



*Diffusive Phosphorus Flux
and Sediment Characteristics in
Big Traverse, Lake of the Woods*

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SUMMARY

Replicate intact sediment cores collected at a station located in the eastern of basin of Big Traverse Lake (48.92182 -94.72825) of the Lake of the Woods (LOTW) in July and late August, 2014, and February and late May, 2015, were incubated at 18 °C, 25 °C, 5 °C, and 11 °C, respectively, under aerobic or anaerobic conditions for laboratory determination of diffusive phosphorus (P) flux. The objectives were to develop regression relationships between temperature and P flux for more accurately quantifying and predicting internal P loading in Big Traverse Lake and other basins in LOTW. Under aerobic and anaerobic conditions, mean diffusive P fluxes increased in an exponential pattern as a function of temperature. Fluxes were greatest under anaerobic conditions, ranging between 0.8 mg/m² d (\pm 0.13 standard error, SE) at the lowest temperature (5 °C) to the 16.8 mg/m² d (\pm 2.2 SE) at 25 °C. Diffusive P fluxes quantified under summer temperature conditions (i.e., 18 °C to 25 °C) fell within to above the upper 25% quartile compared to anaerobic P fluxes determined for other Minnesota Lakes. Under aerobic conditions, mean diffusive P fluxes varied between 0.05 mg/m² d (0.01 SE) at 5 °C and 0.36 mg/m² d (0.06 SE) at 25 °C. Summer aerobic diffusive P fluxes for Big Traverse Lake sediment were moderate and fell near the median relative to P fluxes measured for other Minnesota Lake sediments.

The mean total P concentration in the upper 5-cm sediment layer was moderate at \sim 0.78 mg/g (\pm 0.012 SE). Biologically-labile P (i.e., the sum of the loosely-bound P, iron-bound P, and labile organic P fractions; subject to recycling and diffusive P flux to the overlying water column) accounted for \sim 45% (0.354 mg/g), while biologically-refractory P (i.e., aluminum-bound P, calcium-bound P, and refractory organic P; relatively inert to recycling and subject to burial) represented \sim 55% (0.427 mg/g) of the sediment total P. Iron-bound P (i.e., P bound to iron oxyhydroxides; active in diffusive P flux under anaerobic and reducing conditions) was the dominant biologically-labile P fraction (\sim 61%). The mean iron-bound P concentration was moderate at 0.214 mg/g (\pm 0.011 SE). Mean labile organic P (i.e., cellular polyphosphates and readily mineralized organic P)

and loosely-bound P (i.e., porewater P and P loosely adsorbed to calcite) accounted for ~ 37% ($0.129 \text{ mg/g} \pm 0.005 \text{ SE}$) and 3% ($0.010 \text{ mg/g} \pm 0.002 \text{ SE}$) of the biologically-labile P fraction, respectively. Calcium-bound P was the dominant biologically-refractory fraction at 59% ($0.254 \text{ mg/g} \pm 0.006 \text{ SE}$). Overall, concentrations of most P fractions in Big Traverse Lake sediments were moderate compared to other lake sediments in the State of Minnesota. In addition, concentrations were greater in the 0 – 5 cm than the 5 – 10 cm section, suggesting the accumulation of potentially-mobile P fractions at the sediment water interface in excess of burial and diagenesis.

Vertical sediment profiles of total P, biologically-labile P, and redox-sensitive P (i.e., the sum of the loosely-bound P and iron-bound P fractions), determined from a sediment core collected in late August, 2014, exhibited modest concentration peaks in the upper 5- to 6-cm sediment layer and lower concentrations below this depth. This vertical pattern suggested that surface sediment in the eastern region of Big Traverse Lake has accumulated P in excess of diagenesis and burial (i.e., gross P deposition > diagenesis and burial). Surface peaks reflected elevated concentrations of iron-bound P and labile organic P, suggesting the potential for internal P loading. In contrast, more biologically-inert aluminum-bound and calcium-bound P concentrations were relatively constant with sediment depth over the upper 30-cm sediment profile and did not explain surface layer pattern. Overall, total P, biologically-labile P, and redox-P concentrations were 0.834 mg/g, 0.375 mg/g, and 0.237 mg/g, respectively, in the upper 1-cm and a mean 0.596 mg/g, 0.179 mg/g, and 0.120 mg/g, respectively, below the 5-cm depth.

Experimental estimates of diffusive P flux and vertical P profiles from sediment collected in the eastern portion of Big Traverse Lake suggested that sediment is likely a moderate source of internal P loading. More information is needed on bottom water temperature, dissolved oxygen, and redox dynamics as well as water column mixing and exchange in order to both predict and better understand the role and magnitude of internal P loading contributions within the context of an overall P budget. Vertical sediment P profiles also suggested that past P accumulation has exceeded diagenesis and burial, resulting in the

modest buildup of P that may drive future internal P loading.

OBJECTIVES

Diffusive phosphorus (P) flux from sediment may play an important role in driving excessive cyanobacterial blooms in the Lake of the Woods (LOTW) and needs to be considered in Total Maximum Daily Load (TMDL) development. Previous research in the southern basin (James 2012) indicated that diffusive P fluxes from sediment under aerobic conditions were moderate at 0.2 to 0.6 mg/m² d under summer temperature conditions (20° C). However, it is not known at this point how these sediment internal P loading inputs fit into an overall P budget that quantifies tributary total and soluble P loading as well as sediment P loading to LOTW. Since basins in the LOTW system are generally large and shallow, aerobic conditions may prevail at the sediment-water interface most of the time due to frequent mixing and regulate redox conditions at the sediment-water interface.

This research fills important knowledge gaps to the P budget and empirical modeling of LOTW by assessing the variation in diffusive P fluxes and sediment P pools in Big Traverse Bay seasonally and as a function of temperature. Examination of diffusive P fluxes versus temperature and redox condition will provide modelers with an empirical relationship that can be used to better estimate internal P loading. These relationships will also be important in predicting temperature- and redox-related changes in diffusive P flux due to climate change. Overall, this research provides important supporting data for Phase II of the Historical Nutrient Budget: Thermal Modeling.

Additionally, vertical variations in the concentration of biologically-labile sediment P fractions (i.e., loosely-bound, iron-bound, and labile organic P fractions that are active in internal P loading) provide important information regarding ecosystem balances between P sedimentation and eventual burial and removal from recycling. For instance, Carey and Rydin (2011) contrasted vertical P distribution in sediments of oligotrophic versus

eutrophic systems and found that a peak in sediment P occurred at the sediment surface in eutrophic lakes, suggesting that P burial and diagenetic processes were not in balance with sedimentation of new P. Analysis of variations in sediment P fractions as a function of depth in the sediment column will provide important information on the extent to which sediment processes are at a tipping point with regards to internal P loading and if higher P concentrations at the sediment surface will translate into release during sediment re-suspension.

The goals of this research are to determine: 1) temperature and redox-related variations in diffusive P fluxes and 2) vertical variations in mobile P concentrations in the sediment column of Big Traverse Bay in order to better understand the role of internal P loading to the P economy of LOTW and for the development of the LOTW TMDL.

METHODS

Sampling location and experimental approach

Intact sediment cores (~ 30 cm in length) were collected from a centrally-located station in the eastern basin of Big Traverse Bay in July and late August, 2014, and February and May, 2015, to examine temperature-driven and seasonal variations in diffusive P flux and surface sediment characteristics (Fig. 1 and Table 1). A gravity coring device (Aquatic Research Instruments; Hope, ID), equipped with an acrylic core liner (6.5-cm ID and 50-cm length), was used to collect sediment. Cores were transported vertically on ice and covered to prevent light exposure to the University of Wisconsin – Stout within 24 to 36 hours for sectioning and processing.

