimental parameters and examining the effects of iron application under controlled conditions. The goals of the laboratory column studies were to 1) quantify the appropriate dosage of iron filings necessary for successful reduction of internal phosphorus release, 2) determine the conditions (dissolved oxygen, sulfate/sulfide, temperature) required for iron filings to be effective, and 3) understand the effect of iron amendment on the sediment phosphorus chemistry.

Measurements

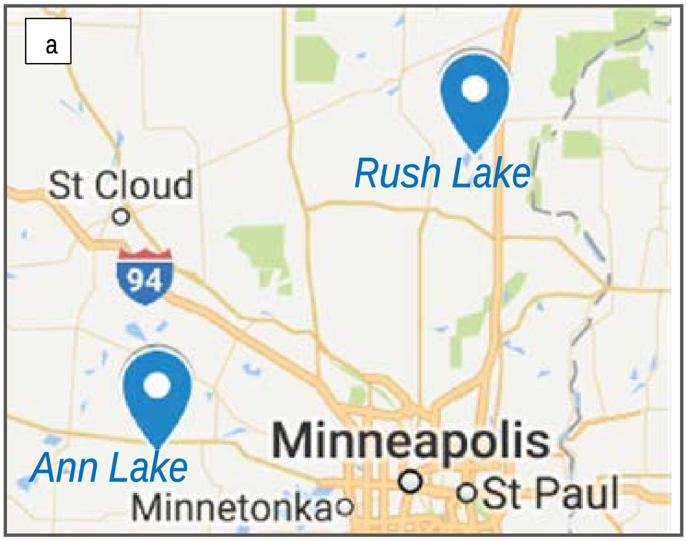
Batch Studies

Batch studies were performed to measure the effectiveness of ten different iron materials in removing dissolved phosphorus (primarily phosphate) from water under controlled experimental conditions. The iron samples were obtained from suppliers in the upper Midwest region. Pyrex borosilicate glass bottles (500 mL) were used for the batch tests. A phosphate solution (400 mL at 250 µg/L), prepared by dissolving potassium phosphate (KH_2PO_4) in deionized water (Milli-Q, 18.2 MΩ·cm), was added to each batch bottle. No other chemical constituent was added to the phosphate stock solution to limit the interaction of the sorbent (i.e., iron material) to the phosphorus in solution. An initial water sample (time = 0) was collected from each bottle before the addition of iron to verify the initial P concentration and identify contamination. Iron (0.343 g) was added to the bottles, and five replicate bottles were used for each iron material. The 'blank' bottles were filled with the standard phosphate solution, without any iron. The batch bottles containing iron and blanks were placed on a Labline Orbital shaker table at 200 RPM. Water samples (~8 mL) were drawn from each bottle after mixing for 1, 5, 10, 24 and 48 hours. The samples were filtered through a 0.45 µm membrane filter to remove particulates, and analyzed for soluble reactive phosphorus (SRP) concentrations colorimetrically using ascorbic acid (Standard Methods 4500-PE; APHA/AWWA/WPCF 1995; detection limit = 10 µg/L). Batch tests with two lower iron quantities, 0.172 g and 0.0343 g iron added to 400 mL of stock P solution each, were performed for two iron samples.

For reference, the 0.343 g, 0.172 g and 0.0343 g iron quantities tested in the batch tests respectively correspond to the 'high', 'medium', and 'low' dosages of iron applied to the lake sediments in the laboratory column studies.

Description of Rush Lake and Ann Lake

Sediments from Rush Lake and Ann Lake in Minnesota were sampled (Figure 1). Rush Lake, located in Chisago County, is in the Lower St. Croix River watershed in the St Croix River Basin. Approximately 80% of the Rush Creek subwatershed land cover is a mix of cropland, grass, woodland, and wetland (MPCA 2015). The surface areas of East and West Rush Lake are 6.0 km^2 (1484 ac) and 6.4 km^2 (1579 ac), respectively. Rush Lake is deep; the maximum water depths are 7.3 m (24 ft) in East Rush Lake and 13 m (42 ft) in West Rush Lake. Ann Lake is located in Wright County and is part of the North Fork Crow River watershed in the Upper Mississippi River Basin. The watershed is primarily agricultural (> 77%) including row crops and animal agriculture (Wenck 2011). Ann Lake is 1.5 km^2 (375 ac) in area, and is a shallow lake with depths varying between 1.5 m (5 ft) and 5.8 m (19 ft) (average depth = 3 m or 10 ft). Rush Lake and Ann Lake are recreational lakes supporting boating and fishing, and they have lake associations comprised of lake shore property owners engaged in management of the lake.



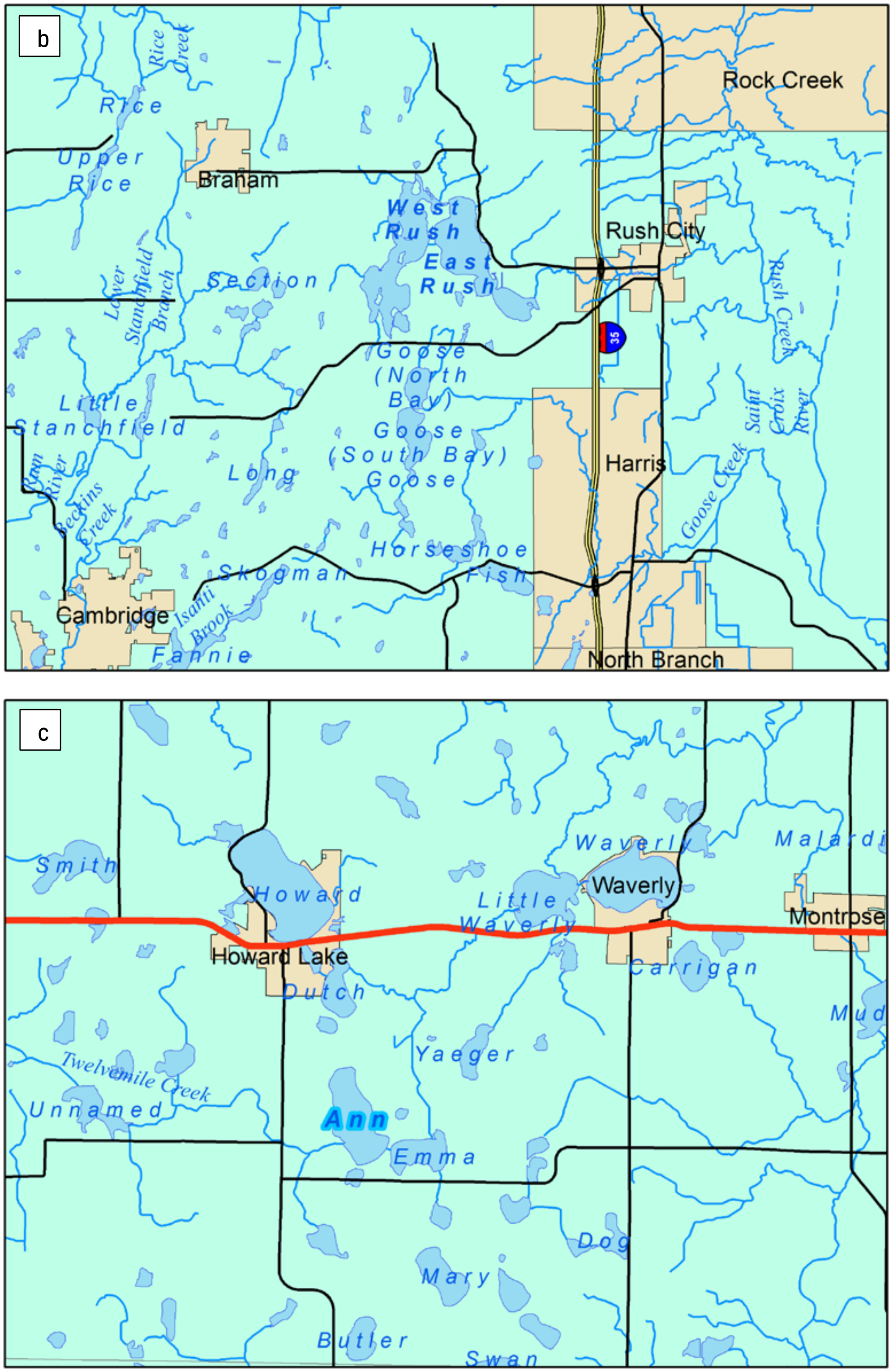


Figure 1. Maps showing the locations of Rush Lake (Chisago County) and Ann Lake (Wright County) in MN (a) (Source: <maps.google.com>), including the area surrounding each lake (b & c).

Both Rush Lake and Ann Lake are listed as ‘impaired’ due to excess nutrients and eutrophication problems in the US EPA’s 303(d) List of Impaired Waters. Ann Lake was placed in the list in 2002, and East and West Rush Lake have been on the list since 2008. Monitoring has shown that the summertime (June through Sep) total phosphorus (TP) concentration ranges between 145 and 395 µg/L in Ann Lake, which exceeds the 60 µg/L standard for shallow lakes in the North Central Hardwood Forest ecoregion (Wenck 2011). In Rush Lake, the TP concentration ranges between 91 and 152 µg/L in summer, higher than the 40 µg/L standard for deep lakes in the ecoregion (Chisago County 2014). Both lakes suffer from invasive curly-leaf pondweed growth, low Secchi depths, and high chlorophyll-*a* that affect the lake water quality (Wenck 2011; Chisago County 2014). The TMDL plan for nutrients was approved in 2012 for Ann Lake (Wenck 2011) and more recently for Rush Lake in 2016 (MPCA 2015).

Water Quality Monitoring of Rush Lake and Ann Lake

Chisago County monitors the water quality of Rush Lake as part of the Water Quality and Aquatic Invasive Species Monitoring program. Water samples are collected using a 1.8 m (6 ft)-long integrated water sampler from the deepest parts of East Rush Lake and West Rush Lake on an approximately monthly basis from May through September for chlorophyll-A, total phosphorus, Secchi disk depth, ammonia nitrogen and surface temperature. Sulfate and total iron were added to these measurements in 2015. Water quality of the lake is evaluated based on the MPCA’s water quality standards established for deep lakes, Carlson Trophic Status Index (Carlson and Simpson 1996), and lake water quality grades (Metropolitan Council 2014). The water samples are analyzed by Pace Analytical Services Inc., Duluth, MN.

Ann Lake water quality is monitored by the Wright Soil and Water Conservation District (SWCD) for dissolved oxygen level, water temperature, total phosphorus, and soluble reactive phosphorus (SRP). Using a Van Dorn sampler, water samples are collected at a sampling station located in the deepest part of the lake with approximately 5.5 m (18 ft) deep water. The dissolved oxygen and temperature profiles are taken using a sonde at 0.30 m (1 ft) intervals from the surface to the bottom of the lake. The chemical analysis of the water samples are performed at RMB Environmental Laboratories, Grand Rapids, MN.

Sediment Core Collection

Initial site reconnaissance of Rush Lake to select the location for sediment coring was conducted in September 2014, with members from the Rush Lake Improvement Association (RLIA). With assistance from RLIA volunteers, 50 intact sediment cores were collected from West Rush Lake in January 2015 (Figure 2). The cores were sampled from a ~16 m × ~16 m (~53 ft x ~53 ft) plot in the lake, where the approximate water depth was 1.5 - 2.1 m (5 - 7 ft). Holes were drilled through the ice with an ice auger, and ~0.61 m (~2 ft) of undisturbed lake sediment along with the overlying water (~0.71 m or 2.3 ft) were collected into 70 mm O.D. (2.75 inch) polycarbonate liner tubes by manually driving a piston corer attached to drive rods into the sediment. This method of sediment core collection preserves the sediment-water interface. The

Limnological Research Center (LRC) at the University of Minnesota provided the coring device and sampling materials. The columns were stored under dark conditions at 4 °C (39 °F) in a temperature-controlled room located in the Civil Engineering building at the University of Minnesota until the laboratory column experiments were set up in March 2015.

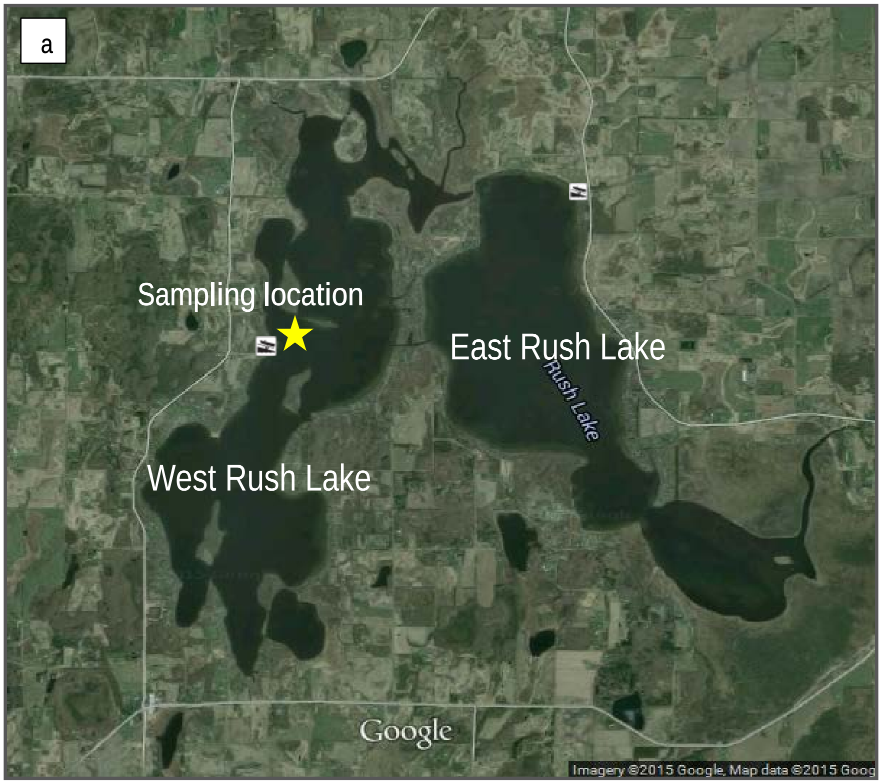


Figure 2. Rush Lake sediment sampling. (a) Sampling location in West Rush Lake (source: <maps.google.com>); (b) RLIA volunteers drilling holes in the lake for sediment coring; (c) Intact sediment core collection using a piston corer (Photographs by D. Cartwright, RLIA, 2014).

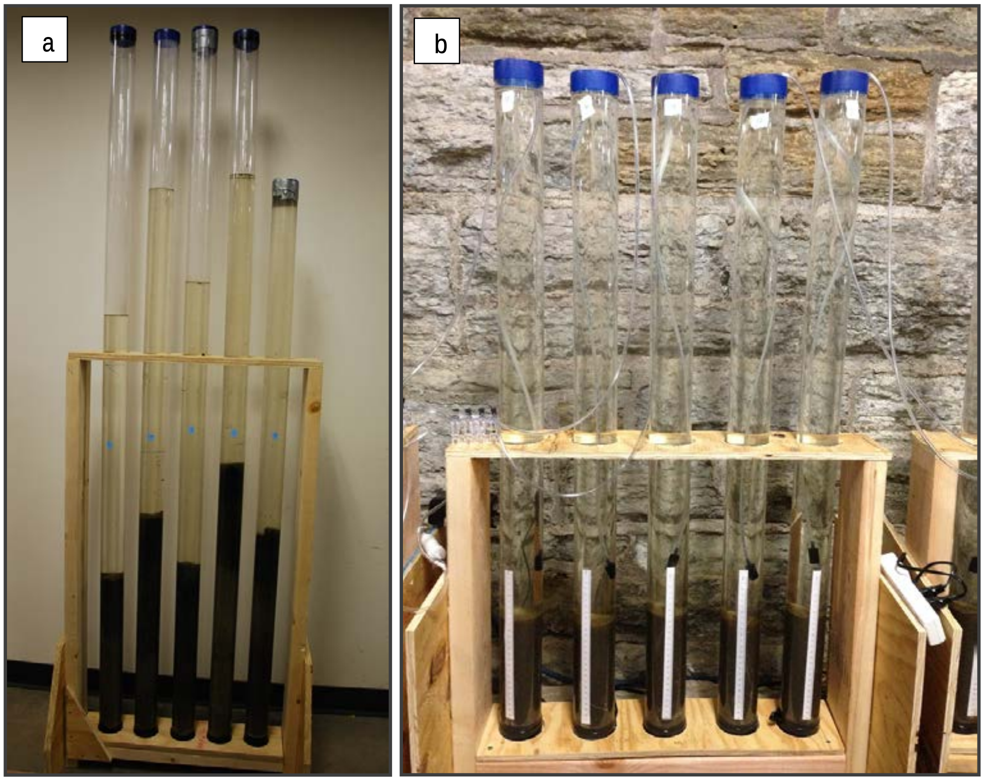
Based on the observations made during the Rush Lake column studies, a different approach was adopted for sampling sediments from Ann Lake in November 2015. Using an Ekman dredge, the top layer (up to ~ 30 cm or 1 ft) of sediment was scooped up from a location in Ann Lake that had mucky sediments and approximately 3.6 m (11 ft) water depth (Figure 3). About 200 L of sediment slurry was dredged and lake water was collected separately in large barrels. The sediment slurry was homogenized in a mortar mixer at the St. Anthony Falls Laboratory (SAFL) and transferred into 19 L (5 gal) buckets. Polycarbonate liner tubes (1 m or 3.3 ft long and 70 mm or 2.75 inch O.D.) were pushed into the sediments such that ~20 cm (~0.66 ft) sediment core was collected and then plugged with end caps. Fifty such cores of homogenized sediments were prepared and allowed to consolidate for two weeks. Periodic measurements of sediment subsidence were taken and no significant depth changes were observed after 10 days. It was expected that homogenizing the sediments prior to setting up the laboratory mesocosm systems would minimize the effects of variation in sediment characteristics on the sediment phosphorus release (as observed in Rush Lake columns, see 'Results' section).

Figure 3. Ann Lake sediment sampling. (a) Sediment sampling location in Ann Lake (source: <maps.google.com>); (b) Collection of lake sediments using an Ekman dredge; (c) Homogenization of dredged sediment in a mortar mixer at SAFL; (d) Sediment coring exercise in the laboratory (Photographs by R. Gabrielson and P. Natarajan, 2015).

Laboratory Column Studies

The water above the sediment in Rush Lake columns was drained, filtered with a 1.2 µm glass fiber filter to remove particulates, and then carefully reintroduced into the columns without causing sediment resuspension. Water collected from Ann Lake was filtered and placed over the sediment after the sediment cores appeared to have consolidated (i.e., after 14 days).

Laboratory mesocosm systems consisting of lake sediments with filtered overlying lake water were then set up for column studies at SAFL (Figure 4). In each column, a porous air stone attached to vinyl tubing was placed in the water column section to serve as bubbler (Figure 4c). The vinyl tubing was connected to manifolds that were either connected to aquarium pumps with an in-line air filter to supply air, or to an ultra-pure grade nitrogen gas cylinder. The dissolved oxygen (DO) status of the water column was regulated by bubbling air (to achieve oxic conditions) or nitrogen gas (to achieve anoxic conditions). Periodic measurements with a DO probe (YSI 58 or YSI ProODO dissolved oxygen meter) indicated that the DO level in the water column was between 0.09 and 0.3 mg/L during N_2 bubbling periods and > 9 mg/L when bubbling air. The air stones were positioned at least 3 cm (1.2 inches) above the sediment surface such that their placement and the gas flow rate did not agitate the sediment during bubbling. The water column was thus fully mixed due to gentle bubbling, which avoided the development of concentration gradient under unmixed condition. The columns were wrapped with aluminum foil to limit exposure to light.



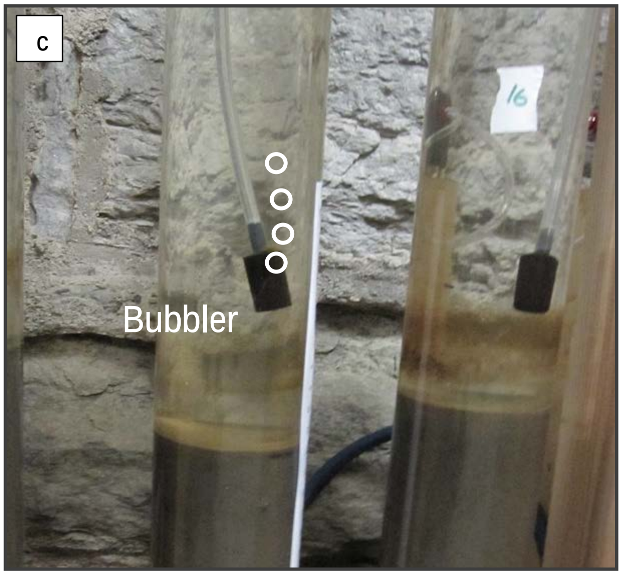


Figure 4. Laboratory mesocosm systems of lake sediments. (a) Intact sediment-water columns collected from Rush Lake; (b) Sediment-water columns of Ann Lake; (c) Bubblers placed in the water column section above sediment to bubble air or nitrogen gas. (Photographs by P. Natarajan, 2015 and 2016).

The overall methodology for the laboratory column studies is presented as a schematic in Figure 5. The entire study was divided into two phases: namely, a pretreatment phase followed by an iron addition phase. Each phase consisted of an oxic period (air bubbling) followed by anoxic period (nitrogen bubbling). In the pretreatment phase, the baseline oxic and anoxic phosphate release potentials of unamended lake sediments were monitored. Application of iron to the sediments was performed right at the beginning of the oxic period of the iron addition phase. One set of columns designated as ‘control’ did not receive iron and was otherwise subject to the same conditions as the iron-dosed columns. The duration of each oxic or anoxic period was at least 30 days but increased as necessary depending on the phosphate flux observations. The objective was to quantify the phosphate release for a given duration but not necessarily wait until steady-state conditions were attained.

The sediment water columns were thus subject to oxic-anoxic-oxic-anoxic cycle during the experimental duration. This is similar to the seasonal stratification and mixing cycle observed in temperate dimictic lakes that result in oxic or anoxic conditions in the hypolimnion.

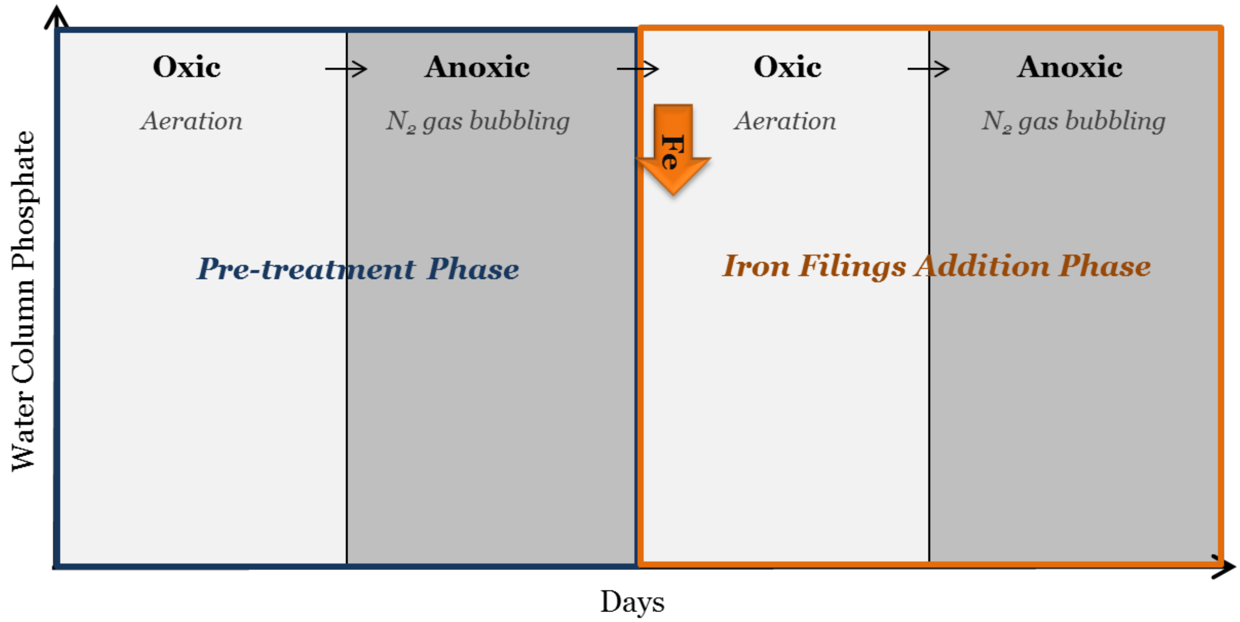


Figure 5. Schematic of experimental approach for the laboratory column studies on Rush Lake and Ann Lake sediments.

The matrix of tests for the Rush Lake and Ann Lake columns is provided in Table 1. The experimental test conditions including DO status of water column, ambient temperature, iron filings (Fe) dose applied, and sulfate level in water columns are provided in the table. The Rush Lake column studies were conducted first (year 1) and minor adjustments were done to the test matrix for the Ann Lake studies (year 2). Five replicates were included for a given set of experimental condition to establish good confidence intervals. The columns set up at 20 °C (68 °F) were kept at SAFL, and the 10 °C (50 °F) columns were kept in the cold room in the Civil Engineering building. The existing sulfate concentrations were ~ 5 mg/L in Rush Lake water and ~11 mg/L in Ann Lake water.

