



Estimation of Internal Phosphorus Loading Contributions to the Lake of the Woods, Minnesota



01 February, 2012

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SUMMARY

Sediment cores were collected in September, 2011, for determination of sediment textural and chemical characteristics and rates of diffusive and equilibrium phosphorus (P) fluxes from bottom and resuspended sediments in the Lake of the Woods system. Intact sediment cores were collected from stations located in the eastern and western basin of Big Traverse Lake, and in Muskeg and 4-Mile Bay. Windy conditions prevented sediment sampling in Little Traverse Lake. The upper 10-cm sediment layer at all stations exhibited relatively high moisture content ($> 60\%$) and a particle size distribution dominated silts and clays. Big Traverse Lake sediment had the highest clay content at $\sim 50\%$ versus $< 25\%$ for Muskeg and 4-Mile Bay. Sand content was $< 7\%$ at all stations. Sediment total P concentrations were modest, ranging between 0.64 and 0.76 mg g^{-1} . Biologically-labile P (i.e., the sum of the loosely-bound, iron-bound, and labile organic P fractions; subject to recycling and biological uptake) accounted for ~ 30 to 50% of the total P. Iron-bound P represented ~ 45 to 60% of the biologically-labile P.

Diffusive P fluxes from sediment were relatively high under anaerobic conditions (8.3 to $12.5 \text{ mg m}^{-2} \text{ d}^{-1}$) and coincided with moderately high concentrations of iron-bound P in the sediment. In contrast, aerobic diffusive P fluxes were over 20 times lower. Nevertheless, rates under aerobic conditions ranged between 0.2 and $0.6 \text{ mg m}^{-2} \text{ d}^{-1}$. Sediment total Fe concentrations were high at ~ 15 - 20 mg g^{-1} for Muskeg and 4-Mile Bay and $\sim 30 \text{ mg g}^{-1}$ for Big Traverse Lake. These concentrations fell within the upper range of concentrations reported in Barko and Smart (1986). The sediment Fe:P ratio exceeded 25. These patterns suggested that diffusive P flux from sediments in the Lake of the Woods was probably coupled with oxidation-reduction reactions associated with Fe cycling.

Equilibrium P studies indicated that sediments probably act as a sink for phosphate and bind P during resuspension events when aqueous concentrations exceed ~ 0.01 to 0.02 mg/L as soluble P. The equilibrium P concentration for sediment in the Lake of the Woods system ranged between near zero to only 0.013 mg L^{-1} . The linear partition

coefficient (k_d) was high (~ 700 to $3,200 \text{ L kg}^{-1}$), suggesting a high buffering capacity for soluble P during P disequilibrium (i.e., deviations from the equilibrium P concentration). Binding sites on sediment particles were also undersaturated with respect to P, as suggested by Langmuir isotherm analysis.

Simulated resuspension experiments indicated that sediment critical shear stress (i.e., force required to initiate sediment resuspension; dynes cm^{-2}) was relatively low ($1.3 - 2.3 \text{ dynes cm}^{-2}$), indicating a high potential for resuspension during wind-generated shear stress. Soluble P concentrations in the overlying water column were $\sim 0.020 \text{ mg L}^{-1}$ during simulated resuspension and close to the independently measured equilibrium P concentration.

OBJECTIVES

The objectives of this investigation were to quantify potential sources of internal phosphorus (P) loading from sediments in the Lake of the Woods, Minnesota. These sources included diffusive P fluxes from deposited sediment and equilibrium P fluxes from resuspended sediment. The results will be important in evaluating the overall P budget of the lake complex.