Diffusive phosphorus flux

Methods for determining diffusive P flux from intact sediment cores were according to James (2010). Twelve replicate cores were collected on each date for replicate

determination of rates of diffusive P flux under aerobic (6 replicates) and anaerobic (6 replicate) conditions. In the laboratory, sediment cores were carefully drained of overlying water and the upper 10 cm of sediment was transferred intact to a smaller acrylic core liner (6.5-cm dia and 20-cm ht) using a core extruder. The additional lake water, collected at the sampling location in Big Traverse Bay, was filtered through a glass fiber filter (Gelman A-E) and 300 mL was siphoned onto the sediment contained in the small acrylic core liner without causing sediment resuspension. Sediment incubation systems consisted of the upper 10-cm of sediment and filtered overlying water contained in acrylic core liners that were sealed with rubber stoppers. The sediment incubation systems were placed in a darkened environmental chamber and incubated at a seasonally appropriate temperature, depending on collection date. Incubation temperatures were 18 °C for July, 2014, 25 °C for late August, 2014, 5 °C for February, 2015, and 11 °C for May, 2015. The oxidation-reduction environment in the overlying water of each system was controlled by gently bubbling either air (oxic or aerobic) or nitrogen (anoxic or anaerobic) through an air stone placed just above the sediment surface. Bubbling action insured complete mixing of the water column but did not disrupt the sediment. Anoxic conditions were verified using a dissolved oxygen electrode.

Water samples for soluble reactive phosphorus (SRP) were collected from the center of each sediment incubation system using an acid-washed syringe and immediately filtered through a 0.45 µm membrane syringe filter. The water volume (10 mL) removed from each system during sampling was replaced by addition of filtered lake water preadjusted to the proper oxidation-reduction condition. These volumes were accurately measured to account for dilution effects. SRP was determined colorimetrically using the ascorbic acid method (APHA 2005). Rates of diffusive P flux from deposited sediment ($\text{mg/m}^2 \text{ d}$) were calculated as the linear change in concentration in the overlying water divided by time and the area of the incubation core liner.

Sediment characteristics

On each sampling date, an additional 6 replicate sediment cores were collected at the Big Traverse Bay station to quantify seasonal variations in sediment textural characteristics and biologically-labile (i.e., subject to recycling) and refractory (i.e., low recycling potential and subject to burial) P fractions in the upper 0 – 5 cm and 5 – 10 cm sections. For examination of vertical variations, a sediment core collected in late August, 2014, was sectioned at 1-cm intervals over the upper 6 cm, 2-cm intervals between 8 and 10 cm, 2.5-cm intervals between 10 and 20 cm, and 5-cm intervals between 20 and 30 cm.

A known volume of sediment was dried at 105 °C for determination of moisture content and sediment wet and dry bulk density and burned at 550 °C for determination of loss-on-ignition organic matter (Avnimelech et al. 2001, Håkanson and Jansson 2002). Porosity (i.e., percent interstitial volume for porewater) was estimated via calculation according to Avnimelech et al. (2001). Sequential P fractionation was conducted according to Hieltjes and Lijklema (1980), Psenner and Puckso (1988), and Nürnberg (1988) for the determination of ammonium-chloride-extractable P (loosely-bound P), bicarbonate-dithionite-extractable P (i.e., iron-bound P), sodium hydroxide-extractable P (i.e., aluminum-bound P), and hydrochloric acid-extractable P (i.e., calcium-bound P; Table 2). A subsample of the sodium hydroxide extract was digested with potassium persulfate to measure nonreactive sodium hydroxide-extractable P (Psenner and Puckso 1988). Labile organic P was calculated as the difference between reactive and nonreactive sodium hydroxide-extractable P. Residual P was estimated as the difference between sediment total P and the sum of the other measured fractions.

The loosely-bound and iron-bound P fractions are readily mobilized at the sediment-water interface as a result of anaerobic conditions that lead to desorption of P from sediment and diffusion into the overlying water column (Mortimer 1971, Boström 1984, Nürnberg 1988; Table 2). The sum of the loosely-bound and iron-bound P fraction represents redox-sensitive P (i.e., the P fraction that is active in P release under anaerobic and reducing conditions; redox-P). In addition, labile organic P can be converted to

soluble P via bacterial mineralization or hydrolysis of bacterial polyphosphates to soluble phosphate under anaerobic conditions (Gächter et al. 1988, Gächter and Meyer 1993, Hupfer et al. 1995). The sum of redox-P and labile organic P collectively represent biologically-labile P. This fraction is active in recycling pathways that result in exchanges of phosphate from the sediment to the overlying water column and potential assimilation by algae. In contrast, aluminum-bound P, calcium-bound P, and residual P are more chemically inert and subject to burial rather than recycling (Table 2).

Additional sediment was dried and ground for determination of total P and total iron (Fe; expressed as mg/g dry mass). A known mass of sediment was burned at 550 °C and digested in 1 N HCl at 110 °C prior to colorimetric determination for sediment total P (Andersen 1976, Ostrofsky 2012a). For Fe, sediment was digested with nitric acid, hydrochloric acid, and peroxide (30%) and analyzed using atomic absorption spectroscopy (EPA Method 3050B).

RESULTS AND DISCUSSION

Variations in diffusive phosphorus flux as a function of temperature and redox condition

P (as SRP) mass and concentration rapidly increased in the overlying water column of replicate sediment incubation systems subjected to anaerobic conditions. For example, rates of P mass and concentration increase were approximately linear over the 7-day incubation period for systems maintained at 25 °C (Fig. 2). Concentration increases were also variable between replicates, ranging between 0.65 and 1.70 mg/L at the end of the incubation period. Rates of P mass and concentration increase were much lower in the overlying water column of systems maintained under aerobic conditions at 25 °C (Fig. 2). Nevertheless, P concentrations were significantly elevated at the end of the 23-day incubation period, despite aerobic conditions, and ranged between 0.03 and 0.12 mg/L.

Similar to previous findings (James 2012), mean diffusive P fluxes were much higher under anaerobic versus aerobic conditions for sediment in eastern Big Traverse Lake (Fig. 3). Under summer temperature conditions (i.e., 18 to 25 °C), the mean anaerobic diffusive P flux ranged between 7.78 mg/m² d (\pm 1.00 standard error, SE) and 16.78 mg/m² d (\pm 2.20 SE), respectively (Table 3). These fluxes were high and fell within upper ranges compared to other large lakes in the region (Fig. 4 and Table 4), indicating potentially eutrophic lake sediments (Nürnberg 1988). By comparison, mean aerobic diffusive P fluxes under these same summer temperature conditions ranged between 0.28 mg/m² d (\pm 0.07 SE) and 0.36 mg/m² d (\pm 0.06 SE), falling near the median compared to other lakes in the State of Minnesota (Fig. 4). While much lower than P fluxes under anaerobic conditions, this summer aerobic P flux range still represented a potentially significant P input to the system that needs to be incorporated into an overall P budget. Contrasting redox patterns also suggested that P fluxes from sediments in Big Traverse Lake were probably coupled with Fe cycling. For instance, under oxygenated conditions, Fe is in an oxidized state (Fe⁺³) as an Fe-oxyhydroxide (Fe~(OOH); solid precipitate) and strongly binds phosphate, resulting in lower diffusive P flux from sediments (Mortimer 1971). Under anaerobic conditions, Fe~(OOH) becomes reduced to Fe⁺², resulting in desorption of phosphate and much higher diffusive P flux.