Table 1. Matrix of test conditions for the laboratory column studies on Rush Lake and Ann Lake sediments.

YEAR 1 RUSH LAKE COLUMN STUDIES					
Type	**Water Column Conditions**	**T °C**	**Iron Dose (g iron/cm^2)**	**Sulfate**	**Replicates**
Control	Oxic → Anoxic → Oxic → Anoxic	20 °C	zero	existing	5
Iron (Fe)-dosed	Oxic → Anoxic → Oxic w/ Fe → Anoxic w/ Fe	20 °C	• Set 1: Two-step dosing 0.01 g/cm^2 → 0.1 g/cm^2 • Set 2: Three-step dosing 0.01 → 0.1 → 1 g/cm^2	existing	5 each (10 total)
Control	Oxic → Anoxic → Oxic → Anoxic	10 °C	zero	existing	5
Iron-dosed	Oxic → Anoxic → Oxic w/ Fe → Anoxic w/ Fe	10 °C	Three-step dosing 0.01 → 0.1 →1 g/cm^2	existing	5
Anoxic iron addition	Oxic → Anoxic → Anoxic w/ Fe	20 °C	Three-step dosing 0.01 → 0.1 → 1 g/cm^2	existing	5 each
YEAR 2 ANN LAKE COLUMN STUDIES					
Type	**Water Column Conditions**	**T° C**	**Iron Dose (g iron/cm^2)**	**Sulfate**	**Replicates**
Control	Oxic → Anoxic → Oxic → Anoxic	20° C	zero	existing	5
Iron-dosed	Oxic → Anoxic → Oxic w/ Fe → Anoxic w/ Fe	20° C	• Set 1: 0.01 g/cm^2 • Set 2: 0.05 g/cm^2 • Set 3: 0.1 g/cm^2	existing	5 each (15 total)
Control	Oxic → Anoxic → Oxic → Anoxic	10° C	zero	existing	5
Iron-dosed	Oxic → Anoxic → Oxic w/ Fe → Anoxic w/ Fe	10° C	0.05 g/cm^2	existing	5
Anoxic iron addition	Oxic → Anoxic → Anoxic w/ Fe	20° C	Three-step dosing 0.01 → 0.05 → 0.1 g/cm^2	existing	5
High sulfate-Control	Oxic w/high SO_4 → Anoxic → Anoxic	20° C	zero	100 mg/L (initial)	5
High sulfate-Iron-dosed	Oxic w/high SO_4 → Anoxic → Anoxic w/ Fe	20° C	Three-step dosing 0.01 → 0.05 → 0.1 g/cm^2	100 mg/L (initial)	5

Four iron doses (defined as g iron per sq. cm of sediment surface area) were tested - 0.01 g/cm^2 (low dose), 0.05 g/cm^2 (medium dose), 0.1 g/cm^2 (high dose) and 1 g/cm^2 (very high dose). While the low, high and very high iron doses were tested in the Rush Lake columns, the Ann Lake columns received the low, medium, and high doses of iron. In the Rush Lake studies, iron filings quantities were added in a stepwise manner during the iron addition phase. For instance, the very high iron-dosed columns first received 0.01 g/cm^2, then more iron was added to attain the high dose of 0.1 g/cm^2, and finally the iron quantity was increased to the very high dose level of 1 g/cm^2; thus, that the cumulative iron dose was equal to 1 g/cm^2 at the end of the oxic period. In the Ann Lake studies, iron filings addition was done as a single dose of low, medium, or high dose in the respective designated set of columns. Iron filings were added at the top of the water column and allowed to settle on the sediment surface by gravity. Specifications of the iron filings material are provided in Table 2 (see 'iron filings 1-IL'). This iron sample has been previously used in the iron-enhanced sand filtration technology studies (Erickson et al. 2012).

The concentration of phosphate (SRP) in the water column was monitored over time. Mass of phosphate (mg) was calculated by multiplying the phosphate concentration (mg/L) and the water column volume (L). Water sampling was done on a biweekly basis. A 15 mL water sample was drawn from approximately the center of the mixed water column using an acid-washed syringe attached to Tygon tubing. The sample was then filtered through a 0.45 micron Millipore membrane filter and analyzed for SRP in a Lachat QuickChem 8500 Series FIA system using ascorbic acid (Standard Methods 4500 PG, APHA/AWWA/WPCF 1995). On most occasions, SRP analysis was performed on the day of sample collection. Otherwise, the water samples were preserved by freezing until analysis.

The effect of high sulfate in the water column on the phosphate flux from sediment and iron dosing was tested in the Ann lake columns (Table 1). Ann lake water contained around 11 mg/L sulfate. The water column was spiked with a concentrated sulfate solution, prepared by dissolving sodium sulfate (Na_2SO_4) in deionized water, to achieve the desired high sulfate concentration of 100 mg/L. The 100 mg/L level is considered high for freshwater systems and was chosen based on the range of sulfate concentrations observed in Minnesota lakes (Caraco et al. 1989; Roden and Edmonds 1997; MPCA 2014). The sulfate level in the water column was monitored as a proxy for production of sulfide due to consumption of sulfate throughout the experimental duration. Because the sulfide formed can release as hydrogen sulfide gas or form solids (such as iron sulfide), measurement of sulfate was deemed appropriate for the column studies, as has been done in other studies (Caraco et al. 1993; Roden and Edmonds 1997). Sulfate concentrations were determined in 0.45 micron membrane-filtered water samples on approximately biweekly basis, in a Metrohm 930 Compact IC Flex ion chromatography using 3.2 mM sodium carbonate - 1 mM bicarbonate eluent.

Water column pH was also measured on the sample collection days, using a Jenco Model 60 pH meter. The dissolved oxygen level in the water column was periodically checked using a DO probe, particularly during the anoxic periods to ensure low DO (< 0.3 mg/L) was maintained by the nitrogen gas bubbling.

Sediment Extrusion and Analysis

At the end of laboratory column experiments, the sediment cores were extruded from the columns using a standard incremental core extrusion apparatus (Limnological Research Center, University of Minnesota) (Figure 6). At least two out of the five replicate columns in the iron-amended and control (no amendment) column sets were extruded. For the Rush Lake sediment cores, the upper 0 - 5 cm sediment was sectioned at 0.5 cm intervals, and the 5 - 10 cm sediment was sectioned at 1 cm intervals. The upper 10 cm sediment in Ann Lake columns was sectioned into 1-cm slices. Most of the iron filings visible on the sediment surface were scraped off before sectioning the sediment in the iron-dosed columns. One column each belonging to the control and iron-dosed column sets was held under oxic conditions for approximately 30 days after the conclusion of the iron treatment phase. These columns were also extruded for sediment analysis.

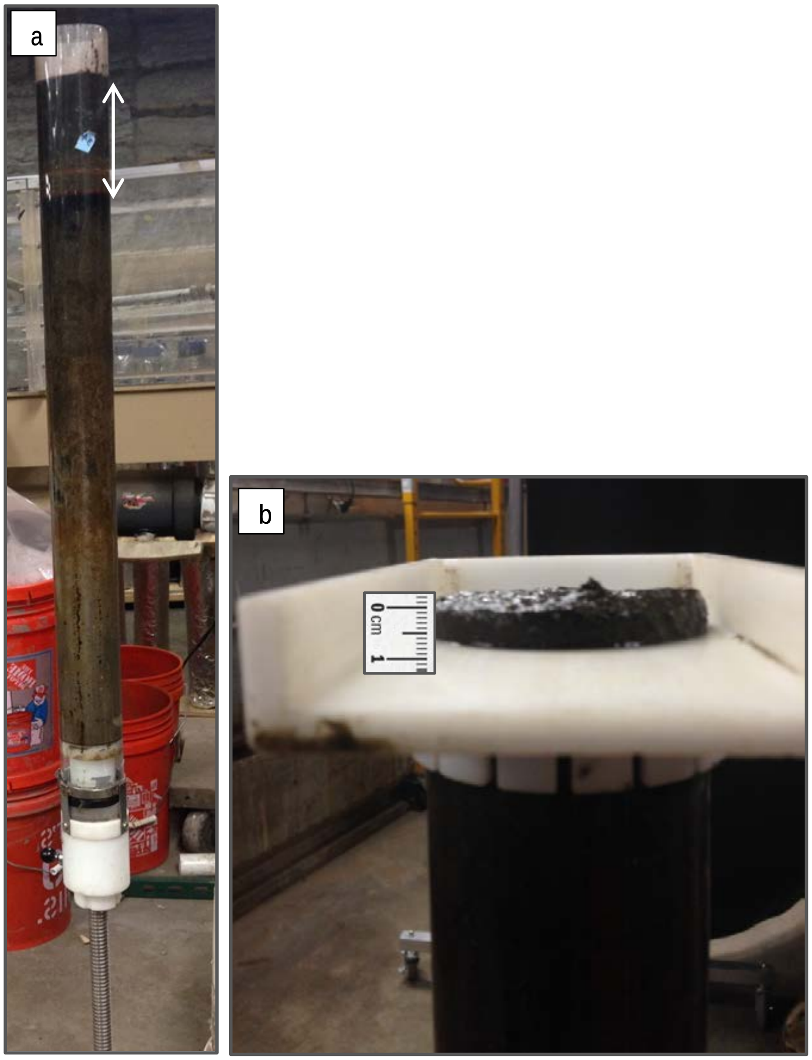


Figure 6. Sediment extrusion from the laboratory columns. (a) Extrusion of a Rush Lake sediment core. (b) 0.5-cm slice of extruded sediment. (Photographs by P. Natarajan, 2016).

The Rush Lake sediment sections were centrifuged at 2500 RPM for 10 minutes to separate out the porewater. The porewater was then filtered through a 0.45 micron membrane filter and analyzed for soluble reactive phosphorus (SRP) concentrations in a Lachat autoanalyzer.

The Ann Lake sediments were subject to sequential phosphorus extraction to quantify the forms of phosphorus in the sediment [method following St. Croix Watershed Research Station's manual on sequential extraction procedure for phosphorus in lake sediments (*personal communication with R. Dietz and M. Natarajan*; method adapted from Hieltjes and Lijklema 1980; Nürnberg 1988; Psenner and Puckso 1988; Kopacek et al. 2005; James 2011). Wet sediments from the top 10 cm depth were combined as 0-1, 1-2, 2-3, 3-4, 4-5, 5-7, 7-10 cm and homogenized by gentle mixing. The sediments were analyzed for loosely-bound P (pore water and $CaCO_3$-adsorbed) (using 1 M ammonium chloride), iron-bound P (using 0.11 M sodium bicarbonate and 0.1 M sodium dithionite), aluminum-bound P (Al-P) (using 0.1 M sodium hydroxide), mineral-bound P (using 2 N hydrochloric acid), and residual P (presumed organic) (using 30% hydrogen peroxide and 2 N HCl). The iron-bound P extraction step was repeated four times due to the increased iron content in the sediments by iron filings addition (Psenner and Puckso 1988). The four-time extraction was performed on the unamended (control) sediments as well for consistency. The P mass (mg/g) extracted in each step was summed to obtain the total iron-bound fraction in the sediment sample. The labile organic P fraction was determined by subtracting the Al-bound P from the nonreactive NaOH-extractable P (Al-P + labile organic P determined by persulfate digestion of the NaOH extract). The extracts from each step were centrifuged at 3500 RPM for 10 minutes and analyzed for SRP concentrations in a Lachat autoanalyzer. The extracts from iron-bound P step were bubbled vigorously with oxygen for 30 minutes before SRP analysis.

Water content (overnight drying at 105 °C) and organic matter content (loss on ignition at 550 °C) determinations were also performed on 2 - 3 g of sediment samples. The dry density (dry mass per volume of fresh sediment) was calculated from moisture content and fixed densities for organic and non-carbonate inorganic fractions (Engstrom 2005).

X-ray diffraction (XRD) (scanning angle of 10 - 90° with 100 s-dwell per step at a step size of 0.0167 degrees 2-theta) was used to determine the mineralogy of the iron layer and sediment sections from select Rush Lake columns. The XRD measurements were performed using a PANalytical X'Pert PRO X-ray diffractometer equipped with a cobalt source (1.7909 Angstroms) and an X'Celerator detector in the Department of Chemistry, University of Minnesota. The iron samples extracted from anoxic sediment columns were dried under N_2-atmosphere in a glove compartment. The sediment samples were triple-rinsed with deionized water, air-dried, crushed, homogenized and sieved prior to analysis. The mineral composition in the samples was, however, not quantified.

Data Analysis

The amount of P in the overlying water did not necessarily reach equilibrium and appeared to slowly increase (or decrease) during a given incubation time. Rates of phosphate release from the sediment (mg/m^2/day) were calculated as the linear change in the mass of phosphate (mg) in the overlying water column over the incubation period [where, mass = concentration (mg/L) × water column volume (L)]; the mass of phosphate was divided by the sediment surface area (same as the core liner area, m^2). P mass data plotted over time for the replicate columns mostly followed linear trends. Regression analysis was used to estimate the P release rate over the linear portion of the data. Confidence intervals (CI; 67%) on the mean for replicates were calculated to represent the variation in the data; 67% CI were used given that the number of replicates used for measurements was only five.

Results and Discussion

Batch Studies

Batch studies on phosphate-sorption were conducted with ten iron materials, six of which are zero-valent cast iron filings or shavings, three are magnetite-rich iron powders, and one silicate-rich iron material. The specifications of the iron materials, as per manufacturer material specification data sheets, are provided in Table 2. The mineralogy of selected samples (iron filings 1-IL, iron powder 1-MN, iron powder 2-MN, iron powder 3-MN, iron tailings-MN) determined by X-ray diffraction are included in Table 2. The manufacturer-specified concentrations of toxic metals such as copper, lead, chromium, nickel, mercury, are very low or below detection in the iron samples tested.

Table 2. Specifications of the iron materials tested in the batch sorption studies.

Material name	Sample photograph	Supplier location	Iron content	Particle size	Type/ Mineral composition	Cost (w/o shipping)
Iron filings 1-IL		IL	90%	0.15 - 2.36 mm	Cast iron/Ferrite, magnetite, hematite, silica	$0.40/lb
Iron filings 2-MI		MI	90%	0.074 – 1.1 mm	Cast iron	$0.41/lb
Iron filings 3-MI		MI	90%	0.10 – 2.1 mm	Cast iron	$0.41/lb
Iron filings 4-NJ		NJ	~95%	~0.044 mm	Cast iron (ZVI reactive iron)	$1.21/lb
Iron filings 5-NJ		NJ	~95%	~0.297 mm	Cast iron (ZVI reactive iron)	$1.03/lb
Iron filings 6-NJ		NJ	~95%	0.015 - 0.5 mm	Cast iron (ZVI reactive iron)	$0.82/lb
Iron powder 1-MN		MN	56%	~0.036 mm	Taconite pellets/ Magnetite, hematite, silica	$0.25/lb
Iron powder 2-MN		MN	89%	N/A	Finishing from castings/ Magnetite, silica	n/a
Iron powder 3-MN		MN	69%	N/A	Magnetite rock/ Magnetite, silica	n/a
Iron tailings-MN		MN		0.074 - 4.76 mm	Taconite tailings byproduct/ silica, hematite, minnesotaite, geothite	n/a

n/a = not available

Results of the batch experiments are shown in Figure 7 and Table 3. The six iron filings materials reduced the dissolved phosphorus (phosphate) in the solution through the test duration. From 67 to 98% of the phosphate was removed by iron filings within a 24-hour contact period, providing removals to below detection limits. The finer gradations of iron filings (iron filings 4-NJ, for example) were highly efficient in removing phosphate due to their larger particle surface area available for surface adsorption. On the other hand, all three iron powders and iron tailings exhibited relatively poor phosphorus removal capabilities, likely due to their mineral composition and surface properties; the phosphate in the batch bottles decreased by only 8.7 to 12% at the end of 48 hours. Two lower quantities of iron (corresponding to the 'medium' and 'low' dosages) were also tested for iron filings 1-IL and iron powder 2-MN (data not shown in Figure 7). Unsurprisingly, the two lower doses of iron powder 2-MN did not impact the phosphate in solution in the 48-hour period. Iron filings-IL provided 18% and 52% reduction in phosphate for the low and medium quantities added, respectively.

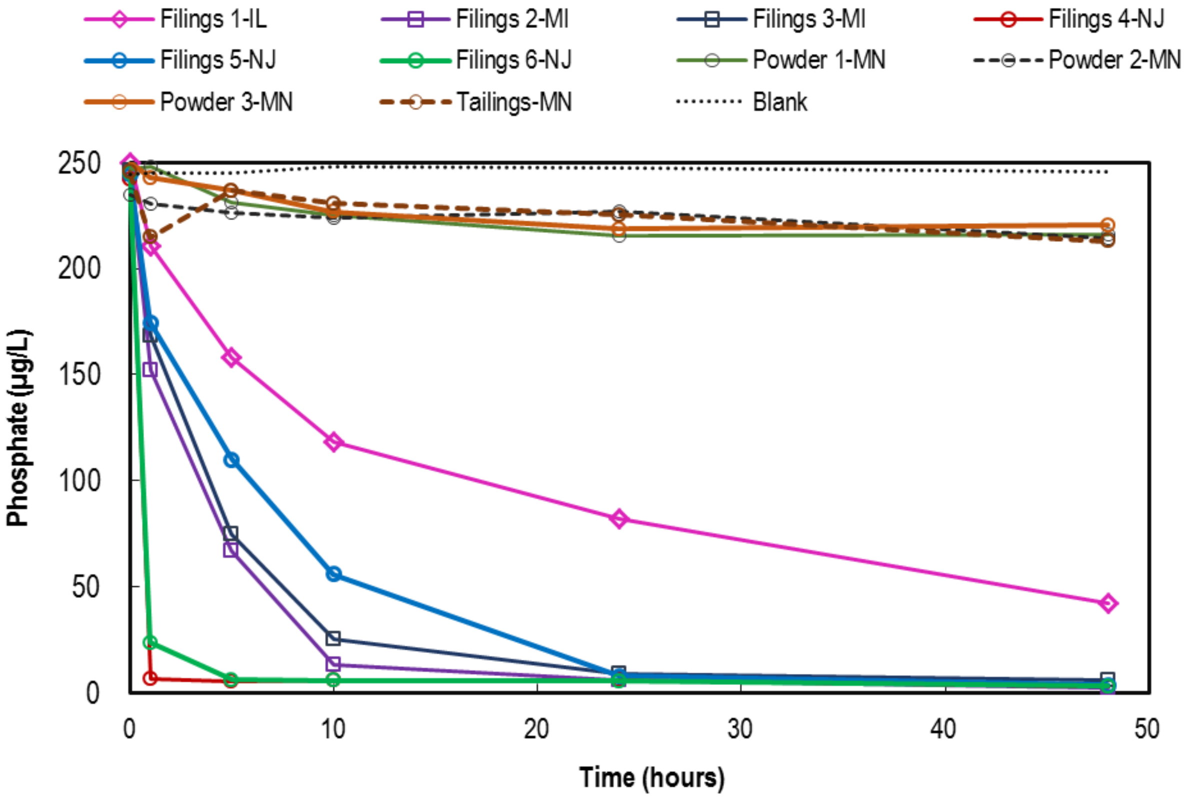


Figure 7. Dissolved phosphorus (phosphate) concentrations in the solution during the batch experiments on ten iron materials. (0.343 g of iron was placed in 400 mL of 250 µg/L standard phosphate solution at time = 0 hour).

Table 3. Dissolved phosphorus (phosphate or P) removal by different iron materials during batch experiments.

Iron Material	Phosphate Mass Reduction	mg P sorbed/g Fe
Iron filings 1- IL	24-h: 67% 48-h: 83%	24-h: 0.195 48-h: 0.242
Iron filings 2-MI	24-h: 98% 48-h: 99%	24-h: 0.278 48-h: 0.282
Iron filings 3-MI	24-h: 96% 48-h: 97%	24-h: 0.277 48-h: 0.280
Iron filings 4-NJ	24-h: 97% 48-h: 99%	24-h: 0.275 48-h: 0.278
Iron filings 5-NJ	24-h: 97% 48-h: 99%	24-h: 0.276 48-hr: 0.281
Iron filings 6-NJ	24-h: 98% 48-h: 99%	24-h: 0.279 48-h: 0.282
Iron powder 1-MN	24-h: 12% 48-h: 12%	24-h: 0.036 48-h: 0.036
Iron powder 2-MN	24-h: 3.4% 48-h: 8.7%	24-h: 0.0094 48-h: 0.0239
Iron powder 3-MN	24-h: 12% 48-h: 12%	24-h: 0.037 48-h: 0.036
Iron tailings-MN	24-h: 8.2% 48-hr: 13%	24-h: 0.024 48-h: 0.038

The batch studies indicate that, in general, zero-valent iron filings have the capacity to effectively remove dissolved phosphorus and are potential materials for treating water containing phosphorus. The magnetite-based iron materials tested (iron powder and iron tailings) were found to be unsuitable for phosphorus treatment.

Rush Lake Laboratory Column Studies (Year 1)

Twentyfive Rush Lake columns were set up at 20 °C at SAFL and ten columns were set up at 10 °C in the cold room of the Civil Engineering Building. At the end of the pretreatment phase, the columns were divided into sets of five replicate columns to serve as control (no iron addition) and iron-dosed columns. As will be discussed later, the pretreatment phosphate (P) release data was used as the basis for the column assignments. Data plots showing water column P mass measurements (P concentration × water column volume) in individual replicate columns through the experimental duration are provided in Appendix A.

Pretreatment Phase: Oxic and Anoxic Sediment P Release at 20 °C

In general, under oxic conditions at 20 °C, increase in phosphate (P) mass in the overlying water column was very low. The P concentration and mass in the water column decreased by a small extent due to aeration in several columns. Oxic P release between 0.054 and 1.69 mg/m^2/day was observed in some of the columns, possibly due to mineralization of labile organic phosphorus in the sediments (Jensen and Andersen 1992), but the water column P concentrations were still < 40 µg/L. Overall, the mean sediment P flux was 0.149 mg/m^2/day (± 0.298 67% CI), and the mean water column P concentration was 23 µg/L for the 25 columns at the end of the 27-day oxic period. The average water column pH was 8.22 (±0.0426 Std Dev).

The columns were then switched to anoxic incubation, and the P mass in the overlying water began to increase due to release of P from the sediments. The water column P concentrations were between 375 and 800 µg/L in the columns that exhibited relatively high P release. Negligible P mass accumulation and concentrations below 20 µg/L were observed in some columns, even under anoxic conditions. The dissolved oxygen levels were verified to be less than < 0.3 mg/L in these columns. Figure 8, showing the P mass in the overlying water in 15 columns, depicts the variable anoxic P release from Rush Lake sediments. Considering data from 25 columns, the P mass increased approximately linearly at 3.22 mg/m^2/day (± 0.714 67% CI) on average over the 49-day anoxic period. This release rate is within the lower 25% quartile of data for other Minnesota lakes (James and Bischoff 2016), and is in the lower range of data reported in international studies (Holden and Armstrong 1980; Nürnberg 1988; Jensen and Andersen 1992; James and Bischoff 2016). The average pH of the water column was 8.35 (± 0.0786 Std Dev); the small increase in pH under anoxic period could be an artifact due to nitrogen bubbling.

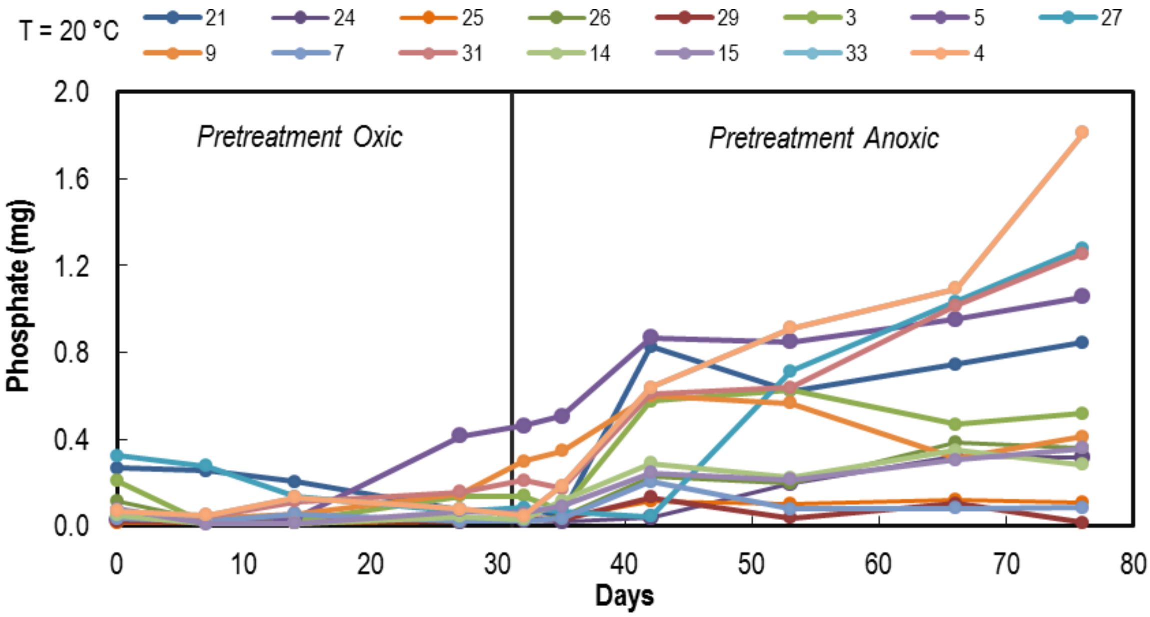


Figure 8. Water column phosphate mass measured during the pretreatment phase in the Rush Lake columns at 20 °C. (Note: Legend shows the number assigned to label a column).