APPROACH

Determination of sediment textural characteristics and biologically labile and refractory phosphorus fractions

The objectives of this task were to quantify sediment textural characteristics and biologically labile (i.e., subject to recycling) and refractory (i.e., low recycling potential and subject to burial) P fractions for sediment samples collected in Big Traverse Lake, Muskeg Bay, and 4-Mile Bay of the Lake of the Woods (Figure 1). An intact sediment core was collected at each station for determination of sediment moisture content, bulk density, organic matter content, and particle size distribution (sand, $\geq 63\mu$; silt, $< 63 \mu$

and $\geq 2 \mu$; clay, $< 2 \mu$) in the upper 10-cm layer. A gravity corer (Aquatic Research Instruments; Hope, ID), equipped with an acrylic core liner (6.5-cm ID and 50-cm length), was used to collect sediment. A known volume of sediment was dried at 105 °C for determination of moisture content and sediment density and burned at 550 °C for determination of loss-on-ignition organic matter (Håkanson and Jansson 2002). The percentages of sand ($> 63 \mu$), silt ($< 63 \mu$ and $> 2 \mu$), and clay ($< 2 \mu$) were estimated using settling columns and pipette techniques (Plumb 1981).

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 1). 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. Refractory organic 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 under anaerobic conditions that result in desorption of P from bacterially-reduced iron compounds (i.e., Fe^{+3} to Fe^{+2}) in the sediment and diffusion into the overlying water column (Mortimer 1971, Boström 1984, Nürnberg 1988). The sum of the loosely-bound and iron-bound P fractions is referred to as redox-sensitive P (i.e., the P fraction that is active in P release under anaerobic and reducing conditions). In addition, labile organic P can be converted to soluble P via bacterial mineralization (Jensen and Andersen 1992) or hydrolysis of bacterial polyphosphates to soluble phosphate under anaerobic conditions (Gächter et al. 1988; Gächter and Meyer 1993; Hupfer et al. 1995). The sum of redox-sensitive P and labile organic P is collectively referred to a biologically-labile P. This fraction is generally 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, calcium-bound, and refractory organic P fractions are more chemically inert and subject to burial rather than recycling.

Additional sediment was dried and ground for determination of total P, total iron (Fe), total manganese (Mn), and total calcium (Ca; expressed as mg/g dry mass). Samples for total P were digested with red mercuric oxide under acidic conditions prior to colorimetric analysis. For metals, sediment was digested with nitric acid, hydrochloric acid, and peroxide (30%) and analyzed using atomic absorption spectroscopy (EPA Method 3050B).

Diffusive phosphorus flux from deposited sediment

Methods for determining rates of diffusive P flux from intact sediment cores were according to James et al. (1995). Six replicate cores were collected at each station for measurement of rates of P release under aerobic (3 replicates) and anaerobic (3 replicate) conditions. The core liners, containing both sediment and overlying water, were immediately sealed with stoppers and stored in protective carrying cases that were cooled during transport to the laboratory. Additional lake water was collected for later incubation with the sediment.

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 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 20°C. 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 (8 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 ($\text{mg m}^{-2} \text{d}^{-1}$) were calculated as the linear change in concentration in the overlying water divided by time and the area of the incubation core liner.

Equilibrium phosphorus characteristics

For each station, wet sediment subsamples (500 mg L⁻¹ dry weight equivalent) were subjected to soluble P (as KH₂PO₄) standards ranging from 0 to 1.0 mg L⁻¹ for examination of P adsorption and desorption after 24 h of exposure. Water obtained from the Lake of the Woods and filtered through a glass fiber filter (Gelman A-E) was used for preparing the P standards to maintain ionic composition. Centrifuge tubes (conical 50 mL capacity) containing sediment and P-amended water were shaken uniformly in a darkened environment at a temperature of ~ 20 °C, then filtered and analyzed for SRP (APHA 2005).