In addition, fluxes strongly varied nonlinearly as a function of temperature (Fig. 5). For instance, the mean anaerobic and aerobic diffusive P flux was only 0.77 mg/m² d (\pm 0.13 SE) and 0.05 mg/m² d (\pm 0.01 SE), respectively, at the lowest experimental temperature of 5 °C. By comparison, diffusive P fluxes were a mean 16.78 mg/m² d (\pm 2.20 SE) and 0.36 mg/m² d (\pm 0.06 SE) under anaerobic and aerobic conditions, respectively, at the highest incubation temperature of 25 °C. Thus, experimentally-derived diffusive P fluxes increased as a function of both temperature and reducing versus oxidized conditions, suggesting these same drivers are important in regulating internal P loading processes in Big Traverse Lake (Table 5). In particular, Lake Traverse bottom temperatures can exceed 20 °C in late summer and there is recent evidence of temporary stratification and development of bottom water hypoxia and anoxia that could drive occasions of anaerobic diffusive P flux (M. Edlund, personal communication, St. Croix Watershed Research

Station, Science Museum of Minnesota). Quantification of stratification patterns and near-bottom temperature, dissolved oxygen, and redox conditions will provide important information that can be used in conjunction with regression equations reported here to predict seasonal and annual sediment P flux contributions to the overall P budget of Big Traverse Lake and other basins of the LOTW.

Subsequent water column mixing during periods of high winds could lead to vertical entrainment of internal P loads and stimulation of cyanobacterial blooms, depending on P availability for algal assimilation. For instance, low bottom water Fe:P ratios ($< 3.6:1$, Gunnars et al. 2002) can result in incomplete binding of SRP during chemical oxidation, resulting in increased P bioavailability for phytoplankton uptake (James et al. 2015, Orihel et al. 2015). In iron-rich systems, however, chemical oxidation and hydrolysis of Fe^{2+} to $Fe(OOH)$ can lead to substantial PO_4 -P binding and precipitation (Hoffman et al. 2013, Kleeburg et al. 2013) and return back to the sediment (i.e., *ferrous wheel*, Campbell and Torgersen 1980). Under this scenario, newly-formed $Fe(OOH)$ -P may not be readily available for phytoplankton uptake (Baken et al. 2014). Thus, an understanding of stoichiometric relationships between Fe and P during mixing and reaeration will be important in assessing the likelihood that internal P loading and vertical entrainment are important recycling pathways driving cyanobacterial blooms in the LOTW.

Sediment composition

Seasonal variations in surface (upper 0-5 cm) sediment textural-physical characteristics, P fractions, and Fe concentrations were relatively minor during the study period (Fig. 6 and 7). Overall, mean moisture content, porosity, sediment wet, and dry bulk densities were moderate in the 0 – 5 cm section, suggesting denser, compacted silts and clays (Table 6). Organic matter content was low at ~ 11.3 to 11.8 %. Mean moisture content and porosity were lower, while sediment wet and dry bulk densities higher, in the 5 – 10 cm section compared to the surface layer as a result of sediment compaction.

Mean biologically-labile P (i.e., subject to recycling and internal P loading; loosely-bound, iron-bound, and labile organic P) concentrations were greater in the 0 – 5 cm than the 5 – 10 cm section, suggesting the accumulation of potentially-mobile P fractions at the sediment water interface in excess of burial and diagenesis (Fig. 8). In contrast, mean biologically-refractory P (i.e., relatively inert to recycling and subject to burial; aluminum-bound, calcium-bound, and residual P) concentrations were similar in the 0 – 5 cm and 5 – 10 cm sections (Fig. 8). Mean total P concentrations were greatest in the upper 0 – 5 cm layer versus the 5 – 10 cm section, primarily as a result of higher concentrations biologically-labile P in the former section (Fig. 8).

Biologically-labile P represented ~ 45% and ~ 36% of the sediment total P composition in the 0 – 5 cm and 5 – 10 cm layer, respectively (Fig. 9). The biologically-labile P fraction was dominated by iron-bound P at 56% to 61% followed by labile organic P, which represented 37% to 40% (Fig. 9). Loosely-bound P, which represents P in the interstitial water and P loosely-adsorbed to calcium carbonate, was lowest in concentration. Calcium-bound P accounted for ~ 60% of the biologically refractory P fraction, indicating a substantial portion of this fraction was apatite (Fig. 9).

Concentrations of most P fractions in Big Traverse Lake eastern basin sediments were also moderate compared to other lake sediments in the State of Minnesota (Fig. 10). For instance, mean loosely-bound P, labile organic P, aluminum-bound P, residual P, and total P concentrations fell below the lower 25% quartile compared to other Minnesota Lake sediments (Fig. 10). Mean iron-bound P also fell within or below the lower 25% quartile. In contrast, mean calcium-bound P concentrations, reflecting apatite, were high, falling above the upper 25% quartile compared to other Minnesota Lake sediments (Fig. 10).

Vertically in the sediment column, moisture content and porosity declined, while wet and dry bulk densities increased, with increasing sediment depth (Fig. 11). Similar to the 5-cm section analyses, moisture content was moderately low in the upper 5-cm sediment column, ranging between 86% at the sediment-water interface to 79%. Moisture content declined further as a function of sediment depth to ~ 62% in the 20 – 25 cm sediment section. Wet and dry bulk densities were relatively high near the sediment-water interface and increased with increasing sediment depth. Organic matter content was relatively low near the sediment-water interface at ~13% and declined with increasing sediment depth. These vertical patterns are typical for lake sediments and caused by sediment compaction over time and degradation of organic matter.

Modest concentration maxima in redox-sensitive P, biologically-labile P and total P were observed in the upper 5-cm layer of the sediment core collected in late August, 2014 (Fig. 12). Concentrations of these constituents declined rapidly to a more constant baseline below a stabilization depth of ~ 5 to 6 cm (Fig. 13). This pattern was important in suggesting the buildup of potentially-mobile P in the upper sediment layer in excess of diagenesis and burial, a pattern typical for eutrophic lake sediments (Carey and Rydin 2011). In contrast, more biologically-inert aluminum-bound and calcium-bound P concentrations were relatively constant with sediment depth over the upper 30-cm sediment profile and did not explain surface layer pattern (Fig. 12). Reasons for the development of a surface P concentration bulge include 1) recent increases in watershed P loading, 2) upward porewater P diffusion and precipitation with $\text{Fe}(\text{OOH})$ at the oxic microzone, 3) deposition of labile organic P, breakdown, and release to $\text{Fe}(\text{OOH})$, 4) microbial storage as poly-P and release to $\text{Fe}(\text{OOH})$, and 5) limited capacity and binding sites to retain and bury P (Carignan and Flett 1981, Hupfer et al. 1995, Gächter and Müller 2003, Carey and Rydin 2011, Rydin et al. 2011, Ostrofsky 2012b). In the case of LOTW, watershed P loading has declined over a period of decades (Hargan et al. 2011) so other mechanisms are likely contributing to the vertical P concentration pattern in sediments of Big Traverse Lake. Buried redox-sensitive P, biologically-labile P, and total P concentrations below the 5-cm depth were a mean 0.12 mg/g, 0.18 mg/g, and 0.60

mg/g, respectively. In contrast, concentrations of these constituents in the upper 1-cm layer were much higher at 0.237 mg/g, 0.375 mg/g, and 0.834 mg/g, respectively.