It is hypothesized that natural spatial variation in the characteristics of the lake sediments is the most likely reason for the variable amount and rate of anoxic P release. High variability in phosphorus release rates owing to natural variation, amount of redox-P, amount of sediment organic matter, sediment composition (calcareous vs. noncalcareous), and artifacts during sampling and incubation have been observed (Holden and Armstrong 1980; Nürnberg 1988; Jensen and Andersen 1992, James 2011). Visual examination of the sediments indicated that the top layer (top 2 to 4 cm) of some Rush Lake sediment cores were rich in organic matter (i.e., muckier) than others appearing more sandy and lighter in color; low anoxic P release were measured in less mucky sediments (Figure 9). The presence of inherent variability in sediment characteristics also highlights the importance of including several lake sediment columns in studies such as this project to assess the internal phosphorus release possible from the sediments.

Figure 9. Intact sediment cores collected from Rush Lake exhibiting natural variation in sediment characteristics. (Note: Sediments in columns labeled ‘b’ and ‘e’ released less P under anoxic conditions compared to other three columns during the mesocosm studies).

Pretreatment Phase: Oxic and Anoxic Sediment P Release at 10 °C

Temperature affects microbial activity in the sediments and hence the rate and magnitude of P release including mineralization of organic-bound phosphorus into the sediment porewater (Bostrom et al. 1982; Jensen and Andersen 1992). The impact of temperature on P release from Rush Lake sediments was investigated by comparing the data from the 10 °C and 20 °C columns.

Figure 10 shows the pretreatment phase oxic and anoxic behavior of the Rush Lake columns kept at 10 °C. During the initial oxic period, P mass accumulation did not occur in most columns and the P concentration in the water was generally low (< 20 µg/L). A very low oxic P release was observed in one column. Gradual P release from the sediments was measured soon after the water column was turned anoxic. Again, as observed in the 20 °C columns, the anoxic P release rates were variable among the 10 °C columns. Out of the 10 columns, sediments in only four columns exhibited significant anoxic P release. The water column concentrations were between 20 and 192 µg/L by the end of the 100-day anoxic duration. The variability in P release rates is attributed to sediment characteristics and the low incubation temperature. Mean pH of the water column was around 8.07 (± 0.0399 Std Dev) and 8.50 (± 0.0778 Std Dev) during the oxic and anoxic periods, respectively.

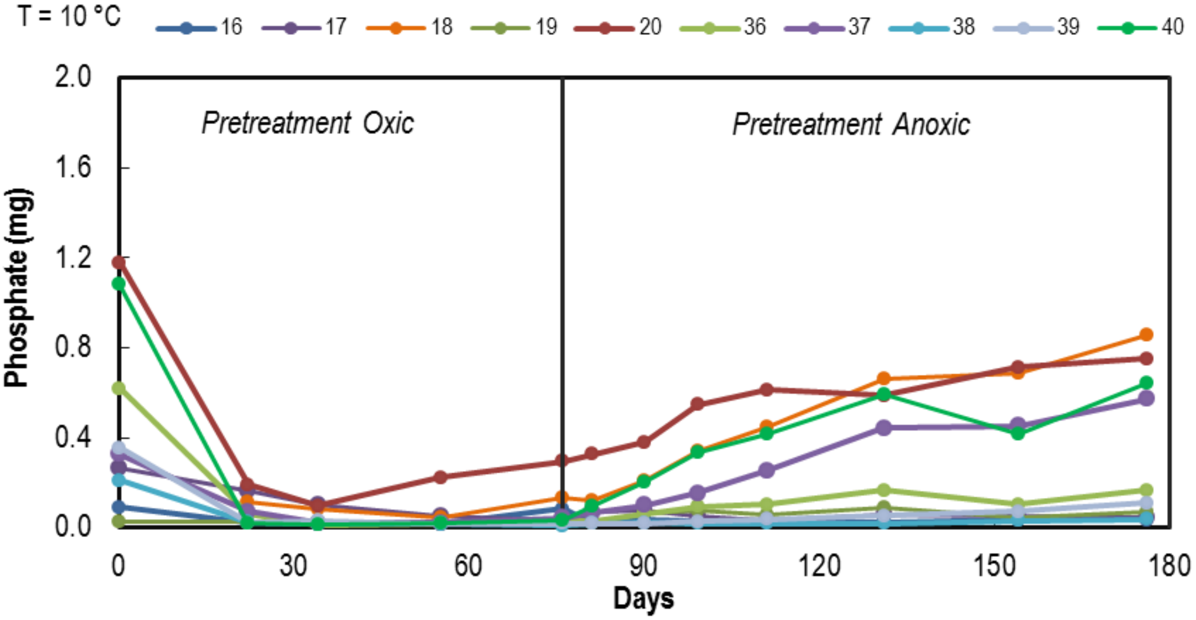


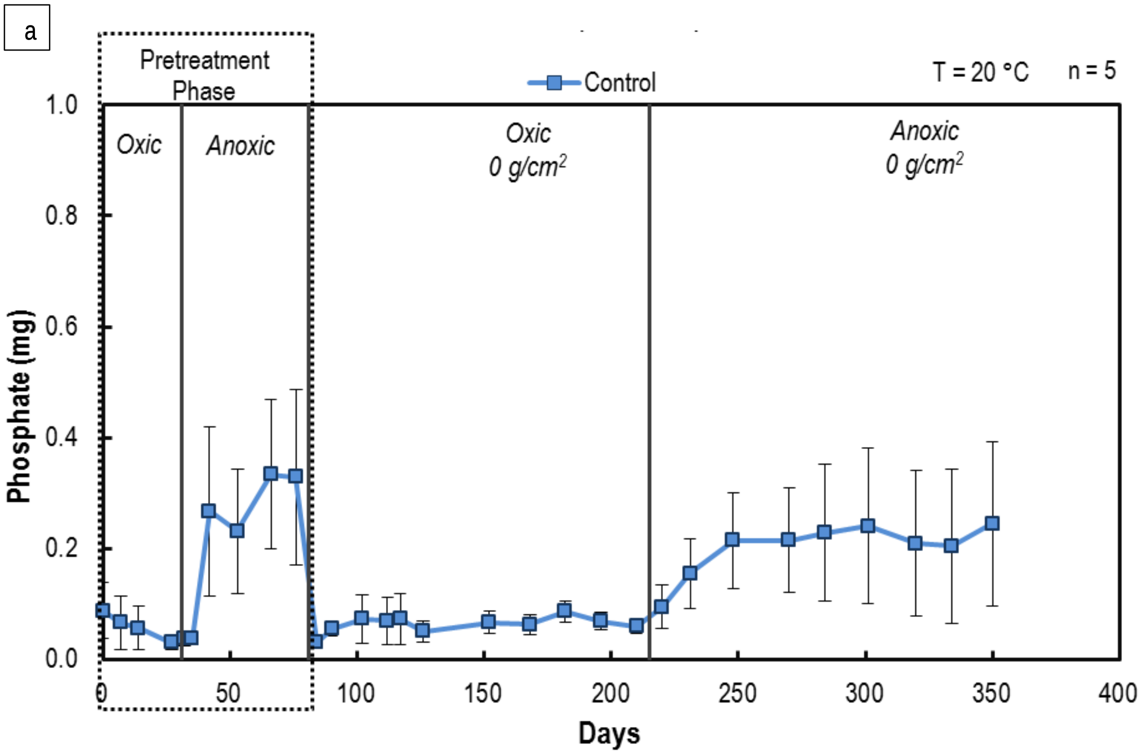
Figure 10. Water column phosphate measured in the Rush Lake columns at 10 °C during the pretreatment phase. (Note: Legend shows the number assigned to label a column).

The overall anoxic sediment P release was lower and slower at 10 °C, resulting in lower P mass added to the water column when compared to at 20 °C (Figure 8 and Figure 10). The average P release rate of 0.714 mg/m^2/day (± 0.289 67% CI) at 10 °C is almost one-fifth the release rate measured at 20 °C. The temperature dependence implies that internal phosphorus flux from lake sediments would vary seasonally and impact deep and shallow lakes differently. Fluctuations in internal phosphorus loading in lakes due to strong correlation between water temperature (0.5 to 21 °C) and seasonal variation in phosphate release rates have been reported (Jensen and Andersen 1992).

Iron Addition Phase

At the end of the pretreatment phase, the 20 °C columns were divided into control (0 g/cm^2), 0.1 g/cm^2 iron-dosed and 1 g/cm^2 iron-dosed columns, with each set comprised of five replicates. The 10 °C columns were divided into control and 1 g/cm^2 iron-dosed columns. The replicates were assigned such that each set included a mix of columns exhibiting high and low anoxic P release per the pretreatment phase data. As a result, the mean release rate for five replicates in a set of columns produced higher standard deviations.

The water column conditions were switched to oxic and the addition of iron filings was performed, except in the control columns. The mean phosphate mass accumulated in the water column over the entire experimental period for the control, 0.1 g/cm^2 iron-dosed, and 1 g /cm^2 iron-dosed columns kept at 20 °C are shown in Figure 11 (replicate measurements are presented in Appendix A). In each plot, the pretreatment phase is marked and the following oxic and anoxic periods fall under the iron addition phase. As detailed in the methods section, step additions of iron filings (0.01, 0.1 and 1 g/cm^2 doses) performed under oxic conditions are also marked in the plots. Error bars represent 67% confidence interval (CI) on the mean. Table 4 summarizes the P release rate data for the iron addition phase for all column sets.



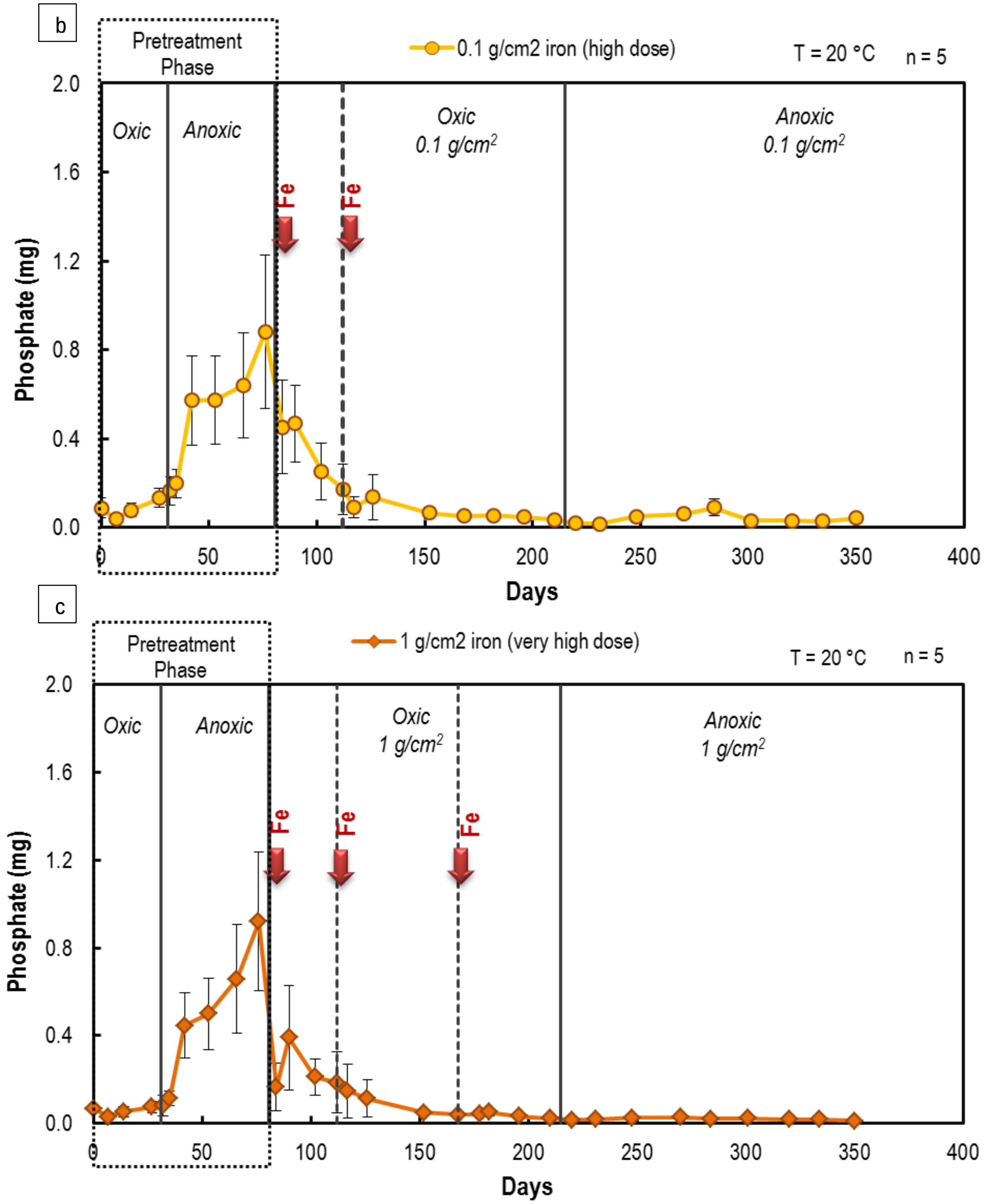


Figure 11. Mean water column phosphate measured during the pretreatment and iron addition phases in the Rush Lake sediment columns at 20 °C. The error bars represent 67% CI on the mean for five replicates. Dark solid line marks the end of an oxic or anoxic period. Red arrows and dashed lines mark the iron filings (Fe) addition step. No iron was added to the control columns. Note difference in Y-axis scale between control (a) and iron-dosed column plots (b & c).

Table 4. Summary of phosphate (P) release rates during the iron-addition phase in the Rush Lake sediment columns at 20 °C and 10 °C. Values provided are mean (± 67% CI) for five replicates.

	20 °C P release rate (mg/m^2/day)		10 °C P release rate (mg/m^2/day)	
Iron filings dose	**Oxic**	**Anoxic**	**Oxic**	**Anoxic**
0 g/cm^2 (control)	0.0413 (± 0.0597)	0.273 (± 0.312)	-0.179 (± 0.235)	1.82 (± 1.29)
0.01 g/cm^2 (low dose)	-3.61 (± 1.77)	n/a	-0.326 (± 0.206)	n/a
0.1 g/cm^2 (high dose)	-0.502 (± 0.417)	-0.00911 (± 0.0109)	-0.442 (± 0.296)	n/a
1 g/cm^2 (very high dose)	-0.192 (± 0.0486)	-0.0206 (± 0.00785)	-0.140 (± 0.120)	-0.131 (± 0.0536)

In the 20 °C columns, once the first 0.01 g iron/cm^2 (low dose) was added, the water column P concentrations decreased from 307 to 49 µg/L over the course of 31 days. The next step addition to 0.1 g/cm^2 iron (high dose) rapidly decreased P mass in the water and P concentration to ~14 µg/L over 56 days. The dosage was increased to 1 g/cm^2 (very high dose) in one set of columns which kept the water column concentrations below 9 µg/L. The columns with high iron dose also maintained 10 µg/L P concentrations. Through the oxic period, water column P mass likely decreased due to the adsorption of P to ferric oxides (and oxyhydroxides) in the sediments (Figure 11 and Table 4; Figure 13).

In the control columns (no iron added or unamended), P concentration decreased from 86 to 16 µg/L through the 129-day oxic period, suggesting that aeration-only was able to reduce P release and lower the P levels in the oxic overlying water. However, it must be noted that at the beginning of the oxic treatment phase, the average mass of P in the overlying water was lowest in the control set (0.33 mg) when compared to the iron-dosed columns (0.90 mg) (Figure 11). This means the extent to which aeration-only can control sediment P release could depend on the P level in the water.

The effect of iron filings application was most evident during the following anoxic period (Figure 11 and Table 4). As soon as the water column turned anoxic, the control (unamended) sediments began to release P at a mean rate of 0.273 mg/m^2/day (± 0.313 67% CI), although this rate was much lower than the 1.96 mg/m^2/day (± 0.927 67% CI) pretreatment anoxic baseline. It is possible that a lack of anaerobic bacterial population in the sediments, and the quite variable release rates in the five replicates lowered the average P release rate.

The sediments amended with 0.1 g iron/cm^2 produced a small initial P release, but the concentration dropped back to < 9 µg/L phosphate over the course of the anoxic period. In the sediments with 1 g iron/cm^2, anoxic sediment P release was not apparent and the net phosphate in the overlying water consistently remained very low throughout the anoxic period. The negative anoxic P release rate in the iron-dosed columns indicates P loss from the water column into the sediments (Table 4). The application of iron filings to sediments not only controlled P diffusion from the sediments but also lowered the water column P level, irrespective of the dissolved oxygen status of the water column.

The positive impact of iron filings addition was observed at 10 °C as well (Figure 12 and Table 4). P accumulated in the water column due to the previous anoxic conditions began decreasing under oxic conditions; the decrease was more consistent in the iron-amended sediments than the control due to the presence of excess iron in the amended sediments. The three-step addition of iron filings to the final 1 g/cm^2 dose controlled P release under oxic conditions and kept phosphate levels to below 4 µg/L. In the following anoxic phase, unlike the control columns, anoxic P release was not evident from the iron-amended sediments.

Water column pH was not affected by iron addition; the mean pH was 8.24 (± 0.0598 Std Dev) in the iron-dosed columns and 8.22 (± 0.0685 Std Dev) in the control columns at 20 °C; and the 10 °C columns had similar mean pH of 8.03 (± 0.101 Std Dev) in the iron-dosed columns and 8.02 (± 0.131 Std Dev) in the control columns.

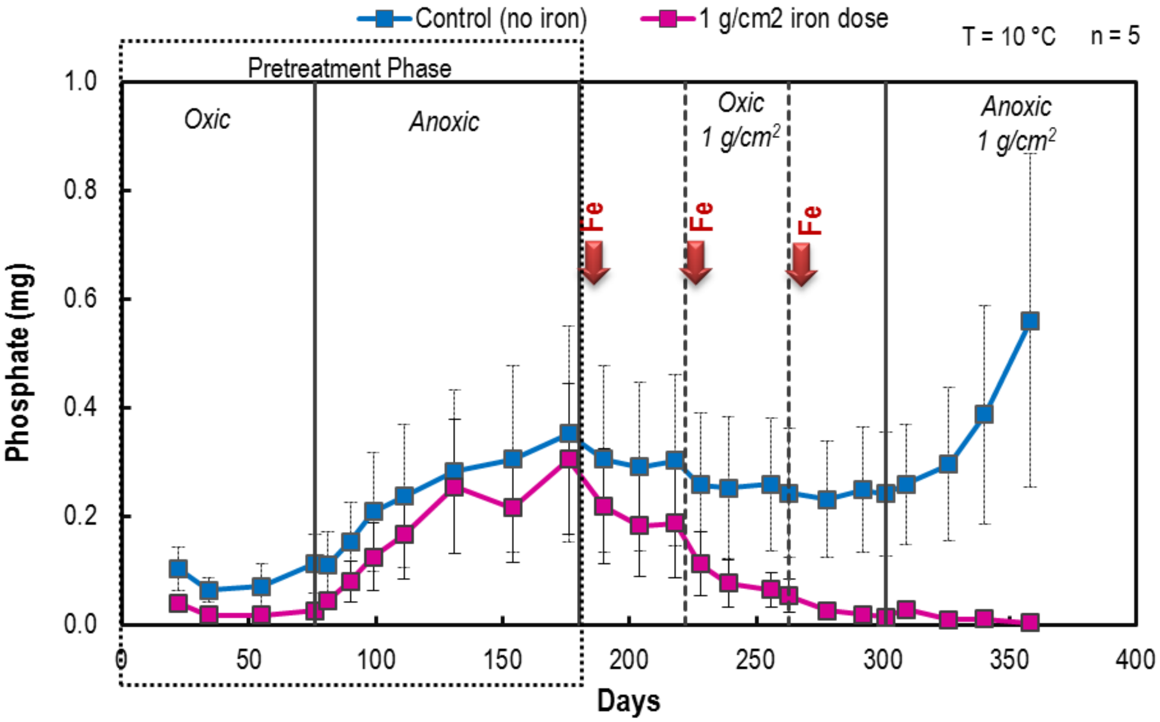


Figure 12. Mean water column phosphate measured during the pretreatment and iron addition phases in the Rush Lake sediment columns at 10 °C. The error bars represent 67% CI on the mean for five replicates. Dark solid line marks the end of an oxic or anoxic period. Red arrows and dashed lines indicate the iron filings (Fe) addition step. No iron was added to the control columns.

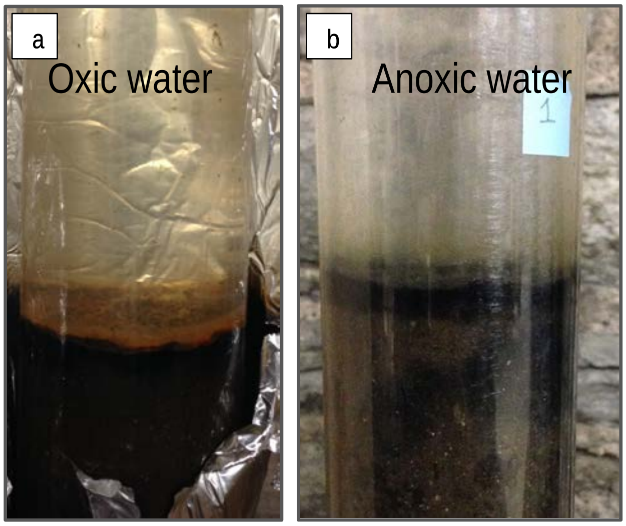


Figure 13. Rush Lake sediment surface amended with iron filings depicting (a) oxidized iron layer under oxic conditions and (b) reduced iron layer under anoxic conditions. (Note: photographs shown are of two different columns).

The mesocosm studies on iron addition to Rush Lake sediments demonstrate that placing sufficient iron filings (at least 0.1 g iron/cm^2) suppresses the release of P from anoxic sediments. Under oxic conditions, oxidation of iron filings to ferric oxides (and hydroxides) provides surface adsorption sites to strongly bind phosphorus in the water (Figure 13). Once conditions turn anoxic, Fe(III) could be converted to gel-like Fe(II) hydroxides that have an increased surface area exposed to sorb phosphate (Patrick and Khalid 1974; Roden and Edmonds 1997). Phosphate in the water column and that available in the sediment porewater is removed by co-precipitation with Fe(II) released from reduction of iron filings to form Fe(II)-phosphate minerals (Kleeberg et al. 2012; Kleeberg et al. 2013). It is hypothesized that these mechanisms, enhanced by iron addition, are together responsible for the observed negative P flux to the iron-dosed lake sediments during the anoxic phase. Subsequent introduction of aerated conditions (i.e., lake overturn) will cause oxidation of free Fe(II) and continue to remove available P.

Timing of Iron Application: Iron Addition Under Oxic Vs. Anoxic Conditions

The oxic-anoxic-oxic-anoxic experimental cycle adopted in the column studies mimics a dimictic lake transition from spring to summer to fall to winter. When iron filings were placed over the sediment under oxic conditions, which corresponds to treating a lake in Spring or Fall, sediment P release was reduced during that oxic phase and in the following anoxic period as well (Figure 11). Both 0.1 g/cm^2 and 1 g/cm^2 iron filings doses were effective to the same extent. Experiments were conducted to test if iron filings application under anoxic conditions, say in late summer, could have similar effects on P release. In other words, the objectives were to determine if the timing (or season) of treating lake sediments with iron filings is important, and if the iron dosing requirements change depending on the season.

Four Rush Lake sediment columns were selected at the end of the pretreatment anoxic phase to study the impact of anoxic iron dosing. The water column contained only ~10 µg/L phosphate due to very low sediment P release under anoxic conditions. Therefore, the water was spiked with concentrated phosphate solution and monitored for three weeks until the overlying water contained ~ 0.92 mg phosphate (~200 µg/L P) in all the columns. Then, 0.01 g/cm^2 iron filings (low dose) was first added to the sediments under anoxic conditions (Figure 14). The phosphate mass in the water column gradually decreased at the rate of 1.45 mg/m^2/day but the average water column concentration was still 138 µg/L by the end of 56 days. Increasing the iron filings amount to 0.1 g/cm^2 dropped the P mass and concentration in the water column further (~48 µg/L P) over the next 52 days. The next step addition of iron filings to the 1 g/cm^2 dose decreased the P mass further and the water column P reduced to less than 17 µg/L by the end of the 60-day anoxic duration. Water pH varied between 8.2 and 8.9 through the anoxic period.