The change in SRP mass (i.e., initial SRP - final SRP; mg) after 24 h of exposure was divided by the dry mass equivalent of the sediment to determine the mass of P desorbed or adsorbed (S; mg P kg⁻¹ sediment). These data were plotted as a function of the final equilibrium SRP (i.e., the SRP concentration after 24 h of exposure) to determine the linear adsorption coefficient (k_d ; L kg⁻¹) and the equilibrium P concentration (EPC; mg P

L^{-1} ; the point where net sorption is zero; Froelich 1988). The k_d and EPC were calculated via regression analysis (SAS 1994) from linear relationships between final SRP concentration and the quantity of P adsorbed or desorbed at low equilibrium concentrations. An example of k_d determination is shown in Figure 2.

Equilibrium data were also fitted to various Langmuir and Freundlich sorption models using the spreadsheet developed by Bolster and Hornberger (2007) to estimate a P sorption maximum for sediment (S_{max} ; the maximum amount of P that can be adsorbed to binding sites on sediment surfaces). Models in the Bolster and Hornberger spreadsheet analysis include the traditional Langmuir, a Langmuir-Freundlich, a 2-surface layer Langmuir, and the Freundlich relationships. The degree of P saturation (DSP; %) for sediments collected in Lake of the Woods was calculated as the redox-P fraction divided by S_{max} estimated from the Bolster and Hornberger spreadsheet. The redox-P was chosen as a surrogate measure of the sediment native exchangeable P pool.

Phosphorus equilibrium concentrations were also determined independently using a water extraction procedure. Water-soluble P was extracted for 1 h using 10 mL of local P-free tap water (to simulate ionic composition) to 1 g dry mass equivalent of wet sediment (modification of Pierzynski 2000). Extractions were centrifuged at 500 g and filtered through a 0.45 μ membrane filter for analysis of SRP using standard colorimetric methods (APHA 2005).

Equilibrium P fluxes during sediment resuspension

Additional intact sediment cores (10 cm in depth) were collected at each station using a 15 by 15 cm box corer (Wildco Wildlife Supply Co., Saginaw, Michigan) for laboratory simulation of sediment resuspension and P equilibrium over a range of shear stresses. A vertically oscillating particle entrainment simulator (PES) developed by Tsai and Lick (1986) was used to subject intact cores to various shear stresses (Figure 3). The PES was programmed to oscillate an acrylic perforated disk above the sediment interface in a stepwise manner from 0 to ~ 4 dynes cm^{-2} at 10-min intervals. At 8 min into each cycle, a

50 mL sample from the overlying water column was collected using a peristaltic pump. Water removed as a result of sampling was simultaneously replaced with filtered lake water using the pump. Samples were analyzed for total suspended sediment, turbidity, and SRP using standard analytical procedures (APHA 2005). Changes in SRP as a function of shear stress were evaluated to estimate soluble P mass transfer and equilibrium SRP due to wind-driven sediment resuspension. The critical bottom shear stress (τ_c ; dynes cm^{-2}) of sediments was estimated as the inflection point where TSS and turbidity increased in the water column above background conditions. The inflection point was interpreted using a segmented linear-linear regression analysis (NLIN; SAS 1994). Natural forces such as wave activity and flow velocity causing a shear stress (τ) at the sediment interface that is greater than τ_c will result in sediment resuspension ($\tau > \tau_c$). This information will be useful for future modeling of potential sediment resuspension in the system.

RESULTS

Sediment Characteristics

Moisture content in the upper 10-cm layer exceeded 75% and density was relatively low at stations in Big Traverse Lake and Muskeg Bay, indicating fine-grained, flocculent sediment (Table 2). In contrast, sediment moisture content was much lower at $\sim 60\%$, with correspondingly higher sediment density, in 4-Mile Bay compared to the other stations in the Lake of the Woods. Sediment organic matter content was moderately low, ranging between ~ 11 and 16% . The particle size distribution was co-dominated by silt ($\sim 48\%$) and clay ($\sim 50\%$) in Big Traverse Lake while silt represented 70% of the particle size range versus 25% clay in Muskeg Bay. For 4-Mile Bay, the silt fraction accounted for $\sim 80\%$ and the clay fraction represented $\sim 14\%$ of the sediment particle size distribution. The sand fraction constituted less than 8% of the particle size distribution at all stations. Overall, there were strong relationships between sediment moisture content and density versus the percent particle size distribution (Figure 4). Sand and silt

percentages decreased, while the clay percentage increased, as a function of higher moisture content and low density.