Rydin et al. (2011) suggested that positive differences between surface and buried P concentrations reflected a long-term average annual internal P loading rate. In effect, the occurrence of concentration maxima in the surface sediment layer provided further indirect evidence that modest internal P loading is likely occurring in Big Traverse Lake despite long-term declines in watershed P loading. Using an approach very similar to that described in Rydin et al. (2011), a simplified annual long-term internal P loading rate was approximated as the difference between the surface and buried P concentration multiplied by a recent annual sedimentation rate of $660 \text{ g/m}^2 \text{ y}$ (D. Engstrom, St. Croix Watershed Research Station, Science Museum of Minnesota). Annual long-term internal P loading ranged between $\sim 80 \text{ mg/m}^2 \text{ y}$ for redox-sensitive P, $130 \text{ mg/m}^2 \text{ y}$ for biologically-labile P, and $160 \text{ mg/m}^2 \text{ y}$ for total P (Table 7). These rates probably underestimate current internal P loading in Big Traverse Lake because 1) they represent a long-term mean over a period of up to 15 y and 2) do not account for sediment-derived P that was incorporated into cyanobacterial biomass and in the water column as of late August, 2014. For instance, vertical P profiles examined in the winter after deposition of the summer cyanobacterial blooms and associated P might have yielded somewhat higher long-term average internal P loading rates.

Because annual deposition is probably not a steady-state and some post-depositional P mobility is likely occurring, caution must be used in interpreting and evaluating these estimates as they provide only a gross approximation using vertical differences in sediment P concentration collected from only one station in Big Traverse Lake. Nevertheless, this approach can be compared against independent estimates of internal P loading based on P mass balance or regression relationships between laboratory-derived diffusive P flux and seasonal variation in temperature-redox conditions above the sediment-water interface (i.e., anoxic factor, Nürnberg 1995). For instance, annual long-term internal P loading estimates derived from vertical variations in P in the sediment

core collected in Big Traverse Lake in August, 2014, are roughly equivalent to mean annual aerobic diffusive P fluxes ranging between 0.2 mg/m² d and 0.4 mg/m² d. Additional vertical P profile analysis from sediment cores collected spatially throughout Big Traverse Lake is needed to more accurately estimate the potentially-mobile P pool that is active in internal P loading.

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REFERENCES

- Andersen JM. 1976. An ignition method for determination of total phosphorus in lake sediments. *Wat Res* 10:329-331.
- APHA (American Public Health Association). 2005. Standard Methods for the Examination of Water and Wastewater. 21st ed. Washington (DC).
- Avnimelech Y, Ritvo G, Meijer LE, Kochba M. 2001. Water content, organic carbon and dry bulk density in flooded sediments. *Aqua Eng* 25:25-33.

- Baken S, Nawara S, Van Moorlegem C, Smolders E. 2014. Iron colloids reduce the bioavailability of phosphorus to the green alga *Raphidocelis subcapitata*. *Wat Res* 59:198-206.
- Boström B. 1984. Potential mobility of phosphorus in different types of lake sediments. *Int Revue Ges Hydrobiol* 69:457-474.
- Burns NM, Ross C. 1972. Project Hypo. CCIW Paper 6 and EPA Tech Rep TS-05071-208-24.
- Campbell P, Torgersen T. 1980. Maintenance of iron meromixis by iron redeposition in a rapidly flushed monimolimnion. *Can J Fish Aquat Sci* 37:1303-1313.
- Carey CC, Rydin E. 2011. Lake trophic status can be determined by the depth distribution of sediment phosphorus. *Limnol Oceanogr* 56:2051-2063.
- Carignan R, Flett RJ. 1981. Postdepositional mobility of phosphorus in lake sediments. *Limnol Oceanogr* 26:361-366.
- Gächter R, Meyer JS, Mares A. 1988. Contribution of bacteria to release and fixation of phosphorus in lake sediments. *Limnol Oceanogr* 33:1542-1558.
- Gächter R, Meyer JS. 1993. The role of microorganisms in mobilization and fixation of phosphorus in sediments. *Hydrobiologia* 253:103-121.
- Gächter R, Müller B. 2003. Why the phosphorus retention of lakes does not necessarily depend on oxygen supply to their sediment surface. *Limnol Oceanogr* 48:929-933.
- Gunnars A, Blomqvist S, Johansson P, Anderson C. 2002. Formation of Fe(III) oxyhydroxide colloids in freshwater and brackish seawater, with incorporation of phosphate and calcium. *Geochim Cosmochim Acta* 66:745-758.
- Håkanson L, Jansson, M. 2002. Principles of lake sedimentology. Caldwell (NJ). The Blackburn Press.
- Hargan KE, Paterson AM, Dillon PJ. 2011. A total phosphorus budget for the Lake of the Woods and Rainy River Catchment. *J Great Lakes Res* 37:753-763.
- Hjieltjes AH, Lijklema L. 1980. Fractionation of inorganic phosphorus in calcareous sediments. *J Environ Qual* 8:130-132.
- Hoffman AR, Armstrong DE, Lathrop RC. 2013. Influences of phosphorus scavenging by iron in contrasting dimictic lakes. *Can J Fish Aquat Sci* 70:941-952.

- Hupfer M, Gächter R., Giovanoli R. 1995. Transformation of phosphorus species in settling seston and during early sediment diagenesis. *Aquat Sci* 57:305-324.
- James WF. 2008. Internal phosphorus loading and sediment phosphorus fractionation analysis for profundal sediments in Jessie Lake, Minnesota.
- James WF. 2010. Nitrogen retention in a floodplain backwater of the upper Mississippi River (USA). *Aquat Sci* 72:61-69.
- James WF. 2012. Estimation of internal phosphorus loading contributions to the Lake of the Woods, Minnesota. Report submitted to the Minnesota Pollution Control Agency. University of Wisconsin – Stout, jamesw@uwstout.edu.
- James WF. 2013. Alum dosage considerations for Halsted's Bay, Lake Minnetonka, Minnesota. University of Wisconsin – Stout, jamesw@uwstout.edu.
- James WF. 2014. Effects of open-lake dredge material placement on sediment characteristics and diffusive phosphorus fluxes in Lake Erie, Western Basin. Report submitted to the U.S. Army Corps of Engineers – Buffalo District, with LimnoTech, Inc. University of Wisconsin – Stout, jamesw@uwstout.edu.
- James WF, Sorge PW, Garrison PJ. 2015. Managing internal phosphorus loading and vertical entrainment in a weakly stratified eutrophic lake. *Lake Reserv Manage* (In press).
- Kleeburg A, Herzog C, Hupfer M. 2013. Redox sensitivity of iron in phosphorus binding does not impede lake restoration. *Water Res* 47:1491-1502.
- Mortimer CH. 1971. Chemical exchanges between sediments and water in the Great Lakes – Speculations on probable regulatory mechanisms. *Limnol Oceanogr* 16:387-404.
- Nürnberg GK. 1988. Prediction of phosphorus release rates from total and reductant soluble phosphorus in anoxic lake sediments. *Can J Fish Aquat Sci* 44:960-966.
- Nürnberg GK. 1995. Quantifying anoxia in lakes. *Limnol Oceanogr* 40:1100-1111.
- Nürnberg GK. 1991. Phosphorus from internal sources in the Laurentian Great Lakes, and the concept of threshold external load. *J Great Lakes Res* 17:132-140.
- Nürnberg GK, LaZerte BD, Loh PS, Molot LA. 2013a. Quantification of internal phosphorus load in large, partially polymictic and mesotrophic Lake Simcoe, Ontario. *J Great Lakes Res* 39:271-279.