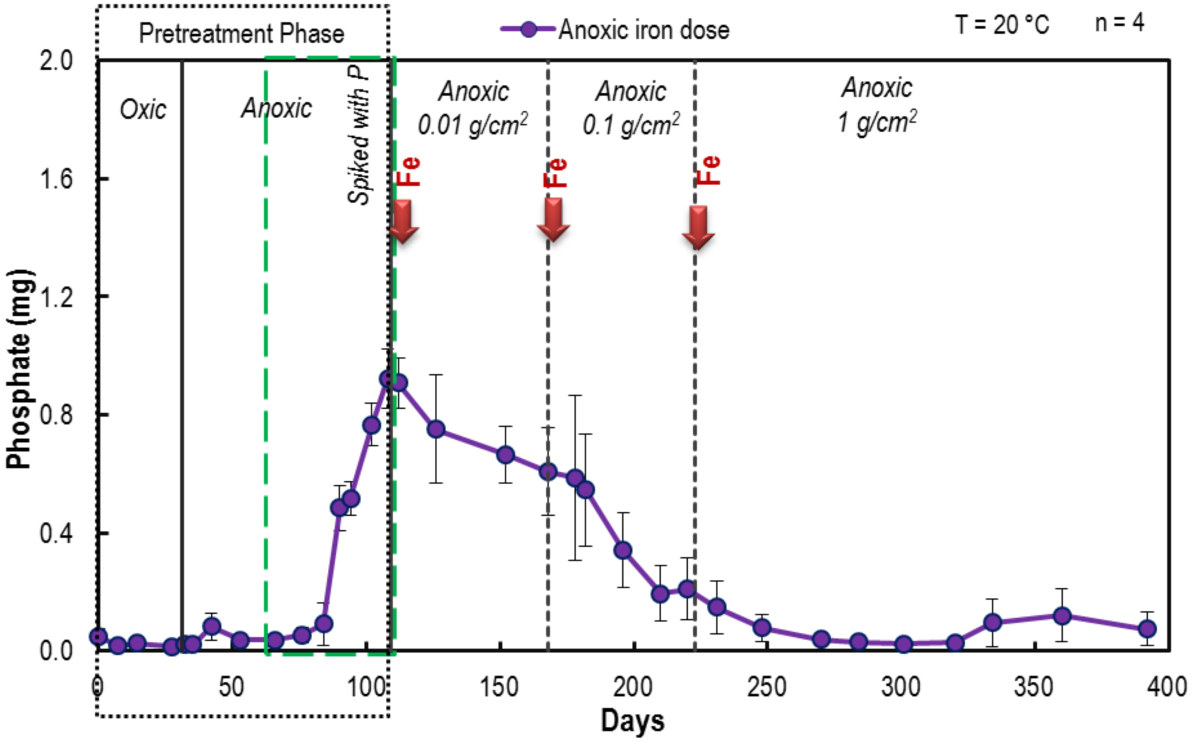


Figure 14. Mean water column phosphate measured during the pretreatment and iron addition phases in the Rush Lake columns dosed with iron filings under anoxic conditions at 20 °C. The error bars represent 67% CI on the mean for four replicates. The timing of step-addition of iron filings (Fe) is marked.

As hypothesized earlier, Fe^{2+} diffusing from the iron filings can precipitate phosphate to form ferrous-phosphate minerals such as vivianite in the sediments and hydrated Fe^{2+} can adsorb phosphate (Rodena and Edmonds 1997; Gächter and Müller 2003; Rothe et al. 2014; Orihel et al. 2016). Depending on the rate of reduction of iron minerals mediated by bacteria and the release of ferrous ions via iron metal corrosion, the P mass in the overlying water gradually decreases. This also means addition of iron filings to anoxic water would act relatively slowly and a higher iron dose may be required to realize immediate significant impact on the phosphorus water quality. Data in Table 5 offer support to this hypothesis; when applied under anoxic conditions, the first 0.01 g/cm^2 iron dose was able to reduce water column P mass (at 1.45 mg/m^2/day), but the 0.1 g/cm^2 iron dose was required to more effectively increase the P flux into the sediments (at 2.88 mg/m^2/day). For the same doses applied under oxic conditions, the first 0.01 g/cm^2 dose alone acted effectively to lower P mass in the water column (at 2.15 mg/m^2/day) and the P mass continued to decrease through subsequent iron addition of 0.1 g/cm^2 dose (at 0.502 mg/m^2/day). The hypothesis is also supported by the observation that adding iron filings under oxic conditions binds the mobile phosphorus in sediment such that the potential for phosphate to release when conditions turn anoxic is decreased and water column P continues to remain low (Figure 11).

Table 5. Phosphate (P) release rates in Rush Lake sediments amended with iron filings under oxic and anoxic conditions at 20 °C. Values provided are mean (± 67% CI).

	P release rate (mg/m^2/day)	
Iron filings dose	**Iron addition under oxic conditions**	**Iron addition under anoxic conditions**
0.01 g/cm^2 (low dose)	-2.15 (± 1.90)	-1.45 (± 0.540)
0.1 g/cm^2 (high dose)	-0.502 (± 0.451)	-2.88 (± 1.16)
1 g/cm^2 (very high dose)	-0.192 (± 0.0489)	-0.174 (± 0.0861)

Ann Lake Laboratory Column Studies (Year 2)

A total of fifty sediment-water mesocosms of Ann Lake were set up as part of Year 2 laboratory column studies: forty columns were kept 20 °C and ten columns at 10 °C. Based on the measured P release responses to iron dosing in the Rush Lake columns, lower iron doses were tested in the Ann Lake sediments. 0.01 g/cm^2 (low dose), 0.05 g/cm^2 (medium dose), and 0.1 g/cm^2 (high dose) iron filings were applied to three sets of columns to isolate the effects of each iron dose under various conditions. The influences of iron dose, temperature, timing of iron dosing, and high sulfate concentration on the sediment phosphorus release were evaluated. Because the sediments had been homogenized, the replicates were randomly assigned to a set of columns. Data plots for replicate columns for the entire study duration are provided in Appendix A.

Pretreatment Phase: Oxic and Anoxic Sediment P release at 20 °C

The phosphate (P) release measured in 20 Ann Lake columns during the pretreatment phase is shown in Figure 15. Under oxic conditions, the P concentrations in the water column were low

(< 16 µg/L) although a small accumulation of P mass occurred over the 41-day duration due to P release from the sediments. The average oxic P release rate was relatively low at 0.102 mg/m^2/day (± 0.0262 67% CI) for 25 columns.

Once the water column conditions were changed to anoxic, P release from the sediments was observed in all of the columns. Formation of black patches in the sediment and/or dark ring at the sediment surface confirmed that the sediments were anoxic (Gunnars and Blomqvist 1997). The P mass increased linearly over the 44-day incubation period, and the mean water column concentration was 304 µg/L (± 26 Std Dev) at the end of the anoxic period. The mean anoxic P release in the 25 sediment columns was 5.60 mg/m^2/day (± 0.104 67% CI). This release rate is near the median P release rates observed in Minnesota lakes (James and Bischoff 2016), and in the range measured in some mesotrophic and eutrophic lakes (Nürnberg 1988; Jensen and Andersen 1992; Pilgrim et al. 2007). One of the observations noticeable in Figure 15 is the minimal variation in the anoxic P release responses among the sediment columns (when compared to the Rush Lake mesocosms) owing to homogenization of the sediments before building the mesocosm systems in the laboratory. The water column pH was 8.21 (± 0.160 Std Dev) under oxic conditions, and 8.68 (± 0.259 Std Dev) under anoxic conditions.

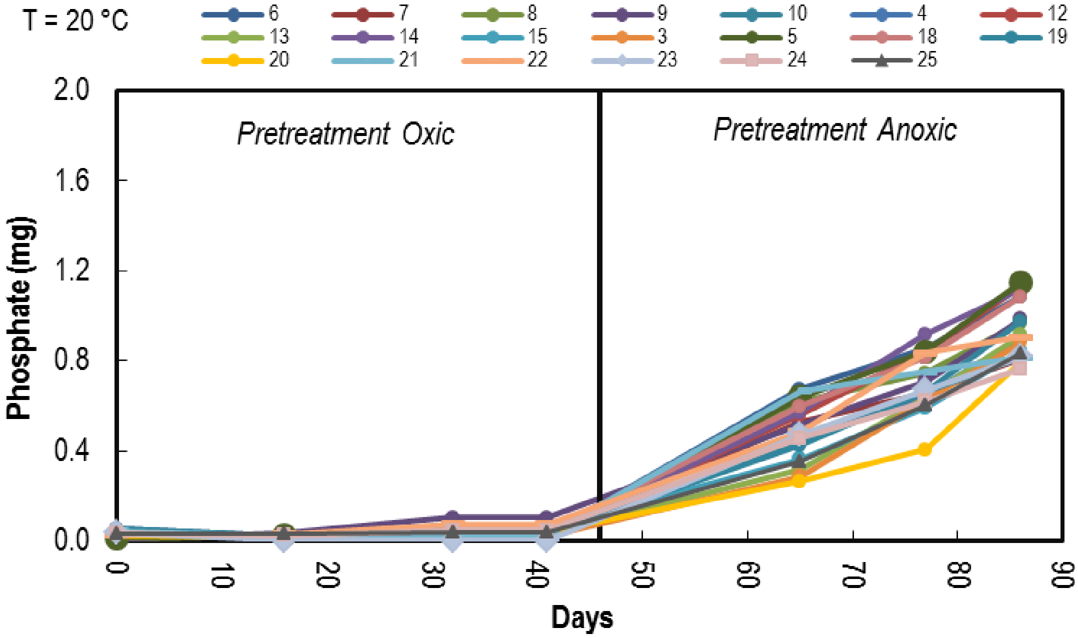


Figure 15. Water column phosphate measured in the Ann Lake columns at 20 °C during the pretreatment phase. (Note: Legend shows the number assigned to label a column).

Pretreatment Phase: Oxic and Anoxic Sediment P Release at 10°C

The Ann Lake sediment columns at 10 °C did not release phosphate under oxic conditions (Figure 16). The water column P concentrations remained less than 9 µg/L in all ten columns during the 43-day oxic period. During the following 57-day anoxic duration, the P mass increased in the overlying water (mean 91 µg/L P). Also, there was minimal variation in P release behavior due to sediment homogenization. The mean anoxic P release rate was 1.34 mg/m^2/day (±0.00392 67% CI) for the anoxic duration.

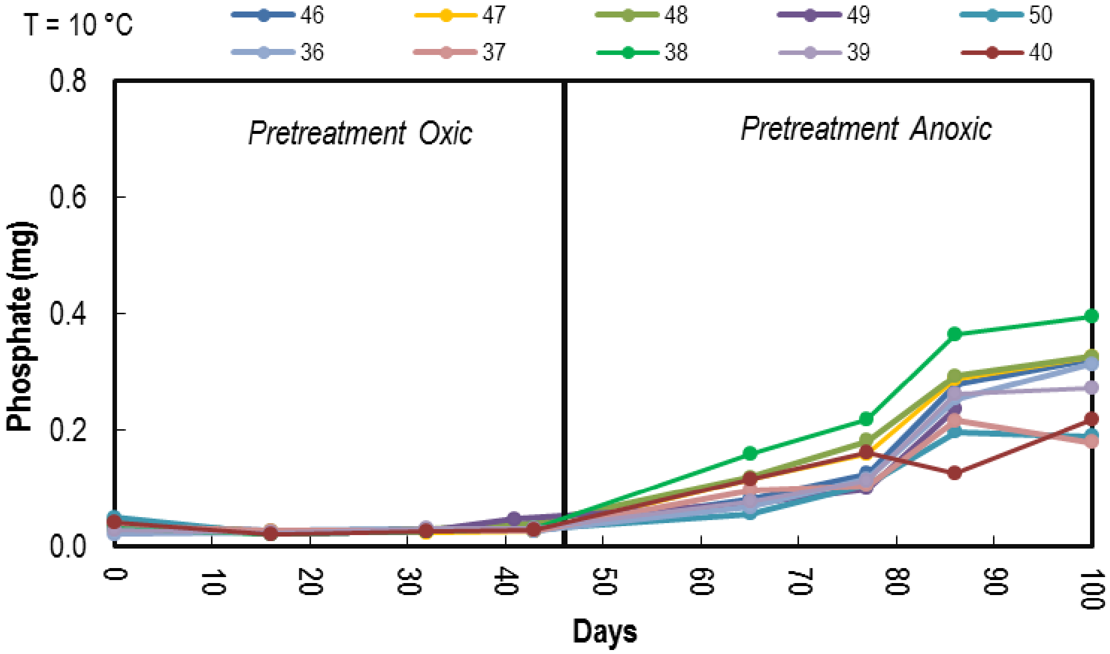


Figure 16. Water column phosphate measured in the Ann Lake columns at 10 °C during the pretreatment phase. (Note: Legend shows the number assigned to label the columns).

The effect of temperature on microbial activity in the sediments and mobilization of redox- and possibly organic-phosphorus across the sediment-water interface was evident in the Ann Lake sediments; the 20 °C anoxic P release from the sediments was greater than four times the release rate measured at 10 °C (Figure 17). Large increase in P release rate corresponding to increase in incubation temperature or water temperature have been measured in several laboratory-scale and in lake-scale studies (Holden and Armstrong 1980; Jensen and Andersen 1992). For example, anoxic release rate at 24 °C was anywhere between 2 to 6 times the rate at 10 °C in some lakes (Lee et al.1977; Holden and Armstrong 1980; Jensen and Andersen 1992).

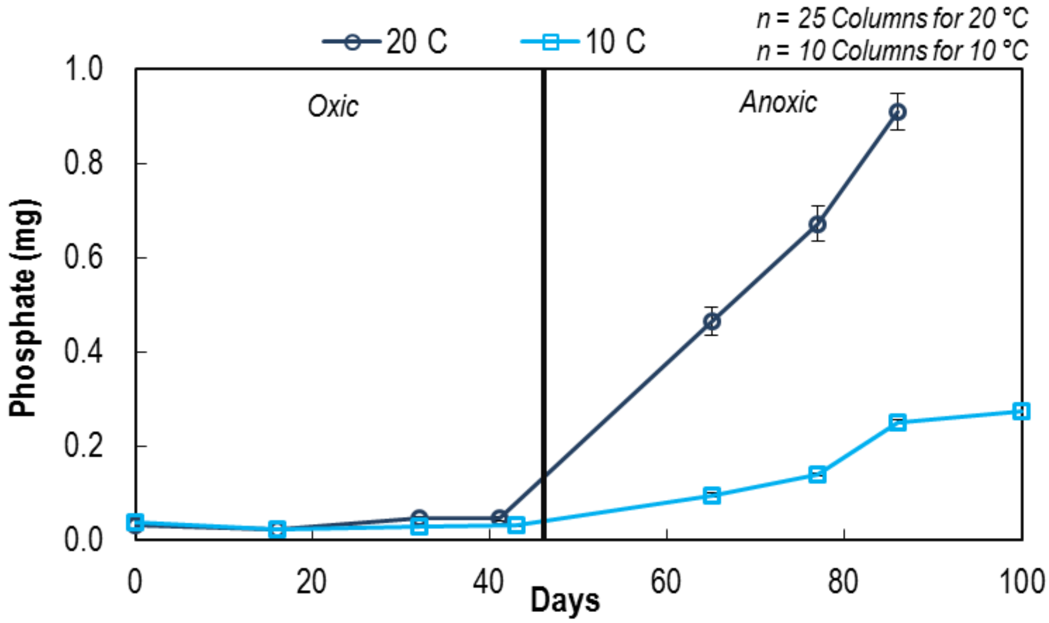


Figure 17. Phosphate release measured in the Ann Lake columns at 20 °C and 10 °C during the pretreatment phase. Error bars are 67% CI on the mean for *n* columns.

Iron Addition Phase

After the conclusion of pretreatment phase, the water column conditions were switched to oxic conditions. 0.01 g/cm^2 (low dose) 0.05 g/cm^2 (medium dose) and 0.1 g/cm^2 (high dose) iron were applied to three separate sets of columns at 20 °C (Figure 18). The accumulated P mass in the water column began decreasing under oxic conditions. At the end of the 44-day oxic period, the mean water column P concentrations were 75 µg/L in the control, 49 µg/L in the 0.01 g/cm^2 iron-dosed columns, 31 µg/L in the 0.05 g/cm^2 iron-dosed columns, and 23 µg/L in the 0.1 g/cm^2 iron-dosed columns. When the water column is aerated, phosphate is immobilized in the sediments more effectively by iron-amended sediments. The formation of oxidized iron layer in the iron-amended sediments capable of adsorbing phosphorus can be seen in Figure 19.

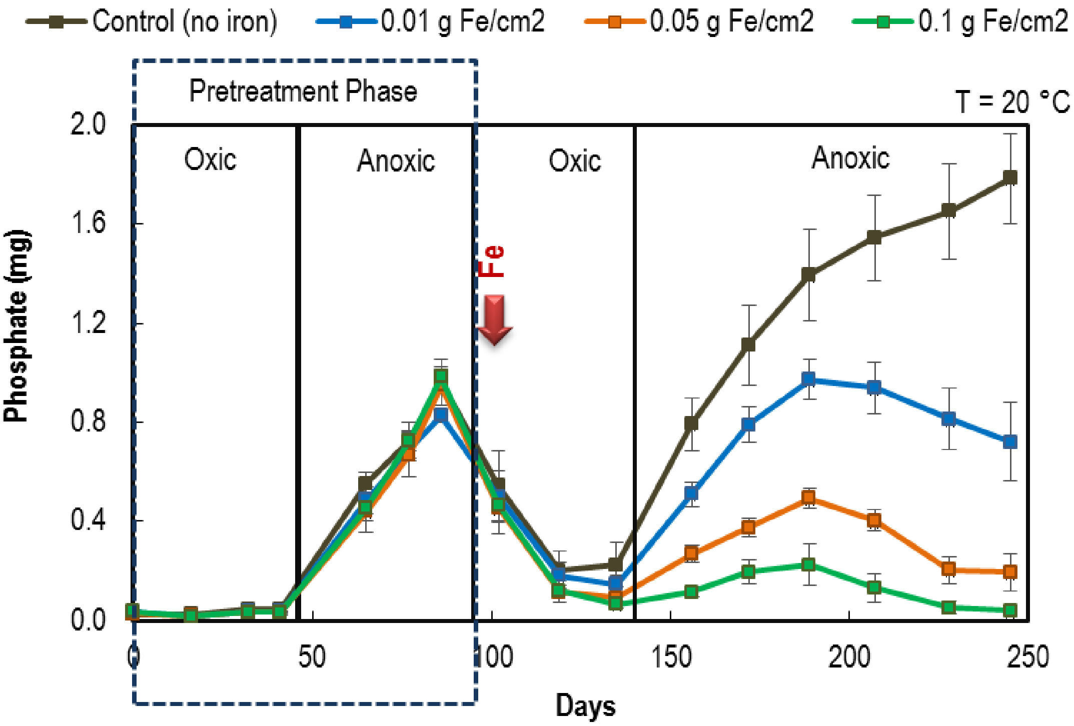


Figure 18. Mean water column phosphate measured during the pretreatment and iron addition phases in the Ann Lake sediment columns at 20 °C. The error bars represent 67% CI on the mean for five replicates. No iron was added to the control columns.

Figure 19. Ann Lake sediments amended with 0.1 g/cm^2 iron filings under oxic water column conditions. The oxidized iron layer can be seen at the sediment-water interface.

The water column conditions were thereafter turned anoxic to measure the impact of iron addition on anoxic sediment P release. As expected, a dose-release response relationship proportional to the quantity of iron filings applied was measured (Figure 18 and Table 6). The influence of iron filings was most evident for the 0.1 g/cm^2 iron dose. Given sufficient time, the 0.05 g/cm^2 dose also reduced the water column P to low levels. At the end of the anoxic phase, the mean water column P concentrations were 572 µg/L in the control, 194 µg/L in the 0.01 g/cm^2 iron-dosed columns, 12 µg/L in the 0.05 g/cm^2 iron-dosed columns, and 6 µg/L in the 0.1 g/cm^2 iron-dosed columns. Water pH was similar in the control (8.70 ± 0.367 Std Dev) and the iron-amended sediment columns (8.58 ± 0.345 Std Dev).

At 10 °C, 0.05 g/cm^2 iron dose was added to one set of columns (Figure 20). Under oxic conditions, the mean water column P decreased to 19 µg/L in the iron-dosed columns and to 33 µg/L in the control columns. In the next anoxic phase, P release was observed in the control columns. In the iron-dosed sediments, anoxic P release was fully controlled including reduction in water column P mass. As discussed earlier, the P mass accumulated in the water column was much lower at 10 °C than at 20 °C at the end of pretreatment anoxic period. Therefore, the 0.05 g/cm^2 dose was sufficient to control anoxic P release in the columns at 10 °C.

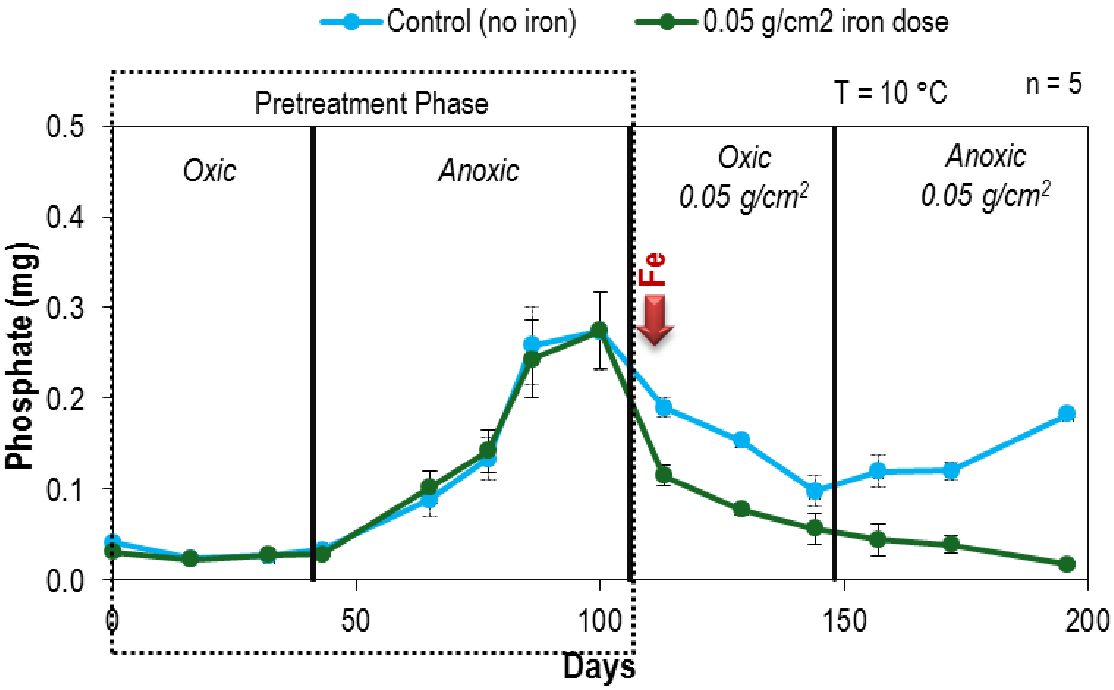


Figure 20. Mean water column phosphate measured during the pretreatment and iron addition phases in the Ann Lake sediment columns at 10 °C. The error bars represent 67% CI on the mean for five replicates in each set. No iron was added to the control columns.

Table 6. Summary of phosphate (P) release rates during the iron addition phase in the Ann Lake sediment columns at 20 °C and 10 °C. Values provided are mean (± 67% CI) for five replicates.

	20 °C P release rate (mg/m^2/day)		10 °C P release rate (mg/m^2/day)	
Iron filings dose	**Oxic**	**Anoxic**	**Oxic**	**Anoxic**
0.0 g/cm^2 (control)	-4.87 (± 0.451)	3.18 (± 0.409)	-1.11 (± 0.111)	0.152 (± 0.196)
0.01 g/cm^2 (low dose)	-4.53 (± 0.383)	0.730 (± 0.345)	n/a	n/a
0.05 g/cm^2 (medium dose)	-5.51 (± 0.562)	-0.289 (± 0.0585)	-1.34 (± 0.227)	-0.200 (± 0.0758)
0.1 g/cm^2 (high dose)	-5.89 (± 0.422)	-0.244 (± 0.0507)	n/a	n/a

At both incubation temperatures, the amount of iron in the sediment directly influenced the rate at which P is mobilized from anoxic sediments (Table 6). As hypothesized for Rush Lake sediments, the presence of an iron source in the sediments enables the suppression of anoxic sediment P release. To reiterate, iron filings provide dissolved iron that removes phosphate in the water column by co-precipitation (ferrous-phosphate) and surface complexation (Fe(II) hydroxide-phosphate). While ferric oxyhydroxides can bind phosphate more firmly than the ferrous form, the hydrated ferrous oxide and/or ferrous hydroxide likely have large surface areas and an increased reactivity with phosphate (Patrick and Khalid 1974).