- Nürnberg GK, Molot LA, O'Connor E, Jarjanazi H, Winter JG, Young JD. 2013b. Evidence for internal phosphorus loading, hypoxia and effects on phytoplankton in partially polymictic Lake Simcoe, Ontario. *J Great Lakes Res* 39:259-270.
- Orihel DM, Bird DF, Brylinsky M, Chen H, Donald DB, Huang DY, Giani A, Kinniburgh D, Kling H, Kotak BG, Leavitt PR, Nielsen CC, Reedyk S, Rooney RC, Watson SB, Zurawell RW, Vinebrooke RD. 2012. High microcystin concentrations occur only at low nitrogen-to-phosphorus ratios in nutrient-rich Canadian lakes. *Can J Fish Aquat Sci* 69: 1457-1462.
- Ostrofsky ML. 2012a. Determination of total phosphorus in lake sediments. *Hydrobiologia* 696:199-203.
- Ostrofsky ML. 2012b. Differential post-depositional mobility of phosphorus species in lake sediments. *J Paleolimnol* 48:559-569.
- Psenner R., Puckso R. 1988. Phosphorus fractionation: Advantages and limits of the method for the study of sediment P origins and interactions. *Arch Hydrobiol Biol Erg Limnol* 30:43-59.
- Rydin E, Malmaeus JM, Karlsson OM, Jonsson P. 2011. Phosphorus release from coastal Baltic Sea sediments as estimated from sediment profiles. *Est Coast Shelf Sci* 92:111-117.

Table 1. Sediment variable list.

Phosphorus flux	Anaerobic and aerobic diffusive P flux
Sediment characteristics	Moisture content
	Wet and dry bulk density
	Organic matter content
	Porosity
	Loosely-bound P
	Iron-bound P
	Labile organic P
	Aluminum-bound P
	Calcium-bound P
	Residual P
	Total P
	Total Fe

Table 2. Sediment sequential phosphorus (P) fractionation scheme, extractants used, and definitions of recycling potential.

Variable	Extractant	Recycling Potential
Loosely-bound P	1 M Ammonium Chloride	Biologically labile; Soluble P in interstitial water and adsorbed to CaCO ₃ ; Recycled via direct diffusion, eH and pH reactions, and equilibrium processes
Iron-bound P	0.11 M Sodium Bicarbonate-dithionate	Biologically labile; P adsorbed to iron oxyhydroxides (Fe(OOH)); Recycled via eH and pH reactions and equilibrium processes
Labile organic P	Persulfate digestion of the NaOH extraction	Biologically labile; Recycled via bacterial mineralization of organic P and mobilization of polyphosphates stored in cells
Aluminum-bound P	0.1 N Sodium Hydroxide	Biologically refractory; Al-P minerals with a low solubility product
Calcium-bound P	0.5 N Hydrochloric Acid	Biologically refractory; Represents Ca-P minerals such as apatite with a low solubility product
Refractory organic P	Determined by subtraction of other forms from total P	Biologically refractory; Organic P that is resistant to bacterial breakdown

Table 3. Mean (1 standard error, SE) diffusive phosphorus (P) flux as a function of temperature and redox condition (i.e., aerobic or anaerobic).

Date	Temp (°C)	Aerobic diffusive P flux (mg/m ² d)	SE	Anaerobic diffusive P flux (mg/m ² d)	SE
7/24/2014	18	0.28	0.07	7.78	1.00
8/19/2014	25	0.36	0.06	16.78	2.20
2/20/2015	5	0.05	0.01	0.77	0.13
5/20/2015	11	0.09	0.02	2.84	0.77

Table 4. A comparison of aerobic and anaerobic diffusive phosphorus (P) fluxes from sediment measured or predicted from large freshwater systems in North America. ND = not detected.

Freshwater aquatic system	Anaerobic P diffusive flux		Aerobic P diffusive flux		Reference
	mean	range	mean	range	
	(mg/m ² d)		(mg/m ² d)		
Big Traverse Lake ¹	12.3	7.8 - 16.8	0.3	0.3 - 0.4	This study
Lake of the Woods (MN)	10.1	6.6 - 14.1	0.3	0.1 - 0.5	James (2012)
Lake Jessie North Basin (MN)	7.2		0.8		James (2008)
Lake Jessie South Basin (MN)	3.9		ND		James (2008)
L Minnetonka Halsted's Bay (MN)	9.6	7.5 - 13.3	2.6	0 - 6.3	James (2013)
L. Erie Western Basin	9.5	2.4 - 20.8	0.4	-0.1 - 1.1	James (2014)
L Erie Western Basin	11.9 ²				Numberg (1991)
L Erie Central Basin	7.4				Burns and Ross (1972)
L Erie Eastern Basin	7.2 ²				Numberg (1991)
L Ontario Central Basin	8.3 ²				Numberg (1991)
Bay of Quinte	10.0				Minns (1986)
L Michigan	2.8 ²				Numberg (1991)
L Huron	0.7 ²				Numberg (1991)
L Simcoe Kempenfelt Bay	9.3	4.3 - 12.8			Numberg et al. (2013a and b)

¹Summer fluxes only (see Table 3)

²Rates were predicted from regression relationships between sediment total phosphorus and the anaerobic P release rate.

Table 5. Regression equations for predicting diffusive phosphorus flux as a function of bottom water temperature.	
Anaerobic conditions	$y = 0.0338x^{1.8988}$
Aerobic conditions	$y = 0.0055x^{1.2977}$

Table 6. Mean (1 standard error, SE) sediment physical-textural characteristics and phosphorus fractions in the upper 0 - 5 cm and 5 - 10 cm sediment section for sediment cores collected in the eastern basin of Big Traverse Lake. n = 24.

Variable		Sediment section			
		0 - 5 cm		5 - 10 cm	
		Mean	SE	Mean	SE
Physical-textural	Moisture content (%)	81.2	0.2	75.8	0.2
	Organic matter (%)	11.8	0.1	11.3	0.1
	Wet bulk density (g/cm ³)	1.114	0.001	1.152	0.001
	Dry bulk density (g/cm ³)	0.212	0.003	0.284	0.002
	Porosity (%)	91.6	0.1	88.8	0.1
Phosphorus fractions	Loosely-bound P	0.010	0.002	0.009	0.001
	Iron-bound P	0.214	0.011	0.135	0.003
	Labile organic P	0.129	0.005	0.097	0.004
	Aluminum-bound P	0.081	0.004	0.075	0.004
	Calcium-bound P	0.254	0.006	0.261	0.011
	Residual P	0.092	0.012	0.090	0.013
	Total P	0.781	0.012	0.662	0.008
Metals	Total Fe	36.41	1.90	34.64	1.61

Table 7. Estimation of annual long-term internal phosphorus (P) loading from a sediment core collected in Big Traverse Lake in late August, 2014, , modified from Rydin et al. (2011) as the difference between surface and buried P multiplied by an average sedimentation rate of 660 g/m² y (D. Enstrom, personal communication, St. Croix Watershed Research Station, Science Museum of Minnesota).

Variable	Total P	Bio-labile P	Redox-P
P concentration in upper 1 cm (mg/g)	0.834	0.375	0.237
P concentration below 5 cm (mg/g)	0.596	0.179	0.120
Sedimentation rate (g/m ² y)	660	660	660
Annual internal P loading (mg/m ² y)	157	129	77



Figure 1. Sediment coring station location in Big Travers Lake, Lake of the Woods, MN.