The high iron dose of 0.1 g/cm^2 worked very well in both Rush Lake and Ann Lake sediments. Nevertheless, the Ann Lake experimental data indicate that the medium dose of 0.05 g/cm^2 iron filings is sufficient to control P flux to the overlying water under anoxic and oxic conditions.

Timing of Iron Application: Iron Addition Under Oxic Vs. Anoxic Conditions

Impact of iron addition performed under anoxic conditions vis-à-vis oxic conditions was investigated in Ann lake sediments at 20 °C (Figure 21 and Table 7). The mean water column concentration was 275 µg/L at the beginning of the anoxic treatment phase. In spite of the first 0.01 g/cm^2 iron addition, P continued to diffuse from the sediments at a low rate of 0.421 mg/m^2/day and concentration increased to about 365 µg/L P in the overlying water by the end of 64 days. Increasing the iron dose to 0.05 g/cm^2 had a moderate effect on the sediments given sufficient time of 104 days; P diffusion occurred during the first 30 days in most columns but was observed to be controlled thereafter. P flux back into the sediments, due to precipitation with or sorption with ferrous products, reduced the mean water column concentrations to 178 µg/L, which is still relatively high. The final increase to 0.1 g/cm^2 iron dose was required to further reduce phosphate to 14 µg/L in the water and prevent net P release.

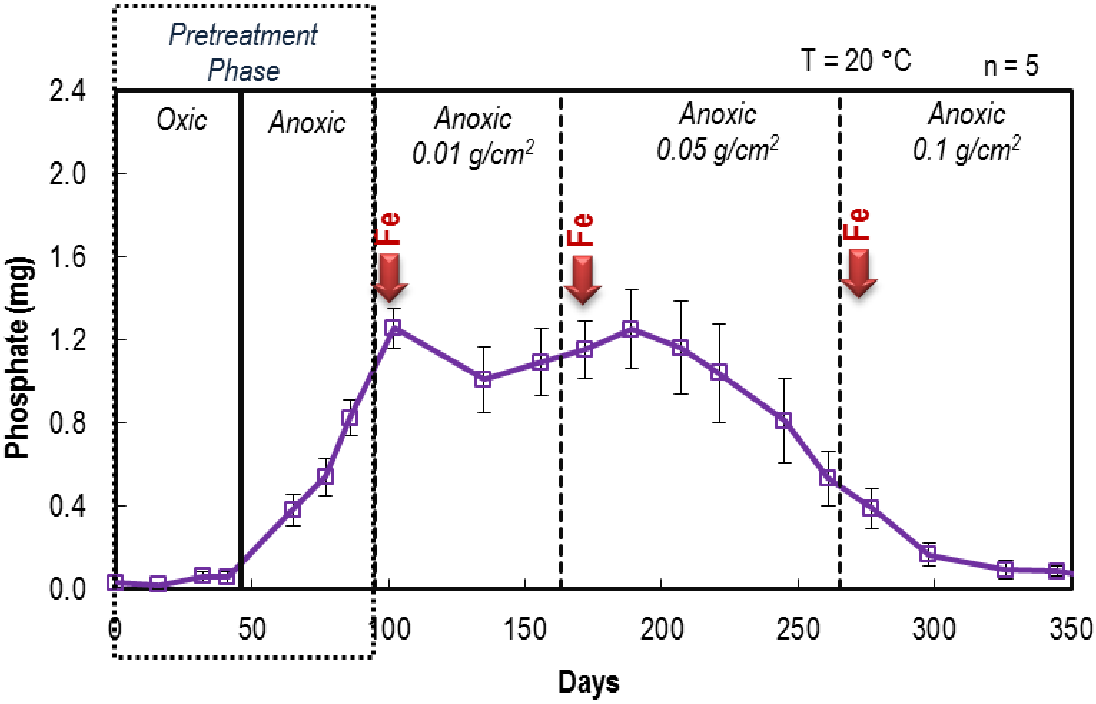


Figure 21. Mean water column phosphate (± 67% CI) during the pretreatment and iron addition phases in the Ann Lake columns dosed with iron filings (Fe) under anoxic conditions at 20 °C.

Table 7. Phosphate(P) release rates in Ann Lake sediments amended with iron filings under oxic and anoxic conditions at 20 °C. Values provided are mean (± 67% CI) for five replicates.

	P release rate (mg/m^2/day)	
Iron filings dose	**Iron addition under oxic conditions**	**Iron addition under anoxic conditions**
0.01 g/cm^2 (low dose)	-4.53 (± 0.383)	0.421 (± 0.828)
0.05 g/cm^2 (medium dose)	-5.51 (± 0.562)	-1.58 (± 0.645)
0.1 g/cm^2 (high dose)	-5.89 (± 0.422)	-1.35 (± 0.360)

On comparing the mean P flux measured in the columns dosed with iron under anoxic conditions to the columns dosed under oxic conditions (Table 7), it can be concluded that iron addition under anoxic conditions will impact the water column phosphate but at a relatively lower rate. Additionally, a 0.1 g/cm^2 iron addition will be required to force significant improvement in the water quality and reduce P release. The 0.05 g/cm^2 dose might work but require a relatively longer duration to control P release.

Effect of High Sulfate on P Release and Iron Dosage

Ten sediment columns, five control and five designated for iron dosing, were incubated at 20 °C to investigate the effects of high sulfate in the water on the phosphate release and iron dosing requirement (Figure 22). The columns were monitored for three weeks with the existing sulfate concentrations (~11 mg/L) and phosphate concentrations (~10 µg/L) under oxic conditions. The water column sulfate levels were then increased to 100 mg/L and maintained under oxic conditions for four weeks during which a very small increase in P mass in the overlying water occurred (0.0671 ± 0.00123 mg/m^2/day). Oxic P release, however, was observed in some columns with low sulfate as well (Figure 15). Competition between sulfate and phosphate for anion sorption sites has been suggested, but clear evidence does not exist (Caraco et al. 1989; Roden and Edmonds 1997).

The water column phosphate mass increased at close to a linear rate under anoxic conditions over the next 47 days. The mean P level was 470 µg/L in the ten columns by the end of the pretreatment anoxic phase. The corresponding mean anoxic P release rate was 8.95 mg/m^2/day (± 0.0278 67% CI) under high initial sulfate concentrations. The release rate is approximately 1.5 times the rate measured under low sulfate concentrations (5.60 mg/m^2/day in 25 columns containing < 11 mg/L sulfate). Under anoxic and abundant sulfate conditions, sulfide (from sulfate reduction) could bind the existing iron in the sediments and decrease the iron supply for ferrous-phosphate compounds, thereby increasing phosphate release from anoxic sediments (Caraco et al. 1989; Roden and Edmonds 1997; Rozan et al. 2002; Gächter and Müller 2003). A mean pH value of 8.66 (± 0.427 Std Dev) was measured in the 10 columns.

Anoxic conditions were continued in all columns for the next phase. The first low dose of 0.01 g/cm^2 iron filings was applied to five columns. During the next 30 anoxic days, P diffused from the low iron-dosed sediments into the overlying water and increased the P mass at the rate of 4.45 mg/m^2/day (± 0.395 67% CI) and concentration to 635 µg/L P by the end of the phase. The control sediment columns also contained a similar P level (622 µg/L), suggesting the 0.01 g/cm^2 iron addition did not have a measureable impact on the sediment with enhanced sulfides. The next addition of iron filings to 0.05 g/cm^{2}dose reduced the anoxic release of P. Over the 70-day duration, P mass in the overlying water was removed, producing a negative P flux of 2.73 mg/m^2/day (± 0.670 67% CI) to the sediment. Application of the next dose to reach 0.1 g/cm^2 iron further decreased P mass (-2.14 mg/m^2/day) and also prevented new anoxic P release. The water columns contained about 64 µg/L phosphate by the end of 100 days. The unamended control sediments continued to release phosphate throughout the anoxic period; the mean water column concentrations were around 700 µg/L P at the conclusion of the mesocosm experiment.

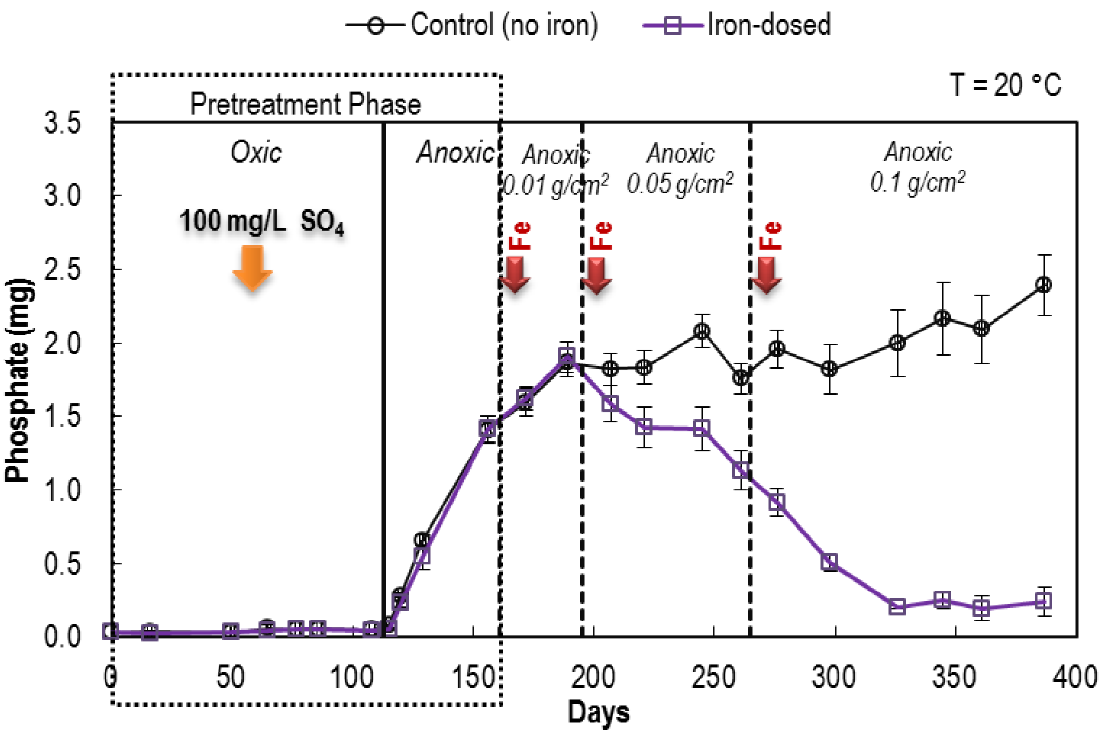


Figure 22. Mean water column phosphate (± 67% CI) in the control and iron-amended Ann Lake sediment columns with high sulfate in the overlying water. Control columns did not receive iron.

The bacterial reduction of sulfate caused the sulfate concentrations in the overlying water to decrease throughout the anoxic periods (Figure 23). When compared to the control, sulfate decrease was accelerated in iron-dosed columns after the addition of medium iron dose, likely due to the formation of iron-sulfide minerals in addition to iron-phosphate minerals in the sediments (Smolders et al. 1995). As seen in Figure 23, the jet-black bands in the sediments presented visual confirmation of the sulfide formation (Roden and Edmonds 1997), and the presence of pits or craters on the sediment surface were possibly caused by ebullition of hydrogen sulfide and/or methane gas bubbles from the deeper highly-reduced sediments (Smolders et al. 2006). The water column contained 65 mg/L sulfate in the control and 50 mg/L sulfate in the iron-dosed columns. Mean pH of the water column was about 8.45 (± 0.355) in the iron-dosed columns.

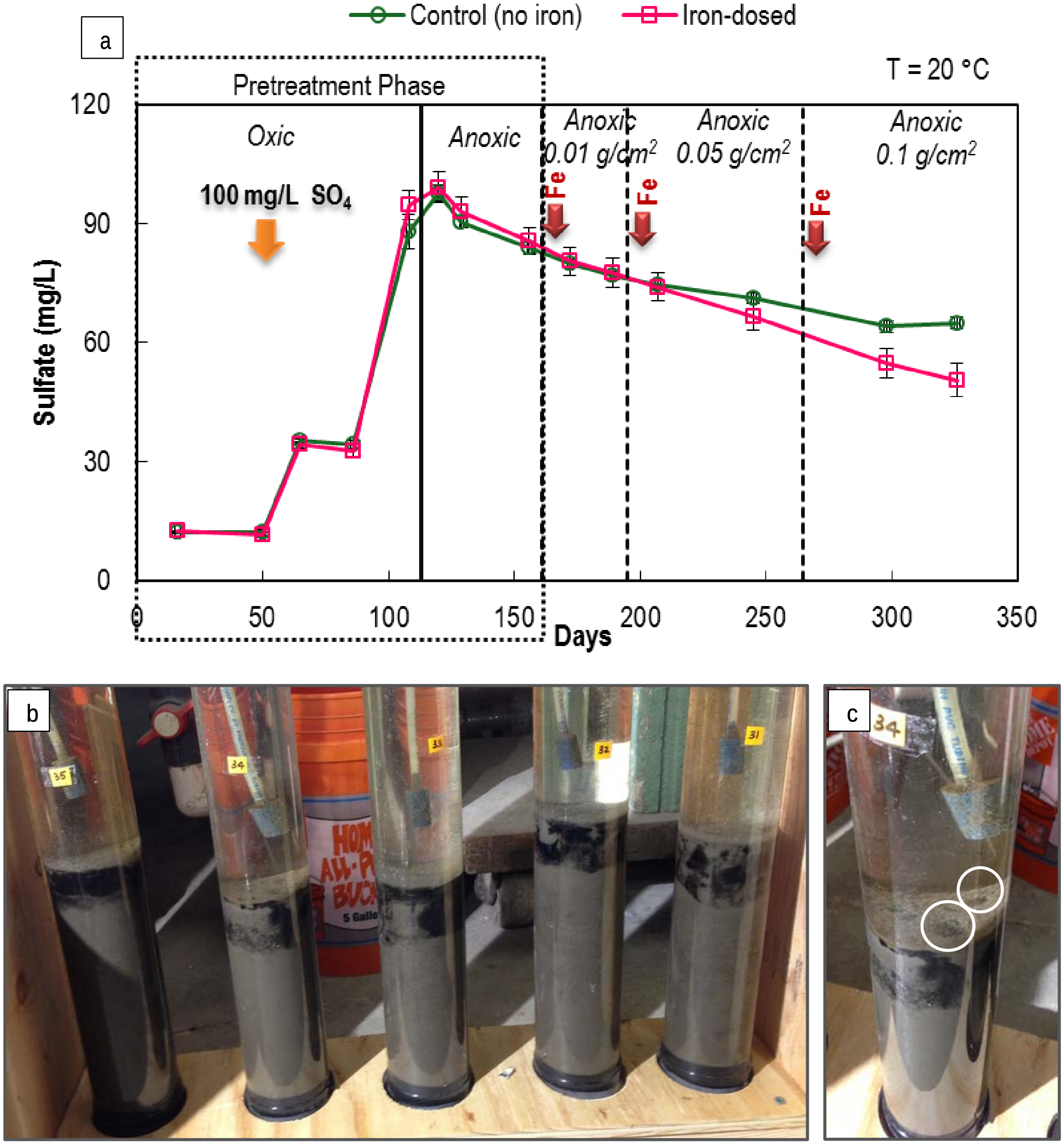


Figure 23. Ann Lake column studies on high sulfate in the water column. (a) Mean water column sulfate concentrations (± 67% CI) in the control and iron-amended sediment columns. (b) Photograph of control columns containing high sulfate in the water. (c) Photograph depicting craters on the surface of the sediment due to gas ebullition.

The P flux measurements after iron addition in columns with existing (low) sulfate and high sulfate were compared to determine the impact of sulfate on iron dosing requirements (Table 8). Without the iron amendment, the rate of P mass accumulation in the water column was larger with high sulfate concentrations. Addition of 0.01 g/cm^2 iron dose had much greater impact on P release in the low sulfate columns than the high sulfate columns. Only after the 0.05 g/cm^2 and 0.1 g/cm^2 iron doses were added, no net release of P and reduction of water column P mass were observed in both low sulfate and high sulfate water. The relatively steep P flux rates after iron addition in the high sulfate columns is because of the higher P mass in the water column before (1.42 mg) and after each iron addition step. The low sulfate columns contained a much lower initial P mass (0.826 mg) that continued to decrease after iron addition.

Table 8. Anoxic P release rates in Ann Lake sediments amended with iron filings containing low (~11 mg/L) and high sulfate concentrations (100 mg/L) in the water column at 20 °C. Values provided are mean (± 67% CI) for five replicates.

	Anoxic P release rate (mg/m^2/day)	
Iron filings dose *(iron added under anoxic conditions)*	**Low sulfate columns**	**High sulfate columns**
0 g/cm^2 (control)	4.82 (± 0.712)	8.95 (± 0.0278)
0.01 g/cm^2 (low dose)	0.421 (± 0.828)	4.45 (± 0.397)
0.05 g/cm^2 (medium dose)	-1.58 (± 0.645)	-2.73 (± 0.674)
0.1 g/cm^2 (high dose)	-1.35 (± 0.360)	-2.14 (± 0.260)

When dosed under anoxic conditions, a high iron dose of 0.1 g/cm^2 is required to control anoxic P release irrespective of sulfate concentrations. However, as the remaining sulfate (~50 mg/L) diffuses into the sediment and is reduced, more Fe(II) from iron filings will be used up to precipitate sulfide and phosphate. This means a dose greater than 0.1 g/cm^2 iron might be required to maintain the supply of iron in the sediments with high sulfate in the overlying water.

Effects of Iron Amendment on Sediment Phosphorus (Year 3)

The effects of addition of iron filings on the lake sediments were further investigated by analyzing the sediment porewater phosphate concentrations, the fractions of bioavailable and refractory forms of phosphorus in the sediment and the types of minerals present in the sediment.

Sediment Porewater Phosphate Profile

The porewater phosphate (P) profiles in Figure 24 show the effect of the iron amendment on Rush Lake sediments. In the sediments that received 0.1 g/cm^2 and 1 g/cm^2 iron filings dose (Figure 24a and b), the P concentrations were very low in the top 4 cm, sometimes even up to 7 cm depth. The sediments are typically anoxic/anaerobic at these depths. The measured concentrations were in fact mostly around the 10 µg/L P-laboratory detection limit. The porewater profiles were similar in columns that were kept anoxic or oxic in the last phase. Porewater P concentrations gradually increased in the lower sediment depths. The unamended sediments contained much higher P concentrations in the porewater, generally peaking around the 5 cm depth (Figure 24c).

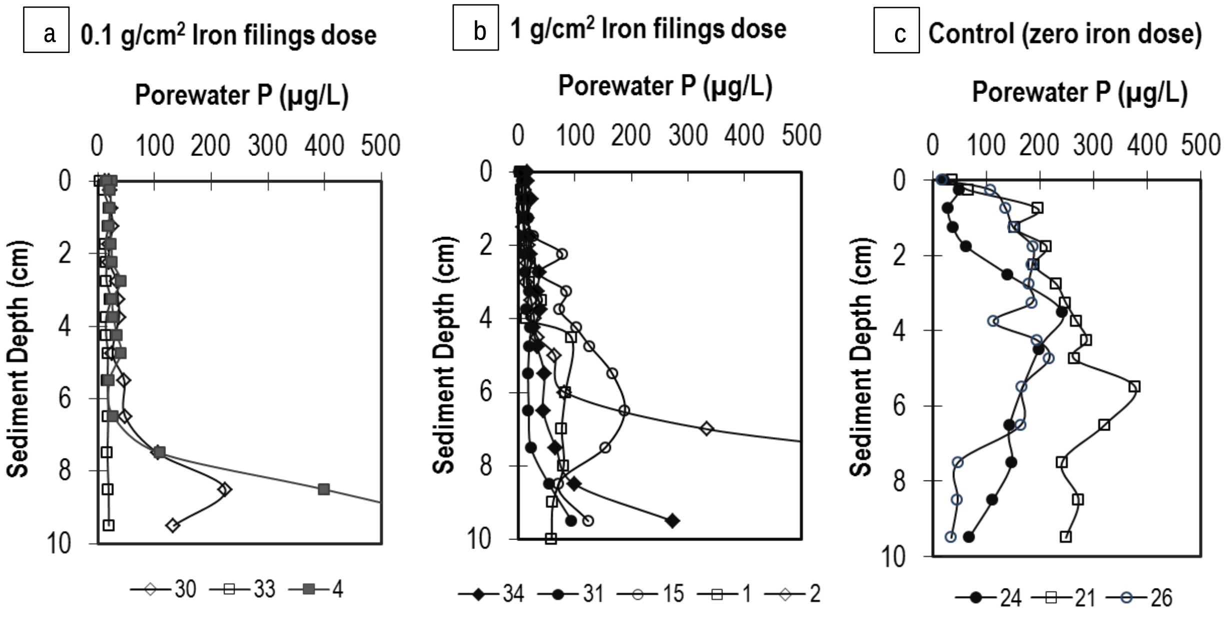


Figure 24. Sediment porewater phosphate concentrations in the Rush Lake sediments amendment with (a) 0.1 g/cm^2 iron dose (3 mesocosms); (b) 1 g/cm^2 iron dose (5 mesocosms); (c) zero iron dose (3 mesocosms). Legend represents column labels.

The diminished porewater P levels in the top 4 cm of iron-amended sediments of Rush Lake confirm that the increased iron supply from the iron filings was able to sequester the mobile phosphorus in the sediments. This is in agreement with the significantly lowered P in the water column and the decreased diffusive P flux measured during the mesocosm studies. Precipitation of the most stable ferrous-phosphate mineral, vivianite ($Fe^{2+}Fe_2^{2+}$ $(PO_4)_2.8H_2O$), occurs in anoxic sulfide-free sediments that are saturated with Fe and P (Gächter and Müller 2003; Murphy et al. 2001; Orihel et al. 2016). Evidence of vivianite formation in reduced lake sediments has been reported in a number of lakes (Rothe et al. 2014; Orihel et al. 2016).

Visual examination of the sectioned sediment offered some support to this hypothesis. Traces of iron filings were present in the top 1 or 2 cm of the iron-dosed sediments. Due to the high water-content in the upper sediments (~87%), the iron filings likely deposited deeper in the sediment during the surficial application. The iron filings present a source of Fe(II) that can diffuse to the upper sediments and water column as well as the lower depths due to a concentration gradient. This can explain the low porewater P concentrations even up to 7 cm below the sediment surface.

Sediment Phosphorus Fractions

The impact of iron filings on sediment phosphorus storage in Ann Lake sediments was evaluated by examining the pools of available and unavailable forms of P in the sediment. The mean water content was 82% (± 3.4% Std Dev) in the upper 4 cm of sediments, and almost uniform at 80%

(± 2.9% Std Dev) through the 10 cm depth. Mean organic matter content of 15% (± 1.1% Std Dev) and dry bulk density of 0.213 g/cm^3 (± 0.0352 Std Dev) were measured in the sediments.

Figure 25a shows the depth distribution of various P fractions in the control (unamended) Ann Lake sediments. The dominant P form is mineral-P followed by residual organic-P, Fe-P, loose-P, labile organic-P, and Al-P. In terms of total sediment phosphorus (TP), the mean composition in the upper 10 cm sediment is 33% mineral-P, 22% residual P, 21% Fe-P, 12% loose-P, 8.6% labile organic P and 3.9% Al-P. The redox-P fraction (loose-P + Fe-P) thus constitutes 33% of sediment TP. Together with labile organic P, which can be degraded and released from the sediment by mineralization or organic matter decomposition (Rozan et al. 2002; Reitzel et al. 2007; James 2011), the total biologically-labile P is nearly 42% of the TP. The difference in P concentrations along the 0 to 10 cm sediment depth is small in Figure 25a because of the homogeneity introduced by sediment mixing before the laboratory mesocosms were setup.

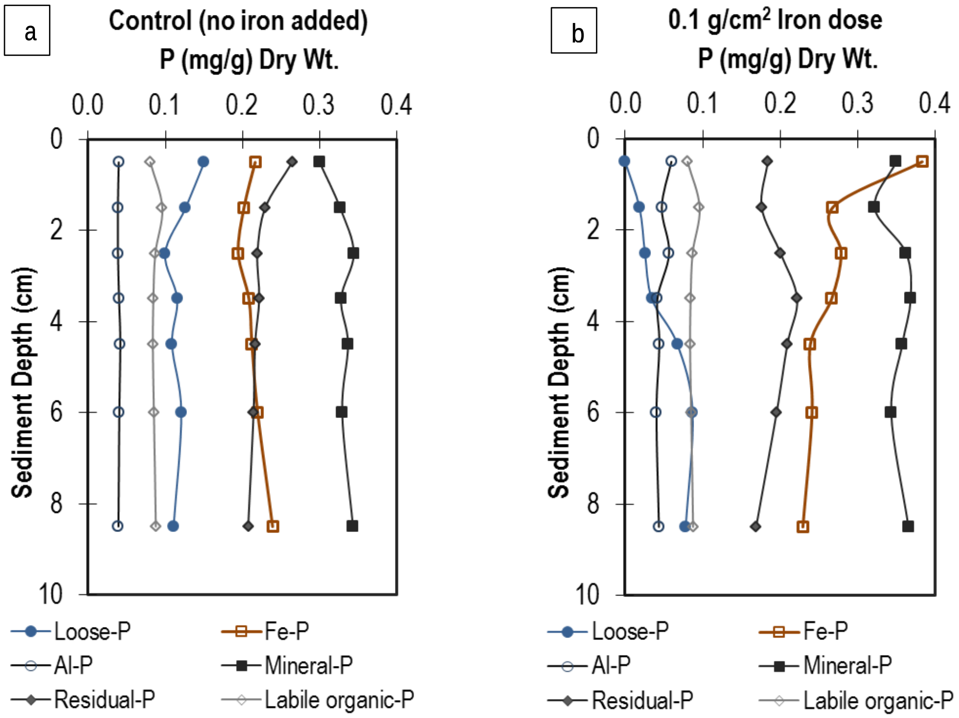


Figure 25. Concentrations of various sediment P fractions in the upper 10 cm sediments from (a) control (unamended) columns and (b) 0.1 g/cm^2 iron-dosed columns of Ann Lake. Concentrations shown are average for two mesocosms in each set. Values are plotted at the midpoint for the depth analyzed (e.g. P in 1-2 cm depth is plotted at 1.5 cm).

The addition of iron filings significantly impacted the loose-P concentration, especially in the 0 - 4 cm sediment layer, as shown in Figure 26a. Loose-P was not detected in the top 2 cm of the sediments that received 0.05 g/cm^2 and 0.1 g/cm^2 iron filings dose. The effect of 0.1 g/cm^2 iron dose on loose-P concentrations was evident until 6 cm depth. The decrease in loose-P virtually manifested as an increase in the iron-bound P fraction (Fe-P) (Figure 26b and c), suggesting capture of the mobile porewater P by iron. The addition of iron increased the average Fe-P concentration from 0.209 mg/g (± 0.0093 Std Dev) to 0.293 (± 0.0440 Std Dev) mg/g in the upper 4-cm sediment. Figure 26c essentially shows the movement of P from loosely-bound form to iron-bound form because of iron addition, and hence the total redox-P concentrations are similar in the iron-amended and control sediments. The increased quantity of reactive iron capable of forming Fe (II)-phosphate minerals in anoxic sediments (Gächter and Müller 2003; Kleeberg et al. 2013; Rothe et al. 2014) is hypothesized as the reason for lowering porewater P and limiting P release even under anoxic conditions.

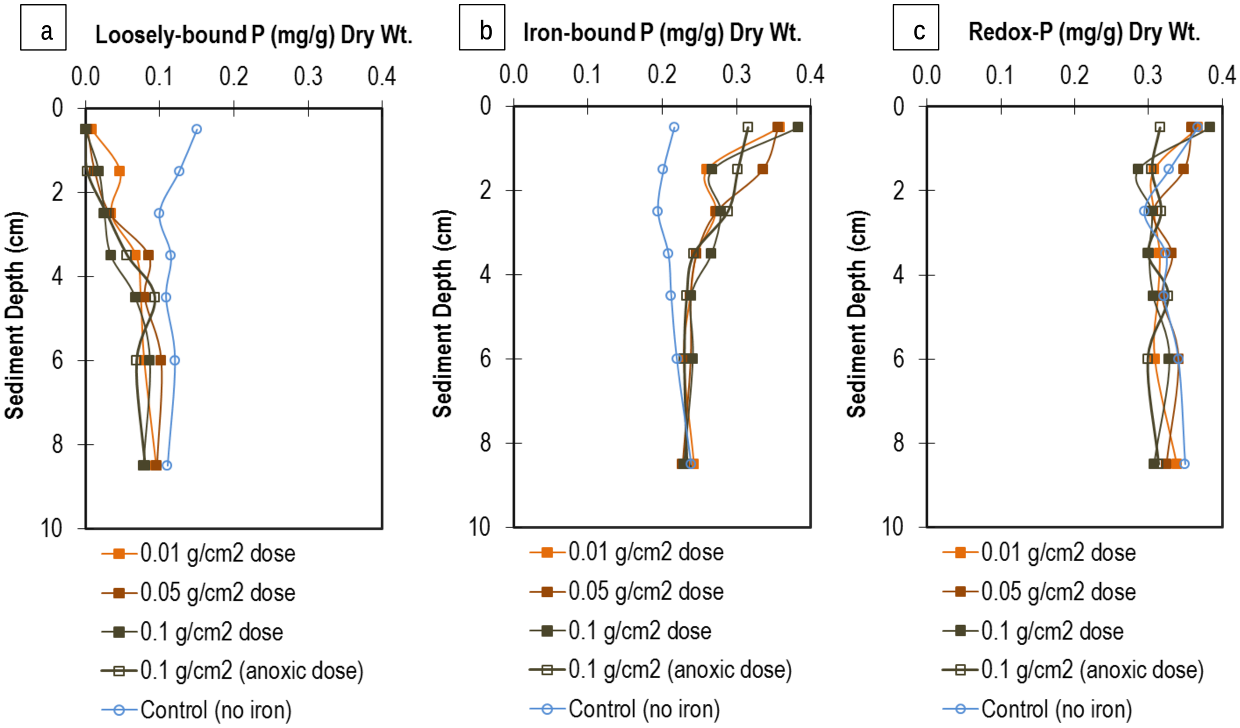


Figure 26. Concentrations of (a) loosely-bound phosphorus (P), (b) iron-bound-P and (c) redox-P (loosely-bound P + iron-bound P) in the upper 10-cm sediments of Ann Lake mesocosms amendment with 0.01 g/cm^2, 0.05 g/cm^2, 0.1 g/cm^2 and zero iron dose. Concentrations shown are average for two mesocosms in each set. Values are plotted at the midpoint for the depth analyzed (e.g. P in 1-2 cm depth is plotted at 1.5 cm).

Concentrations of the remaining sediment P fractions and TP changed minimally due to iron addition (0.1 g/cm^2 iron-dosed sediments shown as example in Figure 25b). This is expected because residual-P and P attached to Al and Ca minerals is insensitive to redox changes and considered refractory. Release of Al-P or Ca-P can occur only if changes in pH induce dissolution of these minerals (Cooke et al. 1993), which is assumed to be negligible during the mesocosm studies conducted because pH did not reach the level of substantial dissolution.

The Rush Lake sediment porewater profiles and Ann Lake sediment phosphorus fractionation show that iron filings have the affinity to bind the mobile, loosely-bound phosphorus. It can be hypothesized that a given iron filings concentration will inactivate mobile P accumulated in lake sediments, even under anoxic conditions, and thus decrease the P release from the sediments, as observed in the laboratory mesocosms.

Sediment Mineralogy

The iron filings and sediments extruded from the Rush Lake columns were analyzed for mineral composition by X-ray diffraction (XRD). The raw sample of iron filings is zero-valent iron containing iron oxide and traces of silica (Figure 27a). In the iron sampled from anoxic sediment surface, iron (II) oxide and iron (III) oxide-hydroxide minerals were detected (Figure 27b).

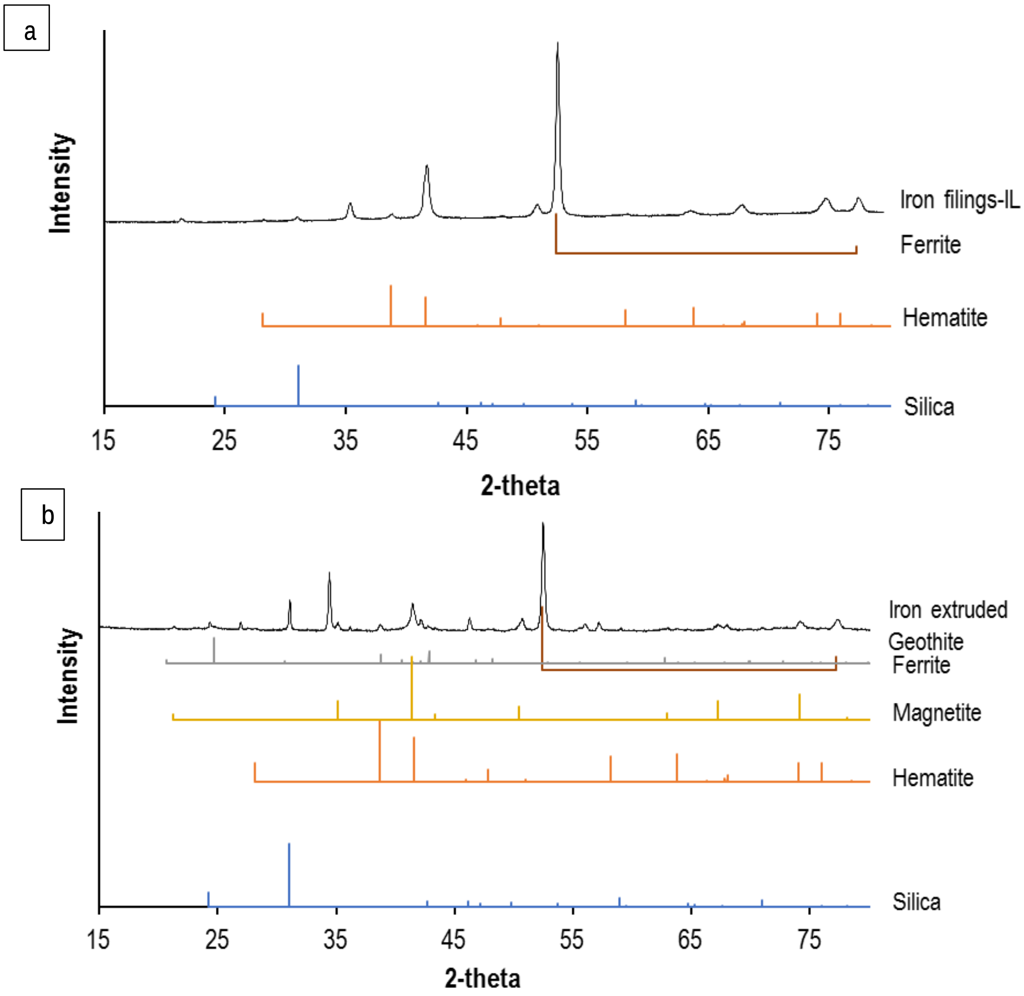


Figure 27. XRD patterns for iron filings (a) raw sample (i.e., before addition to the sediment mesocosm); and (b) iron sampled from anoxic sediment surface (i.e., after addition to sediment mesocosm).

Table 9 summarizes the major mineral composition of the extruded iron filings and sediment samples from Rush Lake columns.

Table 9. Mineral composition of iron filings and sediment samples extruded from the Rush Lake laboratory columns as determined by X-ray diffraction.

Iron filings before application	Iron filings sampled from sediment surface	Sediment depth	Unamended sediments (control)	Sediments amended with 0.1 g iron/cm^2	Sediments amended with 1 g iron/cm^2
Ferrite (Fe) Magnetite ($Fe^{2+}Fe_2^{3+}O_4$) Hematite (Fe_2O_3) Silica (SiO_2)	*Extracted from Anoxic Column* Ferrite Magnetite Geothite ($Fe^{3+}O(OH)$) Hematite Silica *Extracted from Oxic Column* Ferrite Geothite Hematite Silica	0 - 2 cm	Calcite ($CaCO_3$) Silica (SiO_2) Pyrite (FeS_2)	Calcite Ferrite Geothite Magnetite Silica	Calcite Ferrite Geothite Magnetite Silica
		2 - 4 cm	Calcite Silica Pyrite	Calcite Silica Pyrite	Calcite Silica Ferrite Geothite
		4 - 7 cm	Calcite Silica Pyrite	Calcite Silica Pyrite	Calcite Silica Pyrite
		7 - 10 cm	Calcite Silica Pyrite	Calcite Silica Pyrite	Calcite Silica Pyrite

The natural Rush Lake sediments are primarily calcite and silica with traces of pyrite. The presence of iron oxides (ferrite, magnetite and hematite) and iron oxide-hydroxide (goethite) was detected in the top 2 cm of the sediments that received 0.1 g/cm^2 iron filings. Iron oxide minerals were detected until the 4 cm depth in the 1 g/cm^2 iron-dosed sediments. Only the naturally-occurring minerals were detected in the lower depths of the iron-dosed sediments. Nevertheless, evidence of Fe(II)-phosphate mineral formation in the iron-amended sediments could not be confirmed by XRD, likely because the mass formed was likely too low to detect (< 1%). Rothe et al. (2014) concluded that direct identification of vivianite in sediments by XRD is difficult, and an extensive heavy-liquid separation procedure is required to confirm vivianite presence. Orihel et al. (2016) were also unable to show the presence of Fe(II)-phosphate minerals in lake sediments treated with iron chloride. The diffraction patterns of the sediments and the scraped iron layer could not be conclusively assigned to any iron-phosphate mineral. Even if poorly crystalline or amorphous phosphate and iron minerals like $Fe(OH)_3$ were present, they would not be detected by XRD. Because Fe-P minerals were not detected in the Rush Lake sediments, the mineralogy of Ann Lake sediments was not determined.

Nonetheless, the X-ray diffraction patterns support the hypothesis that iron filings will remain in the sediment and act to trap phosphorus in the sediment. The presence of ferrite and iron oxides as the major minerals in the top 2 cm suggests that the iron filings will continue to supply iron (Fe^{2+} and Fe^{3+}), that will control the availability and mobility of phosphorus across the sediment-water interface into and out of the sediment. By binding both phosphate in the porewater and new phosphate diffusing upwards from deeper sediments, the release of phosphate to overlying water will be prevented even if the water contains low dissolved oxygen.

Rush Lake and Ann Lake Water Quality Monitoring

The 2014 to 2016 water quality data for Rush Lake are published in the Chisago County Lake water quality monitoring reports (<http://www.chisagocounty.us/363/Water-Quality>). The water quality parameters like chlorophyll-A, total phosphorus and Secchi disk depth failed to meet their respective standards during the summer months every year in East and West Rush Lake. Severe algae and curlyleaf pondweed growth, and poor recreational suitability were also noted from July. The June to September average total phosphorus (TP) concentrations sampled in East and West Rush Lake, shown in Figure 28, exceeded the 40 µg/L MPCA water quality criterion for deep lakes, and the lake fell under the eutrophic trophic status index in 2014, 2015 and 2016. The highest TP concentrations were measured in August. Sulfate concentrations were low at 5 mg/L. The average total iron concentrations measured in 2015 and 2016 were relatively low at 0.07 and 0.114 mg/L in East Rush Lake, and 0.06 and 0.065 mg/L in West Rush Lake, respectively (2016 data were corrected assuming mislabeling of one concentration unit as mg/L instead of µg/L in the report).

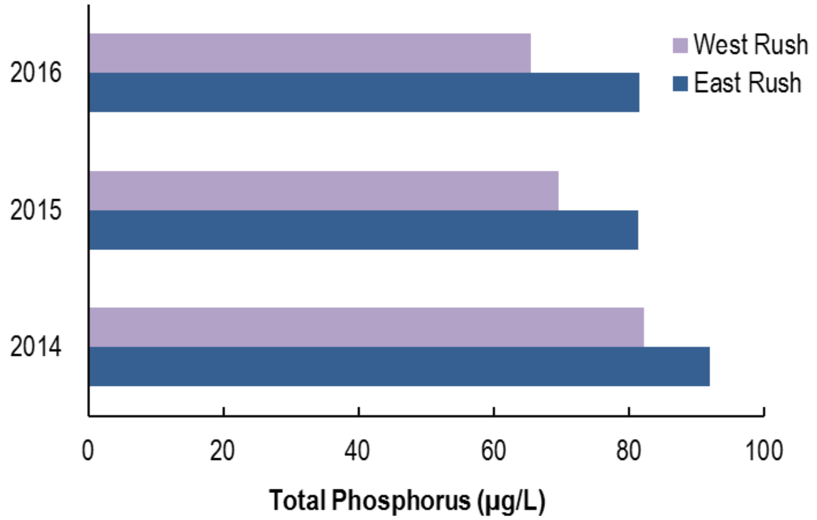


Figure 28. Total phosphorus water quality (June to Sep average) in Rush Lake in 2014 to 2016. (Data source: < http://www.chisagocounty.us/363/Water-Quality>).

Wright County SWCD's weekly monitoring of Ann Lake found that the lake water contained high TP and SRP concentrations in late summer 2016, and these concentrations gradually decreased through Fall (Figure 29). The dissolved oxygen (DO) profile indicated that the lake water column is generally mixed and oxic with 8 to 9 mg/L DO until 5 m (~16 ft) depth from September to December. The DO measurements indicate that the lake water becomes anaerobic with almost 0 mg/L at the lake bottom, although it is possible that the DO sonde is in close proximity of the sediment surface or in the sediments. Presence of a stratified water column was detected between June and August 2017 (Figure 29b).

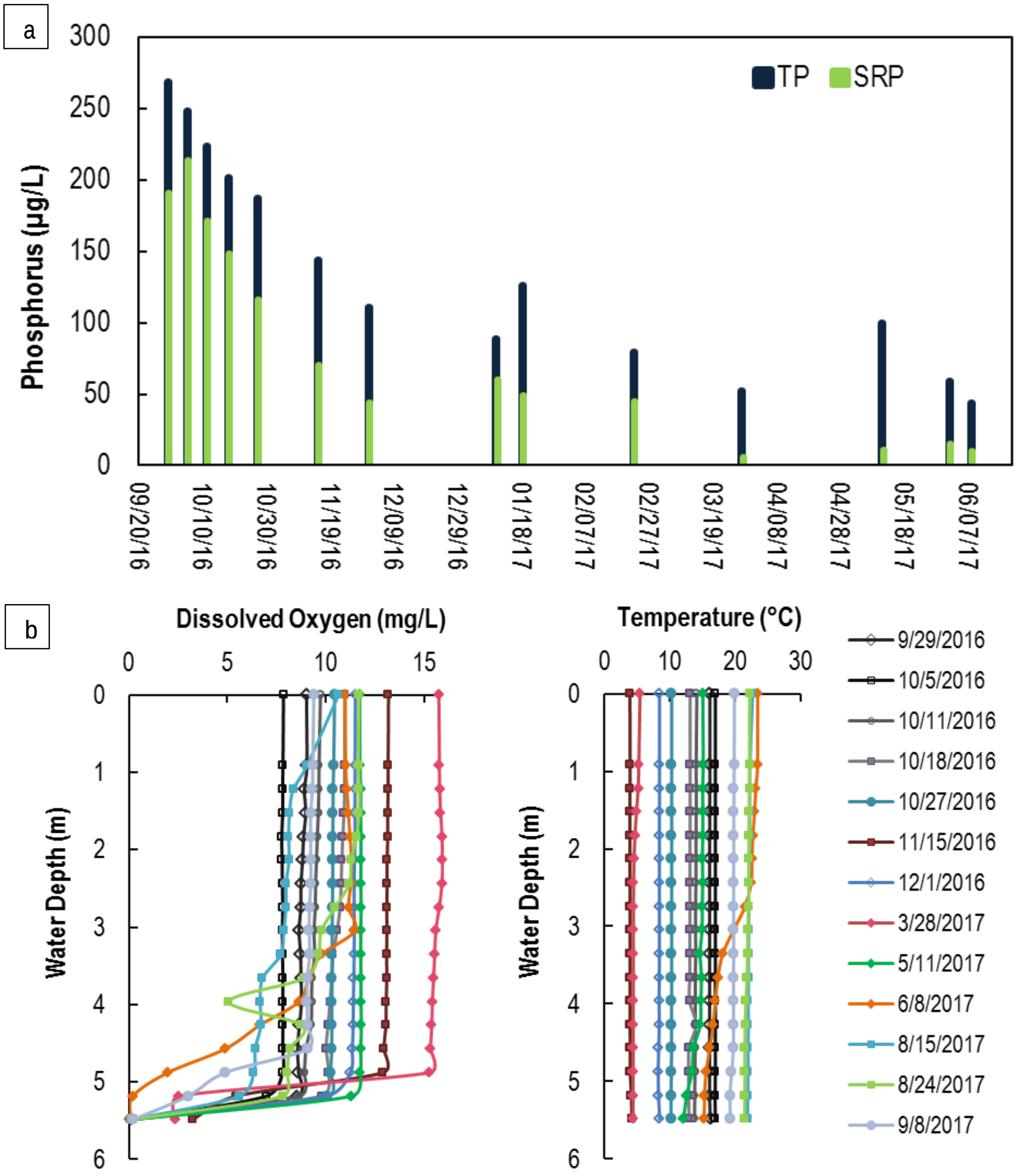


Figure 29. Ann Lake water quality in 2016 and 2017. (a) Total phosphorus (TP) and soluble reactive phosphorus (SRP) concentrations. (b) Dissolved oxygen and water temperature profiles. (Data source: D. Nadeau, Wright County SWCD).

The Rush Lake and Ann Lake monitoring sites have been established in the EQuIS system. Chisago County has been submitting the monitoring data for East and West Rush lake (Location_IDs 13006900-01 and 13006900-02) to EQuIS. The 2016-2017 data collected for Ann Lake has also been submitted to EQuIS (Location_ID 86-0190-00-201 under PRJ08059).

Estimated Internal Phosphorus Loading in Rush Lake and Ann Lake and Potential Impact of Iron Filings Application on P Load Reduction

Rush Lake and Ann Lake water quality monitoring data combined with the laboratory column studies indicate that internal phosphorus loading from anoxic sediments could be important in the two lakes and should be addressed to regulate the lake water quality and trophic status. Anoxic P release is expected to be more significant during summer stratification (~20 °C water temperature) than during winter (~4 °C water temperature), as observed in the laboratory mesocosms. Assuming the lake is mostly oxic during other times of the year, the summertime internal P loading was estimated as the most realistic scenario of annual P contribution from internal loading in West Rush Lake and Ann Lake (Table 10). The internal load calculation method was adapted from Total Maximum Daily Load (TMDL) studies (Wenck 2011; MPCA 2015) and literature (Steinman and Ogdahl 2005; Ogdahl et al. 2014).

First, the number of days (in summer) that an area similar to the lake surface area is actively releasing phosphorus from the sediment was calculated using a relation developed by Nürnberg (2004) based on an international dataset for 70 lakes:

$$Anoxic\ duration = -36.2 + 50.2\ log\ (TP_{summer}) + 0.762\ \frac{z}{A^{0.5}} \qquad (1)$$

where, TP_{summer} is the average TP in the epilimnion (µg/L), z is the mean lake depth (m), and A is the lake surface area (m^2). The June to September average TP of 75 µg/L for West Rush Lake (1998 to 2016 average; MPCA 2015 and Chisago County 2016) and 240 µg/L for Ann Lake (1995 to 2009 average; Wenck 2011) were used to estimate the duration of anoxia in Equation (1) for the two lakes. The experimentally-determined anoxic P release rate ($mg/m^2/day$) at 20 °C from this study was then used to calculate the P load from anoxic sediments as:

$$Anoxic\ P\ load = Anoxic\ duration \times Anoxic\ P\ release\ rate \times Lake\ surface\ area \qquad (2)$$

Oxic P load was computed by considering the oxic P release rate at 20 °C and oxic duration in the lake (122 summer days − Anoxic days predicted by Equation 1). The sum of the anoxic and oxic P loads yields the total summertime internal P loading in the lake.

Table 10. Estimated internal phosphorus loading in West Rush Lake and Ann Lake.

	West Rush Lake	Ann Lake
Surface area (km^2)	6.39	1.52
Average water depth (m)	3.87	3.04
Anoxic duration[1] (days)	59	85
Oxic duration (days)	63	37
Anoxic P release rate[2] (mg/m^2/day)	3.22	5.60
Oxic P release rate[2] (mg/m^2/day)	0.149	0.102
Estimated internal P load (kg/yr)	1269	728
External TP load[3,4] (kg/yr)	2036	2580
Internal load / External load	0.623	0.282

[1] Nürnberg (2004)
[2] P release rates at 20 °C from this study
[3] Wenck 2011; [4] MPCA (2015)

Internal P loading is estimated to be 1269 kg/yr (2978 lb/yr) in West Rush Lake and 728 kg/yr (1606 lb/yr) in Ann Lake. Comparison to the existing annual watershed phosphorus load (obtained from TMDL reports; Wenck 2011 and MPCA 2015) indicates that internal phosphorus loading is relatively significant in both lakes. Internal P load is 62% of the external P load in West Rush Lake, and the ratio is 28% in Ann Lake.

The laboratory sediment mesocosms amended with at least 0.05 g/cm^2 iron filings demonstrated zero net release of phosphate from the sediments to the water column under anoxic conditions. This means application of a similar iron filings dosage on the surface of sediments in West Rush Lake and Ann Lake could potentially eliminate the phosphorus load contributed by internal loading. For the surface area and maximum water depth, the approximate depth of summer mixed layer or thermocline is 6.0 m (~20 ft) in West Rush Lake and 5.1 m (~17 ft) in Ann Lake (Gorham and Dyce 1989; Fee et al. 1996). Assuming the lake becomes anaerobic in the areas deeper than the estimated mixed layer depth, iron filings application should target approximately 60% of West Rush Lake and 30% of Ann Lake surface area to reduce internal loading.