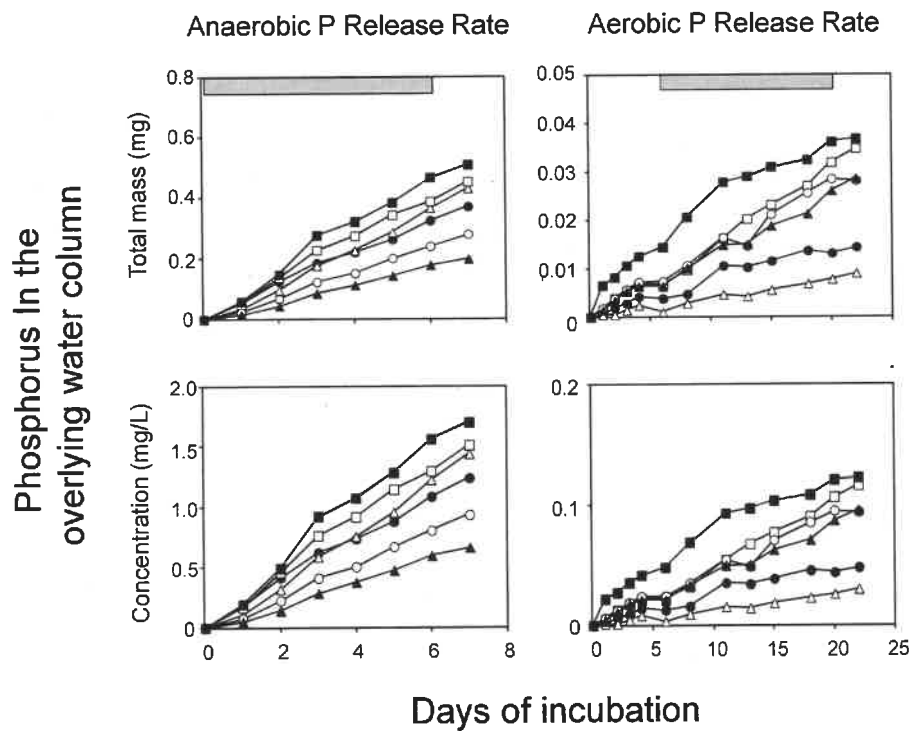


Figure 2. Time series of changes in phosphorus mass (upper panels) and concentration (lower panels) in the overlying water column of sediment cores incubated at 25 °C under anaerobic and aerobic conditions.

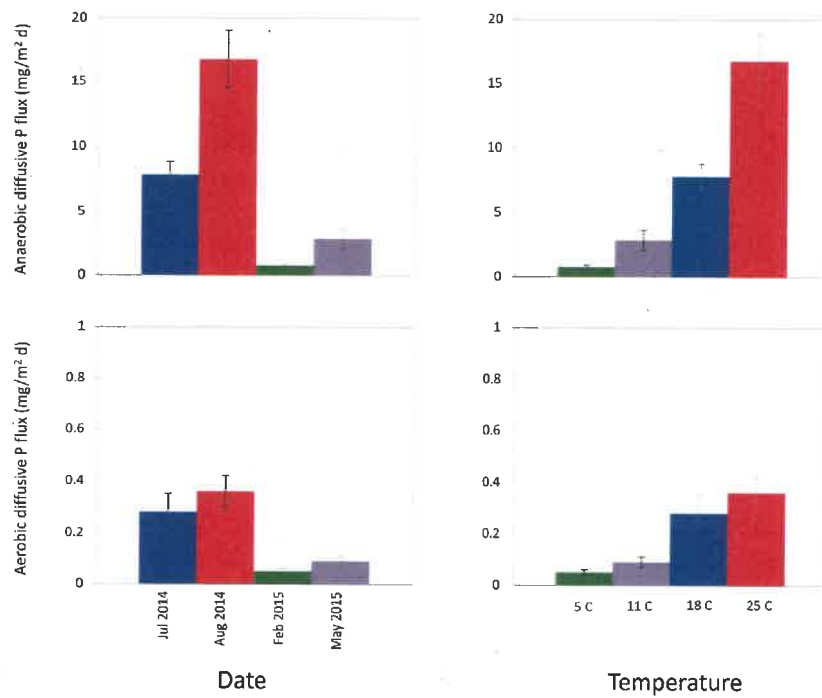


Figure 3. Variations in mean (± 1 standard error, $n = 6$) diffusive phosphorus (P) flux under anaerobic and aerobic conditions versus collection date and temperature.

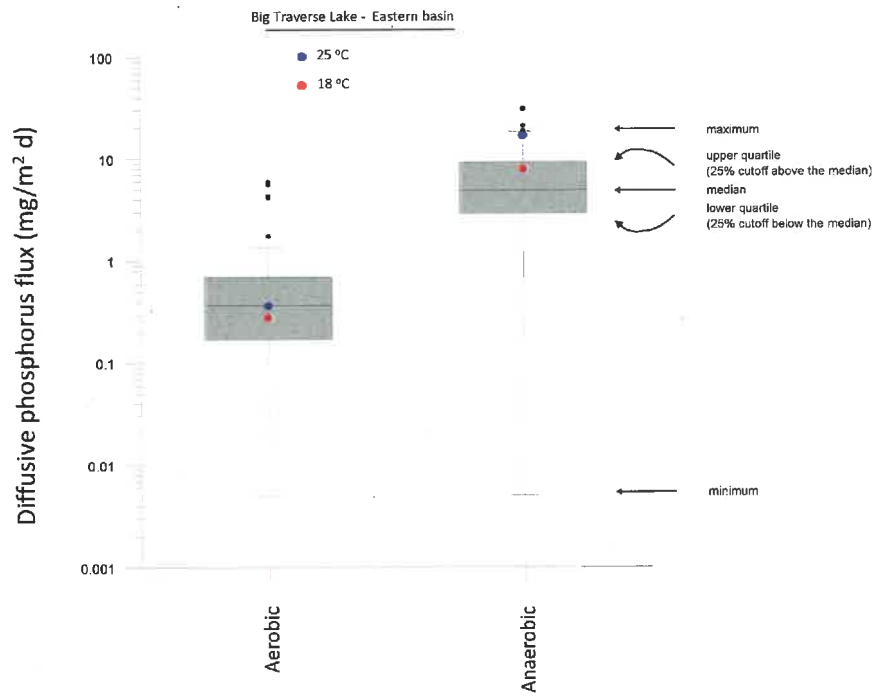


Figure 4. Comparison of mean summer aerobic and anaerobic phosphorus fluxes measured in Big Traverse Lake with statistical ranges for other lakes in Minnesota. Please note the logarithmic scale.

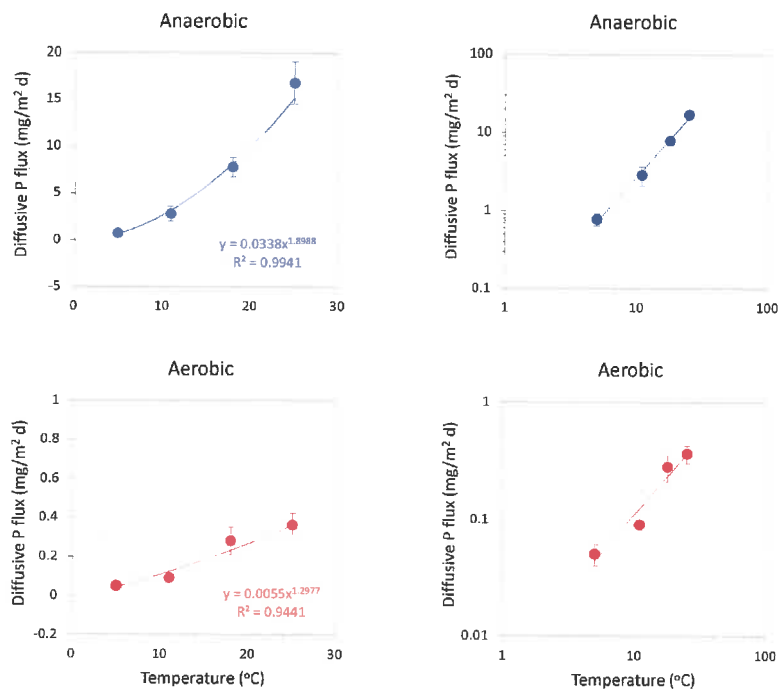


Figure 5. Variations in mean (± 1 standard error, $n = 6$) aerobic and anaerobic diffusive phosphorus fluxes versus temperature.