Major Conclusions and Recommendations on Iron Filings Application for Internal Phosphorus Load Reduction

The major findings and conclusions from the Rush and Ann Lake laboratory column studies on the application of iron filings to reduce internal phosphorus loading in lakes are summarized, as follows:

1) Natural, unamended sediments from Rush Lake and Ann Lake released phosphate (P) when the overlying water had low dissolved oxygen (i.e., under anoxic conditions). The mean P release rates were 3.22 mg/m^2/day in Rush Lake sediments and 5.60 mg/m^2/day in Ann Lake sediments at 20 °C. Such release rates have been measured in some mesotrophic and eutrophic lakes (Nürnberg 1988). Sediment P release under oxic conditions was generally low.
2) The intact sediment cores collected from Rush Lake exhibited variable anoxic P release rates for the five replicates used in this study. The existence of natural variation in lake sediment characteristics highlights the importance of using several sediment cores in the laboratory to calculate redox-sensitive P mass and quantify internal phosphorus loading.
3) Based on the summertime lake water monitoring and the laboratory mesocosm studies, phosphorus contribution from internal phosphorus release from anoxic sediments could potentially be important in Rush Lake and Ann Lake.
4) Temperature is a major factor affecting the magnitude of P release rate. The anoxic P release rate from the sediments at 20 °C was approximately five times the rate at 10 °C in Rush Lake, and four times in Ann Lake. The temperature dependence has implications on internal phosphorus loading with respect to lake depth (deep vs. shallow) and season.
5) Four dosages of zero-valent iron filings, 0.01, 0.05, 0.1, 1 g iron/cm^2 sediment area, were placed on the surface of the sediments with oxic overlying water. Under oxic conditions, all four iron dosages were effective in removing phosphate from the water column indicating that the Fe (III) oxides formed by iron filings acted to lower the water column P and prevent diffusive P flux from the sediment.
6) P release control under anoxic conditions was found to be dependent on the quantity of iron added since a clear iron dose-P release response was measured. Sediments amended with at least 0.05 g iron/cm^2 dose prevented P diffusion from the sediments and lowered P in the water column, even under anoxic conditions. A dose of 0.05 g/cm^2 is effective for low sulfate waters when applied in spring.
7) When the application of iron filings was done under anoxic water conditions at 20 °C, at least 0.1 g/cm^2 iron filings dose was required to impact the water quality and lower P flux from the sediments. This means a dose of greater than 0.1 g/cm^2 may be required if the lake is treated in summer to reduce internal phosphorus loading.
8) Sediment porewater profiles in iron-amended sediments confirmed the absence of available phosphorus (porewater phosphate) in the top 4 and up to 7 cm sediments. The mineral composition of these sediments include a mix of Fe, Fe(II) oxide, and Fe(III) oxide (oxyhydroxide). This means iron filings will continue to supply Fe^{2+} ions to precipitate phosphorus into minerals such as vivianite in reduced sediments.
9) The iron filings layer plays the role of a chemical barrier in the sediment; iron scavenges porewater and redox-sensitive phosphorus migrating upwards from deeper sediments, potentially transforms mobile P into unavailable P, suppresses P release across the sediment-

water interface, and reduces the net P mass in the overlying water. The effectiveness of iron filings amendment even during anoxic periods is one of the important findings of this study.

10) When sulfate concentrations are high in the water (100 mg/L in this study), unamended lake sediments released P at a rate roughly 1.5 times the rate for low sulfate waters (11 mg/L in this study) under anoxic conditions. Mobilization of P is increased due to excess sulfide that competes with phosphate for precipitation with Fe(II) in the anoxic sediments, and possibly due to decomposition of organic phosphorus.
11) An iron filings dose of 0.1 g/cm^2 or greater is required to reduce anoxic P release for high sulfate waters (100 mg/L in this study). Higher iron quantity may be required for higher sulfate/sulfide systems to keep up with the demand for sufficient iron supply for Fe-S-P cycling in the sediments.
12) Addition of iron filings to the sediments did not increase the water column pH above 9 during both oxic and anoxic periods.
13) This study has demonstrated that application of an appropriate dosing of iron filings will sequester phosphorus in lake sediments and control in-lake cycling of phosphorus from anoxic sediments. The iron addition technique has the potential to serve as an effective treatment measure for reducing internal phosphorus loading in eutrophic lakes.
14) Different iron materials were found to have different reactiveness to phosphorus in the batch tests conducted as part of this study. Therefore, a given iron sample must be evaluated before application for phosphorus treatment. A simple jar test, i.e., placing the iron material in water containing phosphorus, periodically shaking the jar, and measuring the phosphorus concentration reduction after 24 or 48 hours, can provide an estimate of the iron sample's potential to remove phosphorus. Additional chemical analysis to screen for the presence of impurities including toxic trace metals in the iron material is strongly recommended. Material availability, material costs and particle size suitable for the given treatment application are some of criteria to be considered before final selection.

Products

This report is the primary product and final deliverable under the contract. The description of the work completed, data collected, results and applications have been provided in the report. As requested, an electronic summary of lake water quality monitoring data collected by the project partners has been/will be provided for the EQuIS database. In addition, at least two peer-reviewed journal publications will be published using data from this project.

Photos

Several photos are provided in this Final Report.

Long-term Results

Long-term Outcomes

High internal loading of phosphorus occurs in many watersheds and is a difficult problem to solve in lakes. This project focused on external addition of iron filings to lake sediment surface as an action designed to augment the iron supply for sequestering phosphorus in the sediments and address internal phosphorus loading. Recommendations on the type of iron, quantity of iron filings needed and the conditions under which the iron dosing would be effective have been developed in this project. Iron filings application has the potential to reduce non-point source pollution of phosphorus released by lake sediments throughout the state. With numerous lakes that experience internal phosphorus loading in Minnesota, the potential impact is substantial.

Partnerships and Alliances

This project involved partnership between the Minnesota Pollution Control Agency, Chisago County, Wright County SWCD, Rush Lake Improvement Association, Ann Lake Association, and the University of Minnesota St. Anthony Falls Laboratory (SAFL). It is anticipated that the findings from this project and dissemination of its results will lead to new partnerships with organizations interested in treatment of lakes with significant internal phosphorus loading. It is expected that application of iron filings to solve internal phosphorus loading and eutrophication problems in lakes will be of interest to lake associations and lake managers in the County and Watershed District level.

Sharing of Results

Results were disseminated through a public seminar hosted by the St. Anthony Fall Laboratory in April 2017, and through a poster presentation at the Association of Environmental Engineering & Science Professors (AEESP) Conference in June 2017. Oral presentations will be given at the MN Water Resources Conference in October 2017 and the North American Lake Management Society (NALMS) Conference in November 2017.

Section III – Final Expenditures

The project was completed on time and within budget. The Final Expenditures can be found in a separate spreadsheet document listing individual Objectives, Tasks, and line items categories.

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Appendix A – Phosphate Release Data Plots

Rush Lake Laboratory Column Data

The plots show the measured mass of phosphate (SRP) in the water column (P concentration × water column volume) above the sediments in the five replicates belonging to a set of columns used in the Rush Lake laboratory column studies. Control sediments were not dosed with iron. High iron-dosed columns received cumulative dose of 0.1 g/cm^2 iron filings. Very high iron-dosed columns received cumulative dose of 1 g/cm^2 iron filings. Explanation of the step addition of iron to the sediments is provided in the 'Laboratory Column Studies' section under 'Measurements'.

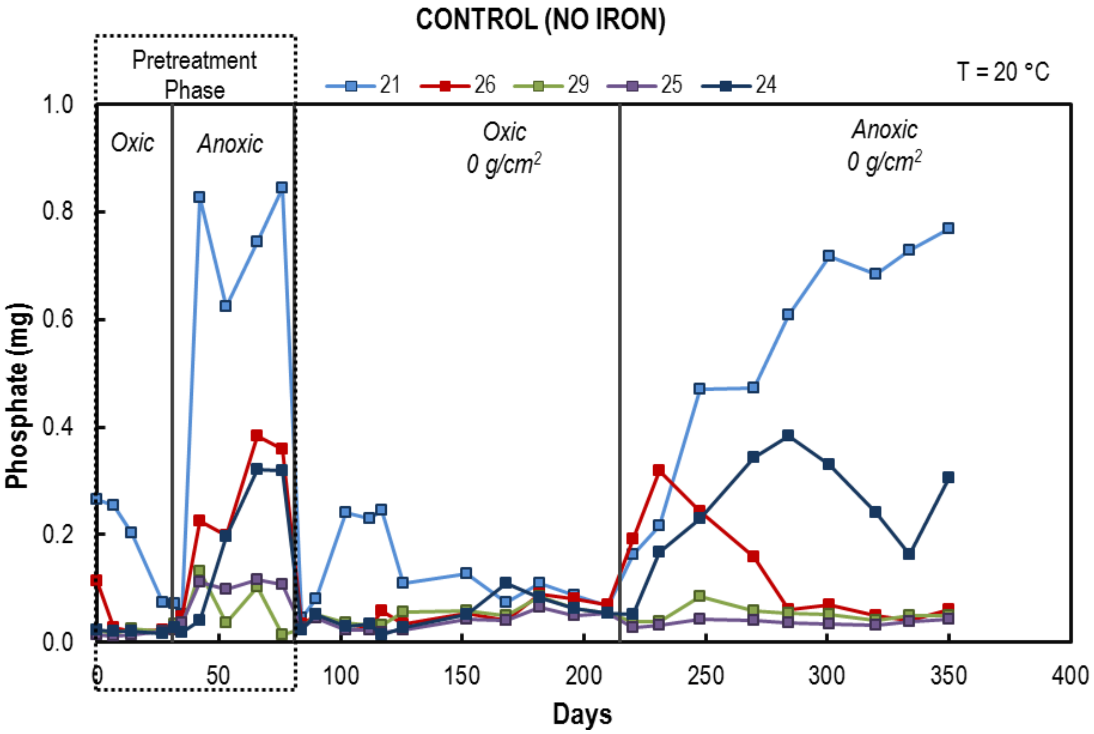

Figure 30. Water column phosphate measured in five control columns of Rush Lake at 20 °C. No iron was added to the sediments. Legend shows number assigned to label columns.

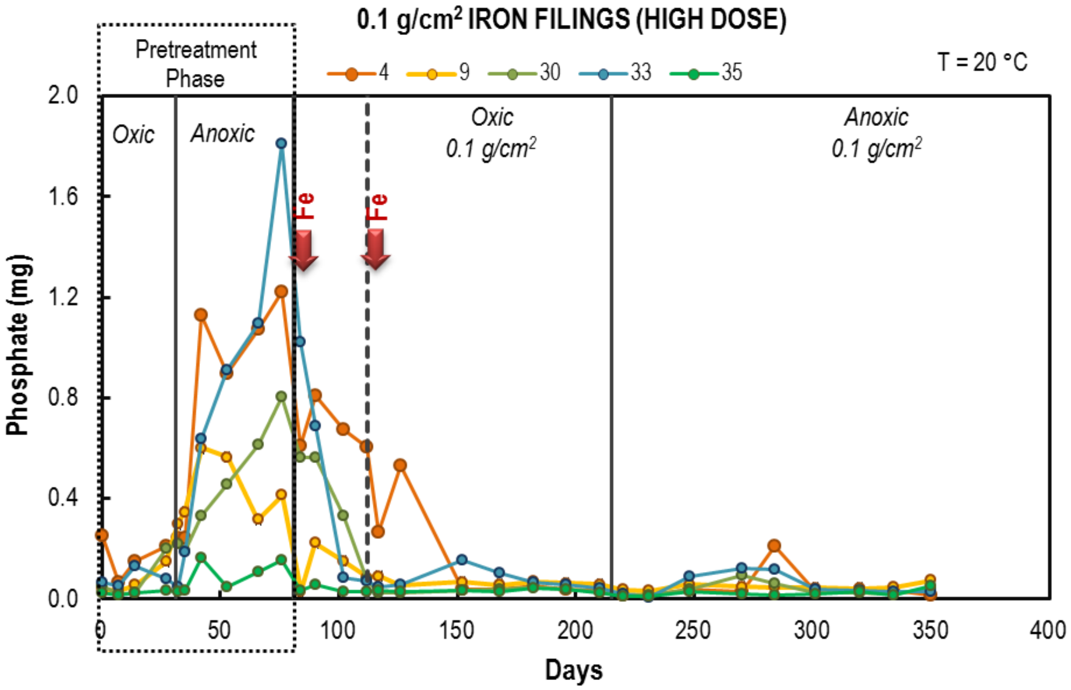

Figure 31. Water column phosphate measured in five Rush Lake columns amended with 0.1 g/cm² iron filings (high dose) at 20 °C. The 0.1 g/cm² iron dose was added to the sediments in two steps. Legend shows number assigned to label columns.

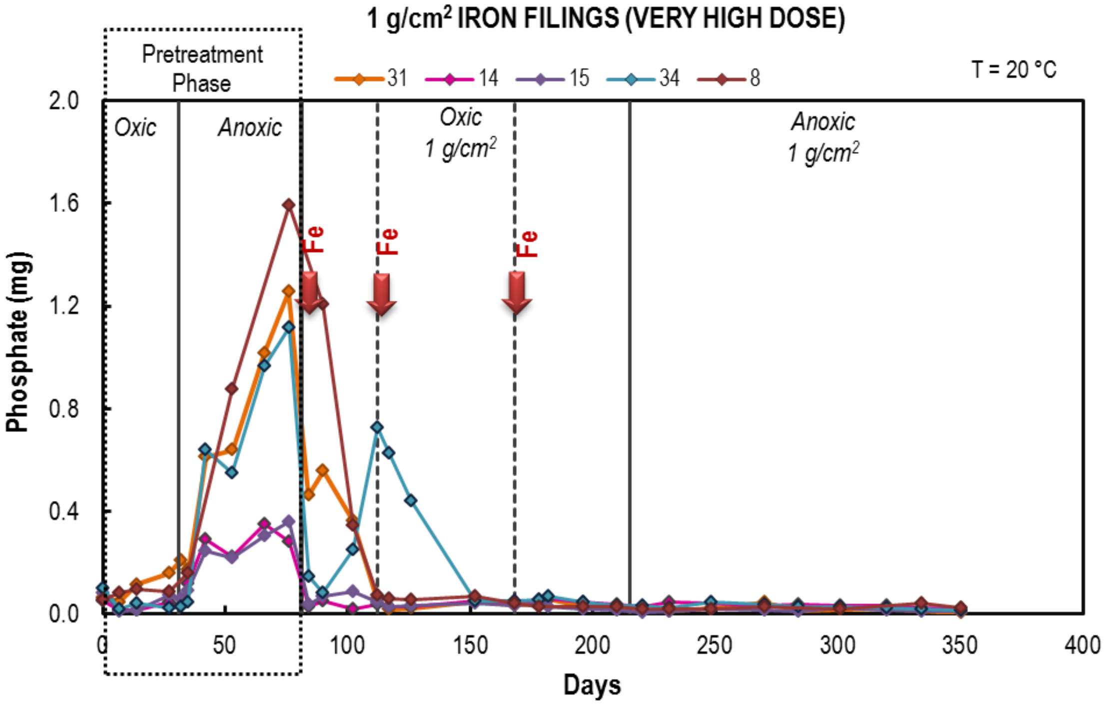

Figure 32. Water column phosphate measured in five Rush Lake columns amended with 1 g/cm² iron filings (very high dose) at 20 °C. The 1 g/cm² iron dose was added to the sediments in three steps. Legend shows number assigned to label columns.

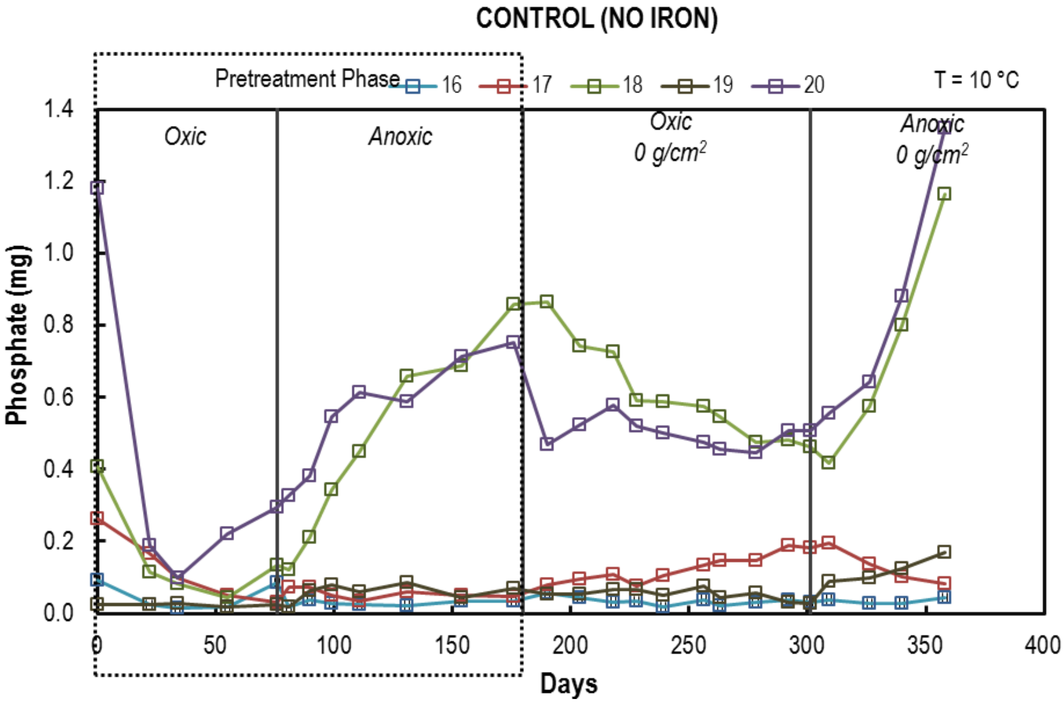

Figure 33. Water column phosphate measured in five control columns of Rush Lake at 10 °C. No iron was added to the sediments. Legend shows number assigned to label columns.

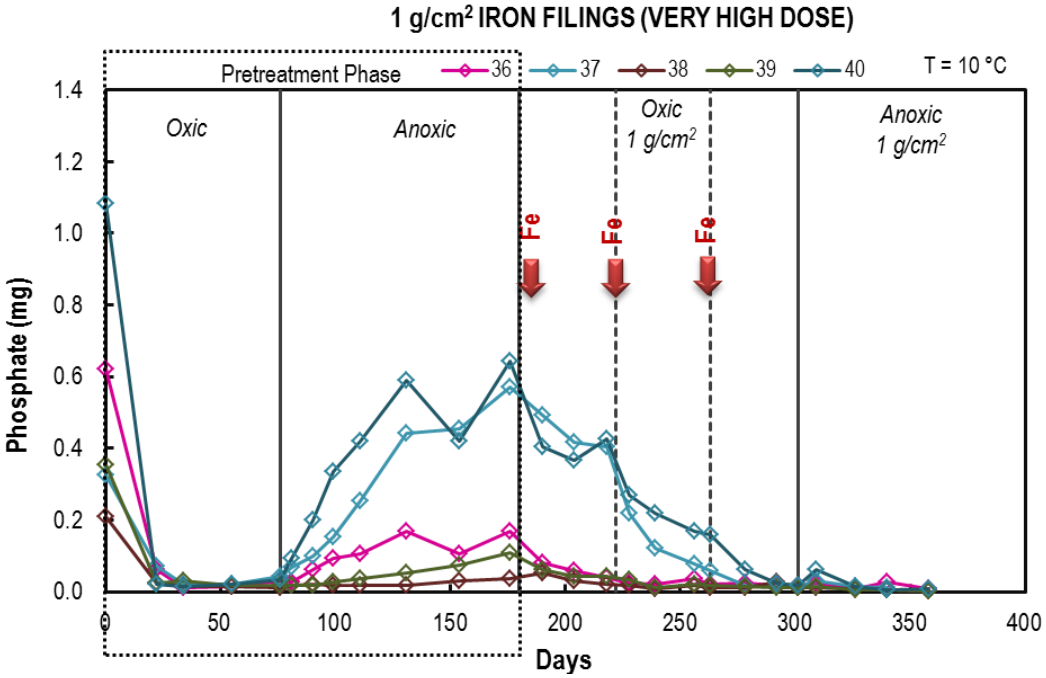

Figure 34. Water column phosphate measured in five Rush Lake columns amended with 1 g/cm^2 iron filings (very high dose) at 10 °C. The 1 g/cm^2 iron dose was added to the sediments in three steps. Legend shows number assigned to label columns.

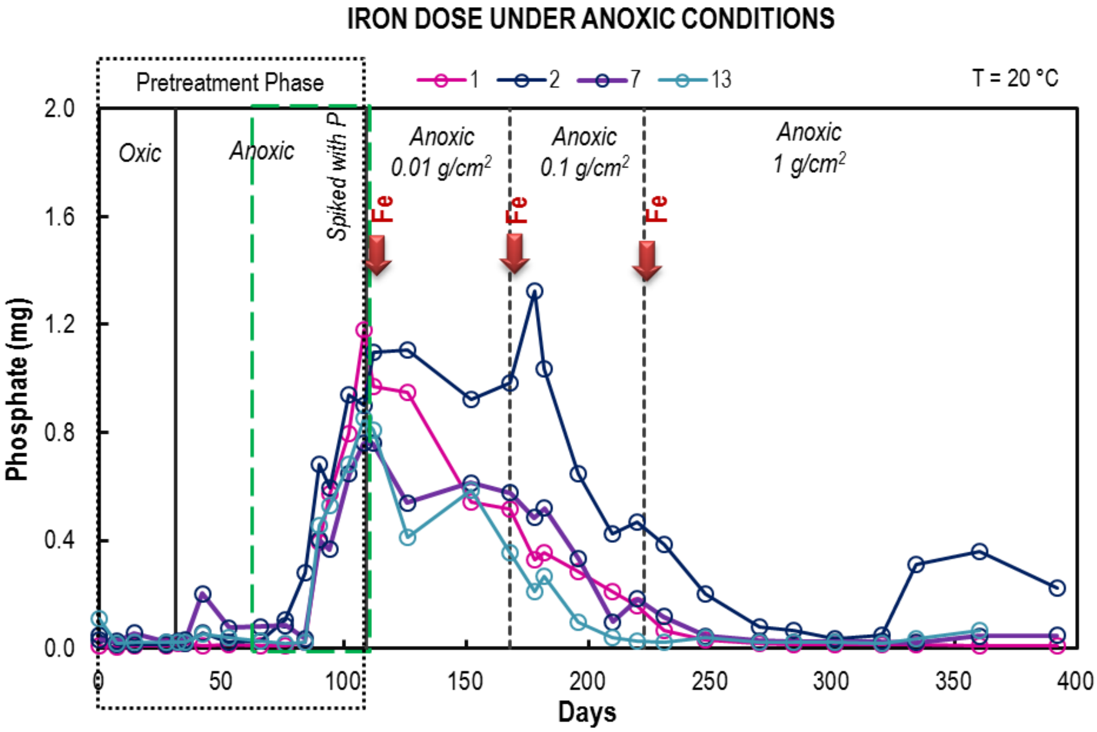

Figure 35. Water column phosphate measured in four Rush Lake columns dosed with iron filings under anoxic conditions at 20 °C. The 0.01, 0.1 and 1 g/cm^2 iron doses were added to the sediments in steps. Legend shows number assigned to label columns.

Ann Lake Laboratory Column Data

The plots show the measured mass of phosphate (SRP) in the water column above the sediments in the five replicates belonging to a set of columns used in the Ann Lake laboratory column studies. Control sediments were not dosed with iron. Low iron-dosed columns received 0.01 g/cm^2 iron filings, medium iron-dosed columns received 0.05 g/cm^2 iron filings, and high iron-dosed columns received 0.1 g/cm^2 iron filings.

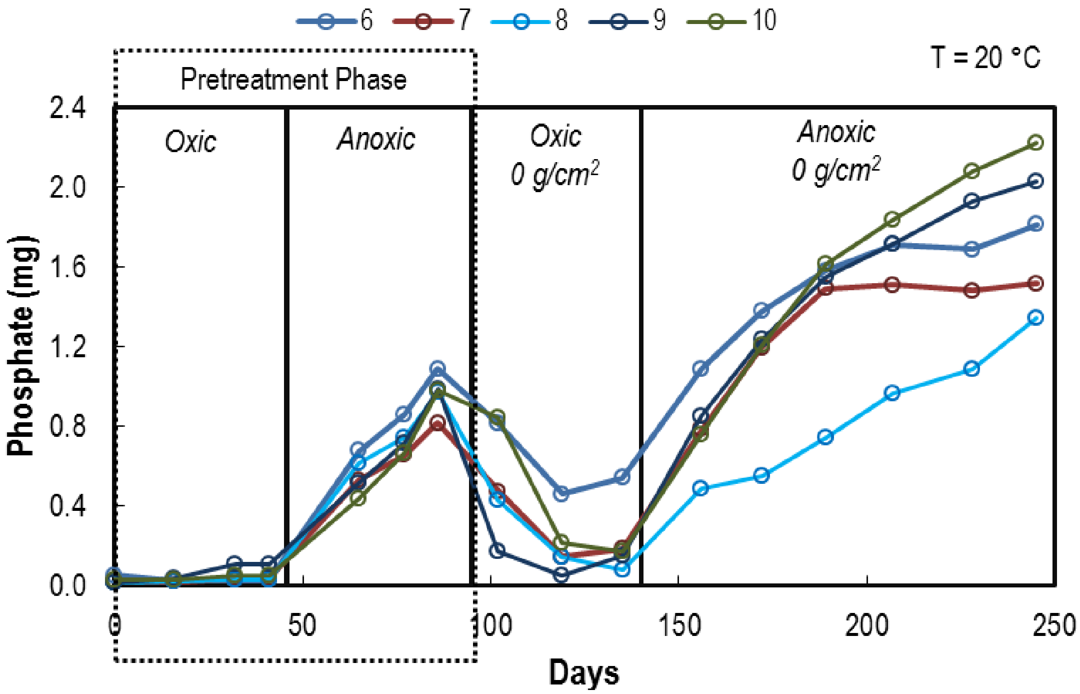

Figure 36. Water column phosphate measured in five replicate control columns of Ann Lake at 20 °C. No iron was added to the sediments. Legend shows number assigned to label columns.