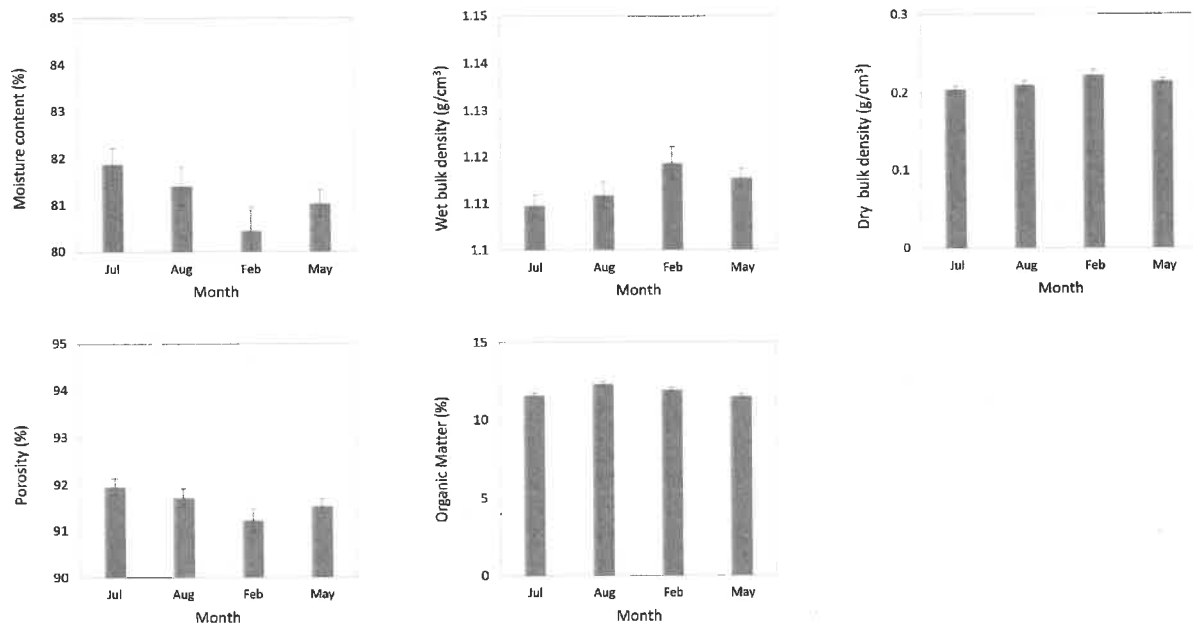
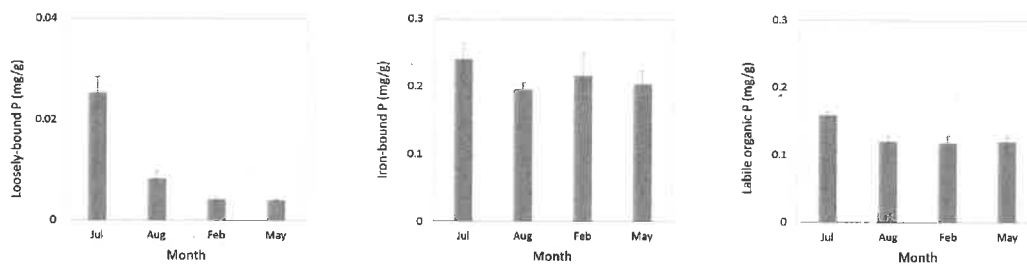


Figure 6. Variations in mean (± 1 standard error, $n = 6$) sediment physical-textural characteristics in the upper 5 cm sediment section of sediment cores collected in July and August, 2014, and February and May, 2015.

Figure 7. Variations in mean (± 1 standard error, $n = 6$) sediment phosphorus fractions in the upper 5 cm sediment section of sediment cores collected in July and August, 2014, and February and May, 2015.



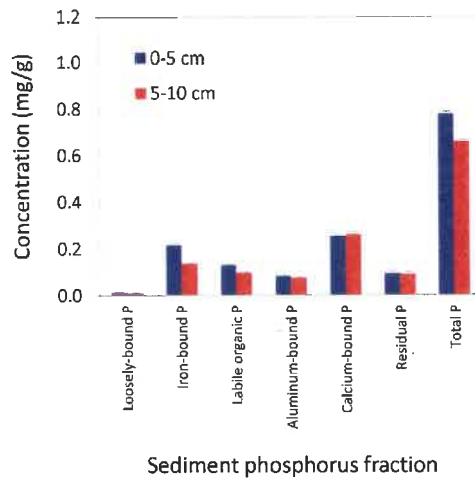


Figure 8. Mean (± 1 standard error, $n = 24$) sediment phosphorus fraction concentrations in the 0 – 5 cm and 5 – 10 cm sediment section of sediment collected in Big Traverse Lake.

0 - 5 cm

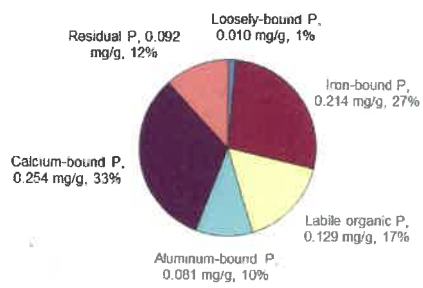
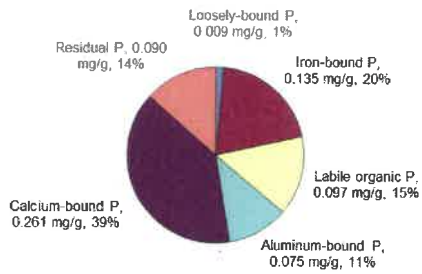


Figure 9. Mean (± 1 standard error, $n = 24$) composition of total phosphorus in the 0 – 5 cm and 5 – 10 cm section of sediment collected in Big Traverse Lake.

5 - 10 cm



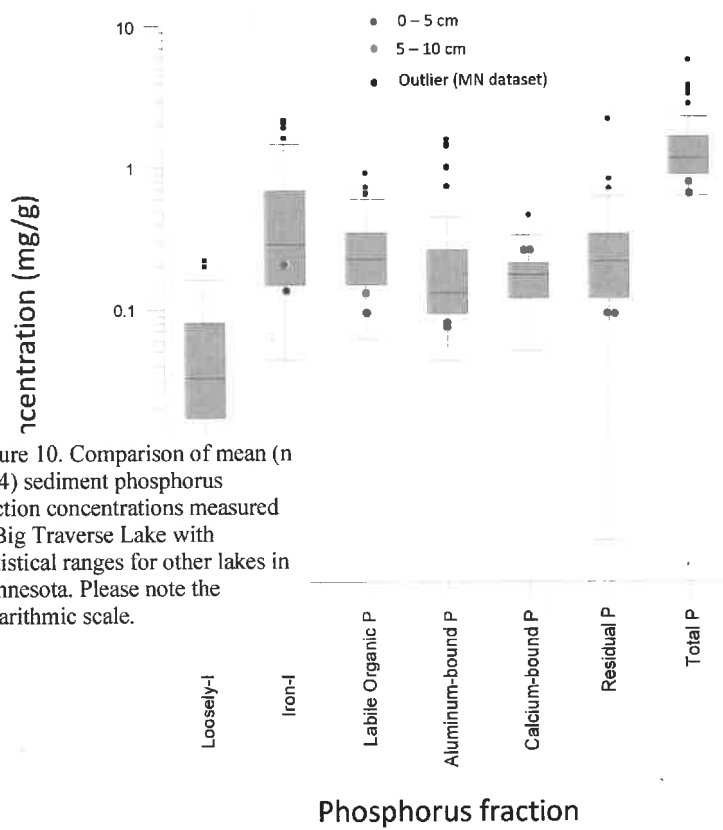


Figure 10. Comparison of mean (n = 24) sediment phosphorus fraction concentrations measured in Big Traverse Lake with statistical ranges for other lakes in Minnesota. Please note the logarithmic scale.