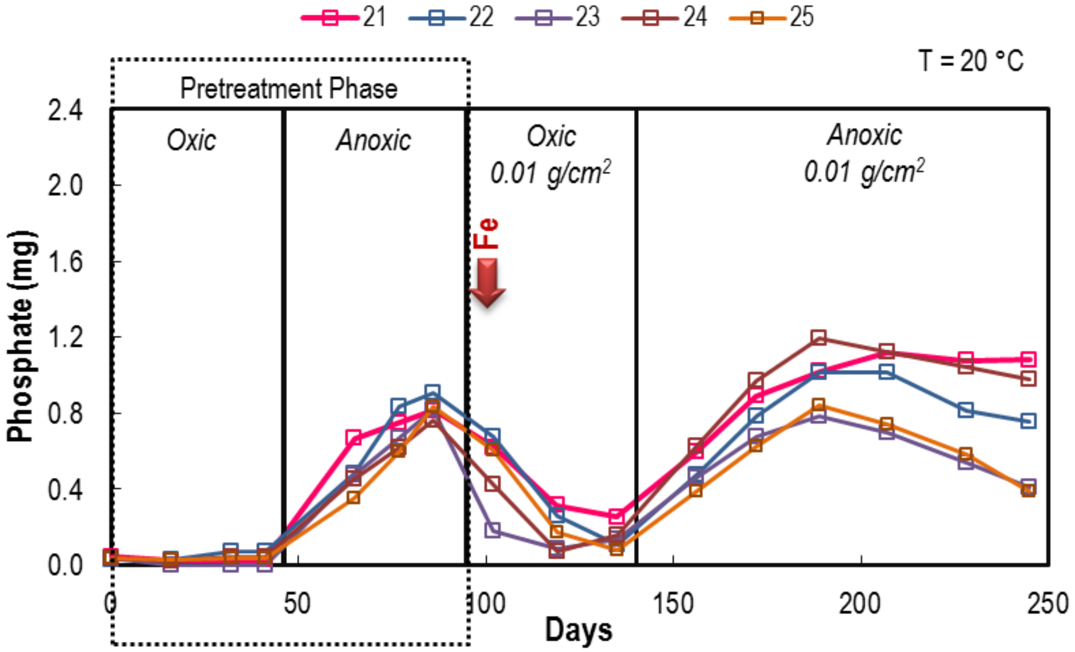

Figure 37. Water column phosphate measured in five replicate Ann Lake columns amended with 0.01 g/cm^2 iron filings (low dose) at 20 °C. Legend shows number assigned to label columns.

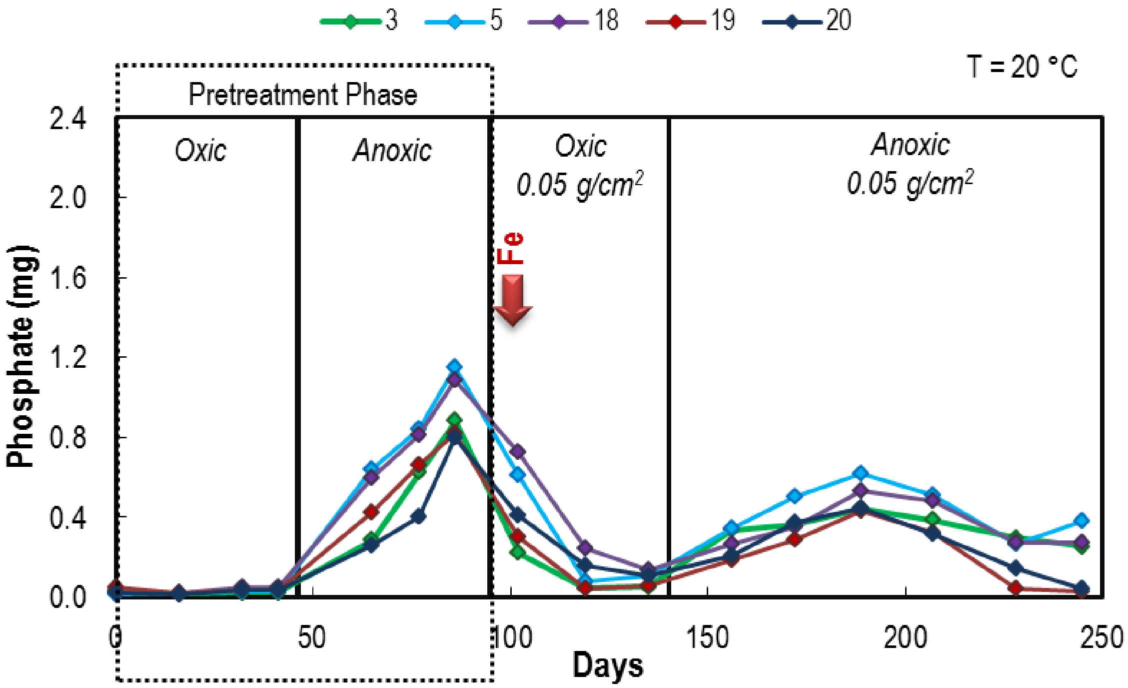

Figure 38. Water column phosphate measured in five replicate Ann Lake columns amended with 0.05 g/cm^2 iron filings (medium dose) at 20 °C. Legend shows number assigned to label columns.

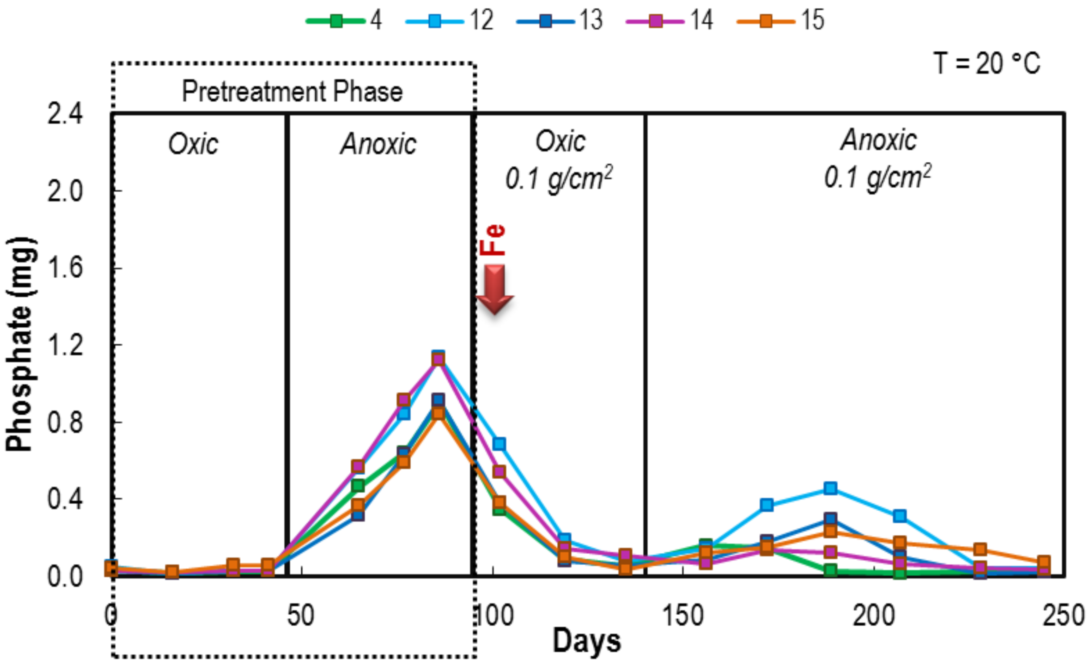

Figure 39. Water column phosphate measured in five replicate Ann Lake columns amended with 0.1 g/cm^2 iron filings (high dose) at 20 °C. Legend shows number assigned to label columns.

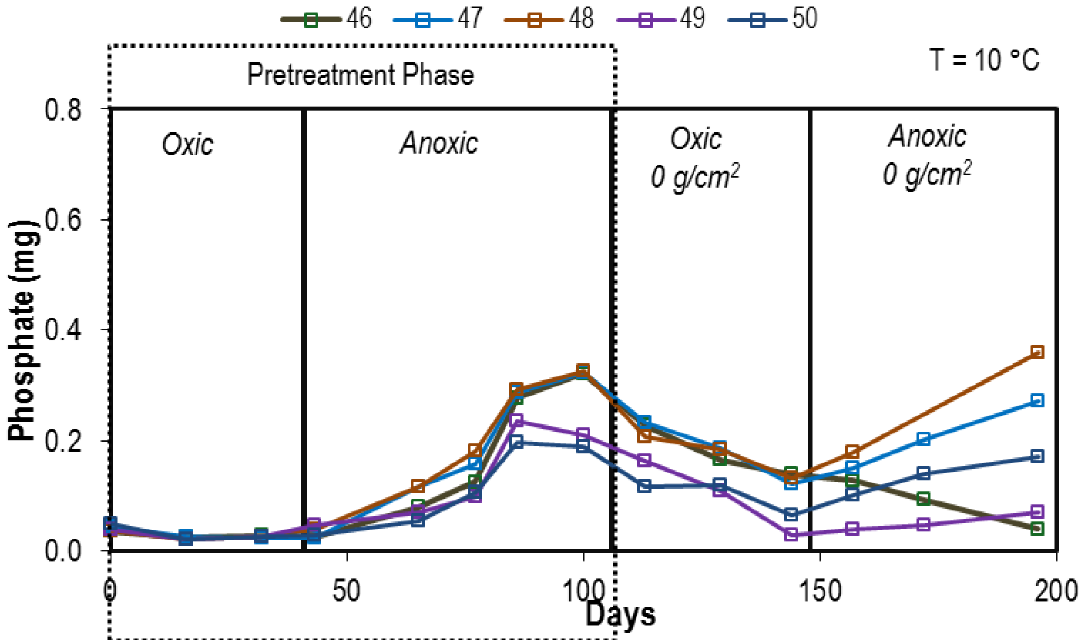

Figure 40. Water column phosphate measured in five replicate control columns of Ann Lake at 10 °C. No iron was added to the sediments. Legend shows number assigned to label columns.

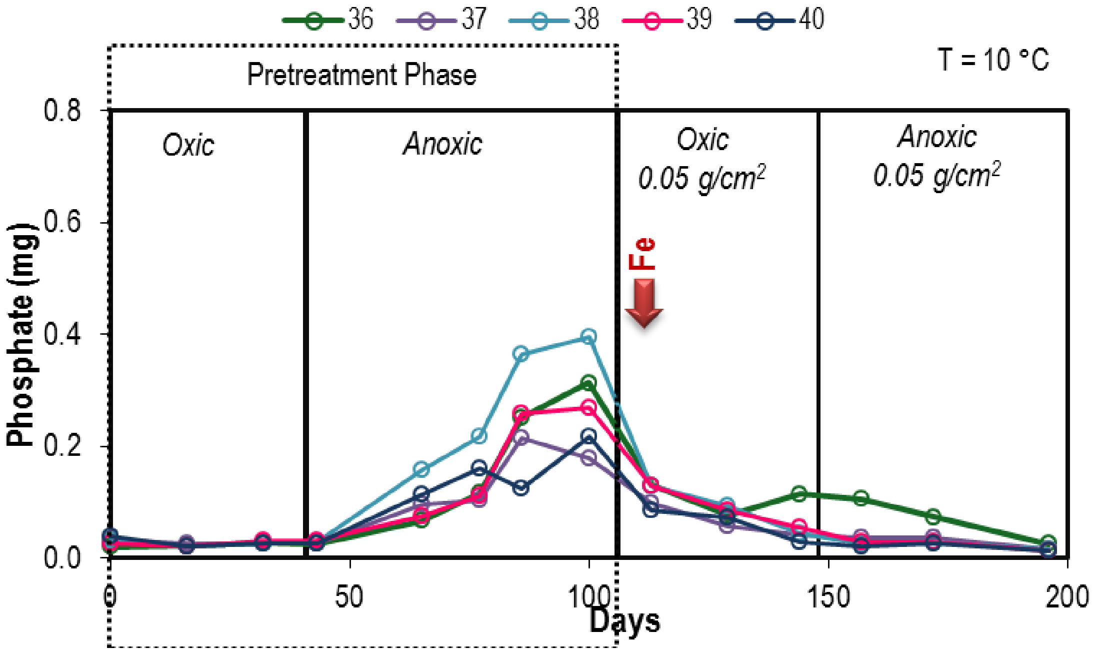

Figure 41. Water column phosphate measured in five replicate Ann Lake columns amended with 0.1 g/cm^2 iron filings (medium dose) at 10 °C. Legend shows number assigned to label columns.

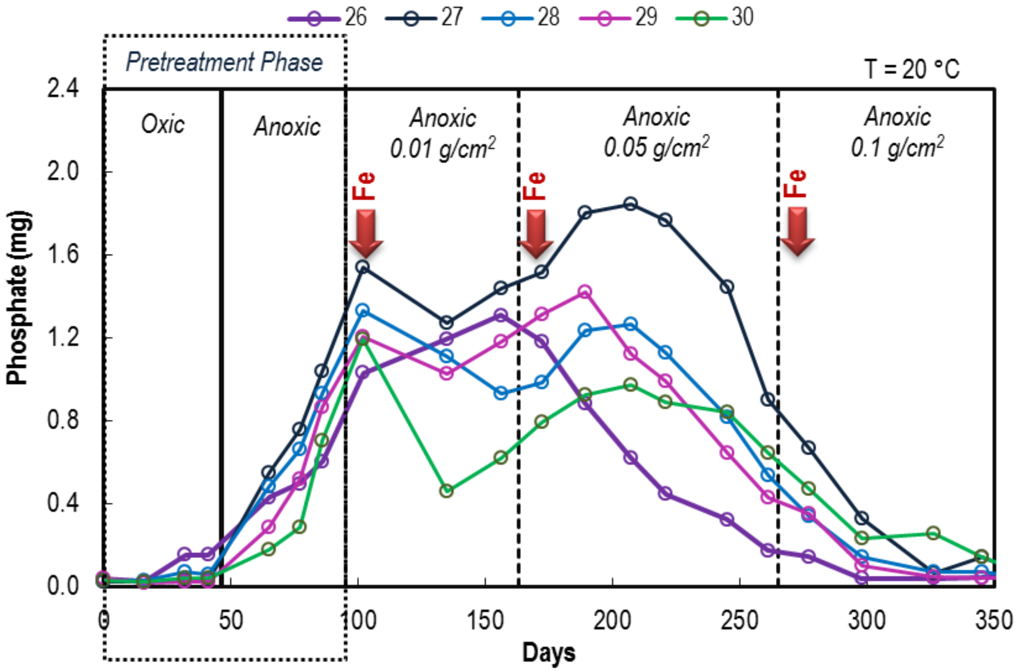

Figure 42. Water column phosphate measured in five replicate Ann Lake columns dosed with iron filings under anoxic conditions at 20 °C. The 0.01, 0.05 and 0.1 g/cm^2 iron doses were added to the sediments in steps. Legend shows number assigned to label columns.

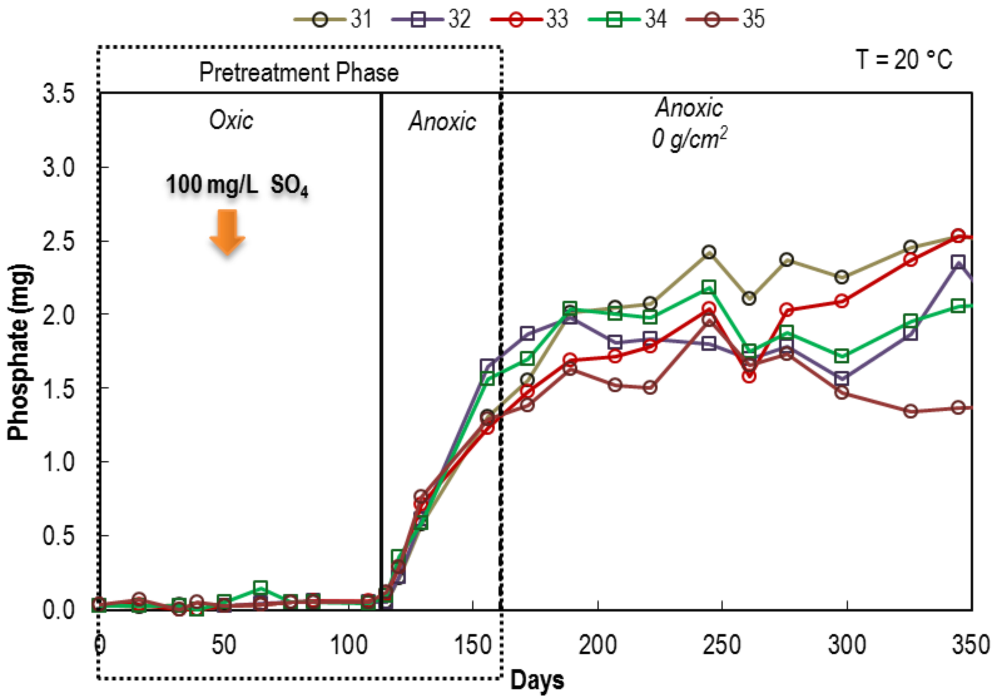

Figure 43. Water column phosphate measured in five replicate control columns of Ann Lake containing high sulfate water at 20 °C. No iron was added to the sediments. Legend shows number assigned to label columns.

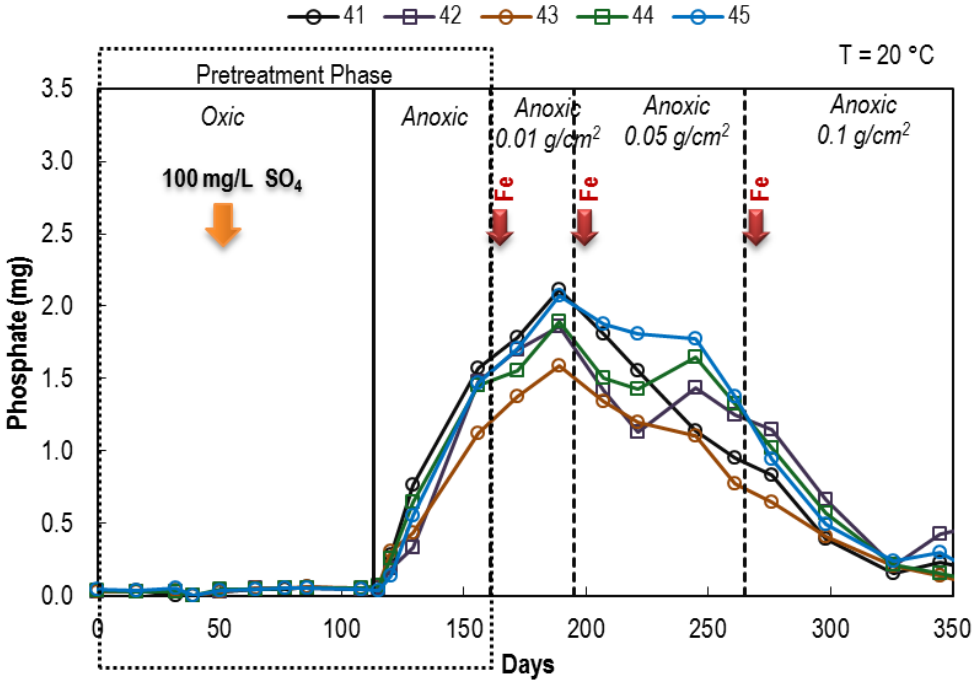

Figure 44. Water column phosphate measured in five replicate columns of Ann Lake containing high sulfate water and amended with iron filings at 20 °C. The 0.01, 0.05 and 0.1 g/cm^2 iron doses were added to the sediments in steps. Legend shows number assigned to label columns.

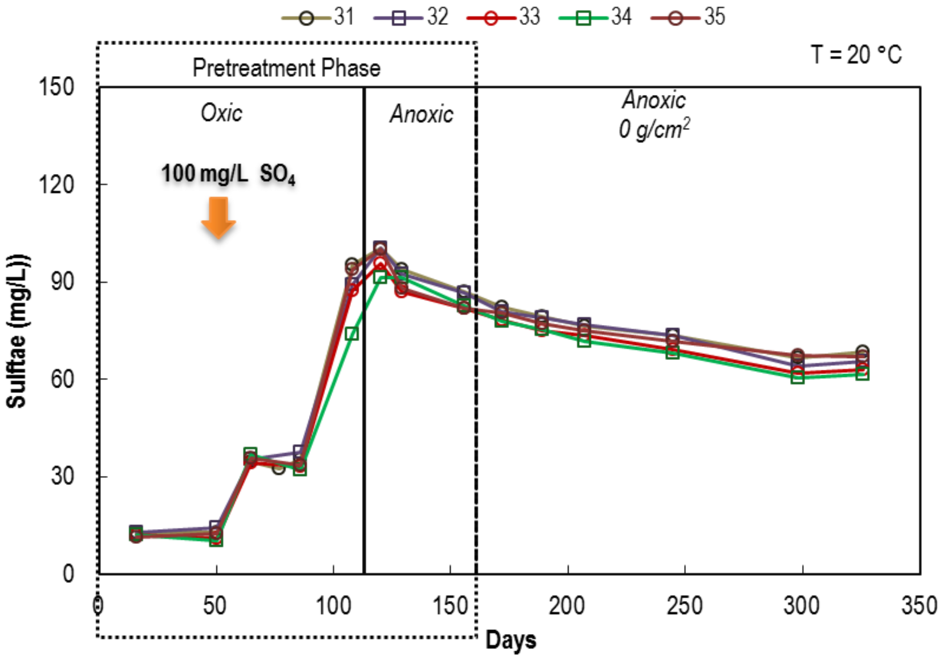

Figure 45. Sulfate concentrations in the water column in five replicate control columns of Ann Lake at 20 °C. No iron was added to the sediments. Legend shows number assigned to label columns.

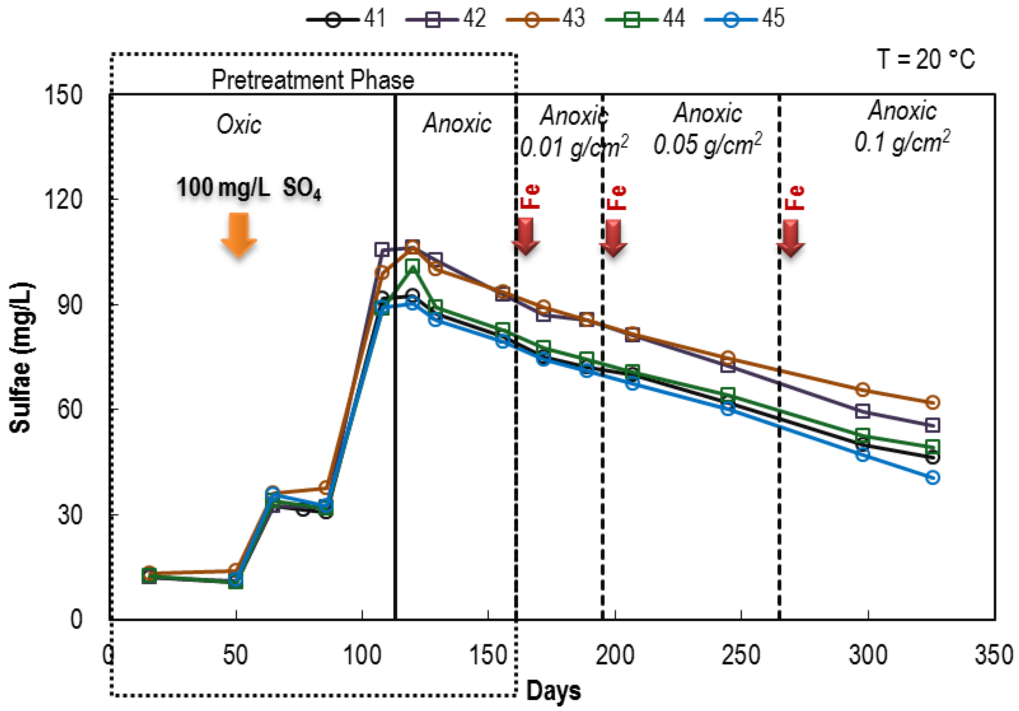

Figure 46. Sulfate concentrations in the water column in five replicate Ann Lake columns amended with iron filings at 20 °C. Legend shows number assigned to label columns.