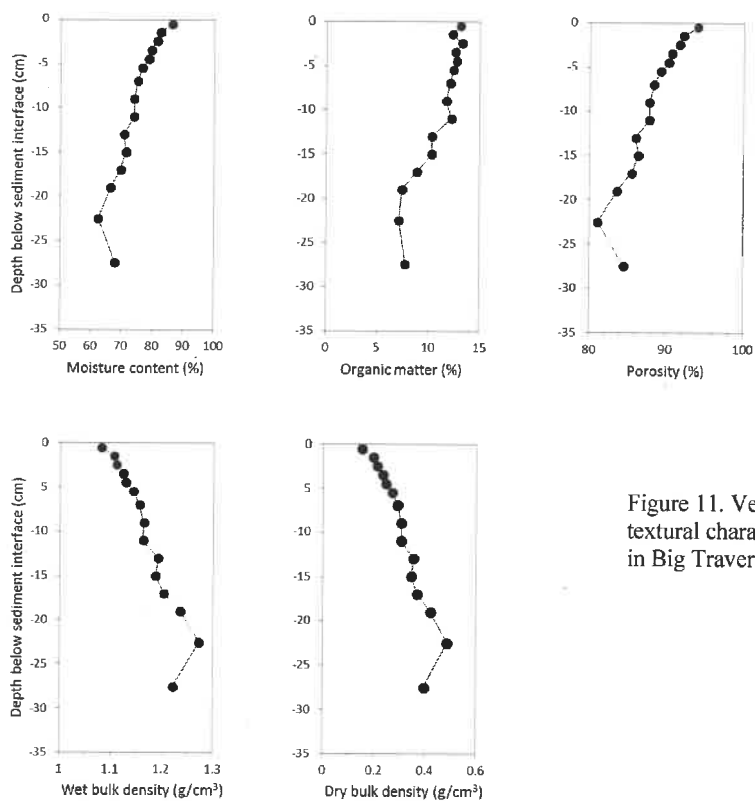


Figure 11. Vertical variations in sediment physical-textural characteristics from a sediment core collected in Big Traverse Lake in late August, 2014.

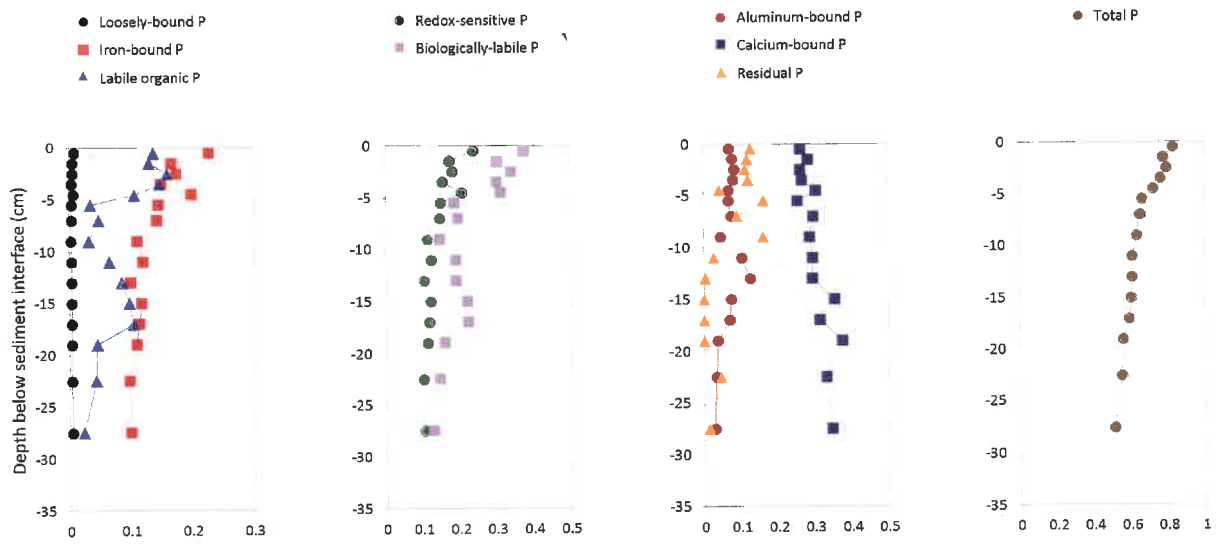


Figure 12. Vertical variations in sediment phosphorus (P) fractions from a sediment core collected in Big Traverse Lake in late August, 2014.

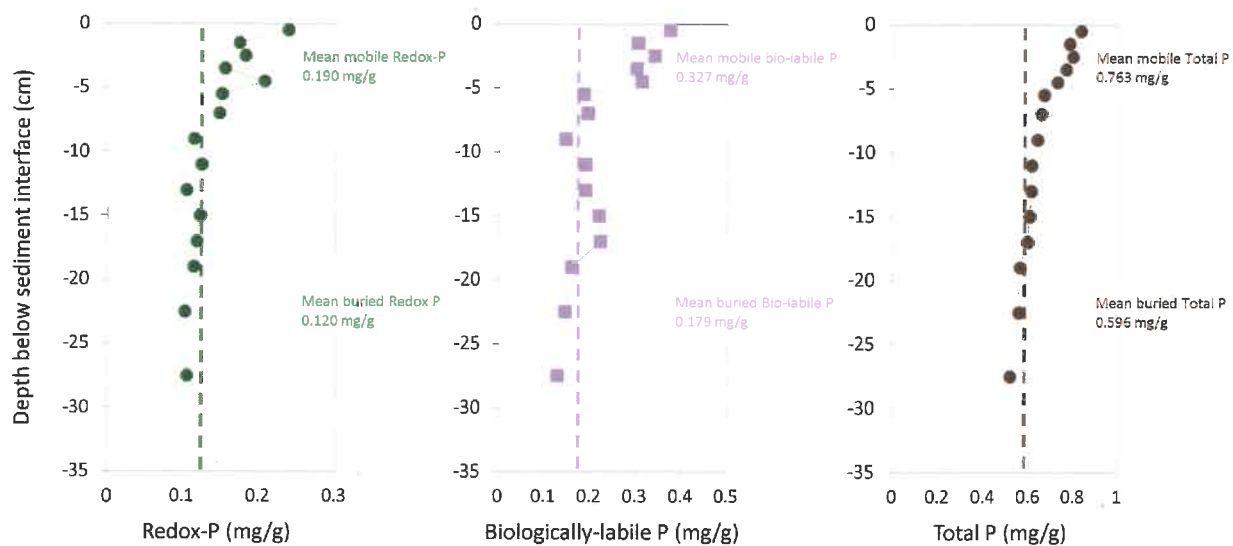


Figure 13. Vertical variations in redox-sensitive phosphorus (redox-P, i.e., the sum of the loosely-bound P and iron-bound P fractions), biologically-labile P (i.e., the sum of redox-P and labile organic P), and total P with a comparison of mean concentrations in the upper ~5-cm sediment layer versus mean concentrations below the 5-cm depth. Dashed lines represent the mean concentration below the 5-cm depth.