In general, sediment total P concentrations for the upper 10-cm layer were modest at the four stations in the Lake of the Woods system (Table 3). Sediments collected in Big Traverse Lake exhibited total P concentrations of $\sim 0.7 \text{ mg g}^{-1}$, while Muskeg and 4-Mile Bay sediments ranged between 0.64 and 0.69 mg g^{-1} total P. Biologically-labile P (i.e., the sum of the loosely-bound, iron-bound, and labile organic P fractions) accounted for 27 to 49% of the total sediment P (Figure 5). Muskeg Bay sediments exhibited the lowest percentage of biologically-labile P while nearly half of the P composition of Big Traverse Lake sediments was biologically-labile (Table 3). Redox-sensitive P (i.e., the sum of the loosely-bound and iron-bound P fractions) accounted for greater than 50% of the biologically-labile P. In contrast, labile organic P represented ~ 32 to 49% of this fraction. The iron-bound P fraction dominated redox-sensitive P (Figure 5) and sediments from Big Traverse Lake generally exhibited highest concentrations of this fraction at $\sim 0.22 \text{ mg g}^{-1}$ versus lower concentrations of $\sim 0.11 \text{ mg g}^{-1}$ for sediments in Muskeg and 4-Mile Bay (Figure 5). When normalized with respect to sediment fresh mass (i.e., a reflection of sediment wet volume concentration), iron-bound P concentrations were relatively high, ranging between 20 and $40 \mu\text{g g}^{-1}$, and fell within the upper range of concentrations reported in Nürnberg (1988) for a variety of North American lake sediments. Biologically-refractory sediment P represented greater than 50% of the sediment total P composition at all stations (Table 3). Refractory organic P accounted for the much of this fraction, followed by calcium-bound and aluminum-bound P.

Total sediment metals concentrations in the Lake of the Woods system indicated that iron was high relative to phosphorus, resulting in Fe:P ratios that ranged between ~ 25 and 40. Sediment iron concentrations were highest in Big Traverse Lake at $\sim 30 \text{ mg g}^{-1}$ versus lower concentrations of 15-20 mg g^{-1} in Muskeg and 4-Mile Bay. Overall, these concentrations were very similar to those measured in nearby Jessie and Swan Lakes, Minnesota (James 2006, 2008). Sediment calcium concentrations were modest in the lake

system; however, they were 2 to 3 times higher in 4-Mile bay versus the other stations. Total manganese concentrations ranged between 0.4 and 1.0 mg g⁻¹.

Diffusive Phosphorus Fluxes

P (as SRP) mass increased rapidly in the overlying water column of replicate sediment incubation systems subjected to anaerobic conditions (Figure 6 and 7; upper panels). P increases were linear throughout the incubation period for sediment cores collected from Big Traverse West and 4-Mile Bay. In contrast, P mass increased linearly over the first 4 to 7 days then exhibited a nonlinear pattern of less increase between days 7 and 14. This pattern is not unusual and likely due to diminishing P concentration gradients at the sediment-water interface that resulted in lower diffusive P fluxes over time. P concentrations in the overlying water column generally approached or exceeded 1.0 mg/L in all systems toward the end of the incubation period (Figures 6 and 7; lower panels).

Mean rates of diffusive P flux under anaerobic conditions ranged between 8.3 and 12.5 mg m⁻² d⁻¹ (Table 3). These rates were high and fell within the high range of P fluxes measured for eutrophic systems in North America (Figure 8; Nürnberg 1988). Sediment collected from Big Traverse West exhibited the highest anoxic P release rate at 12.5 mg m⁻² d⁻¹ (± 0.9 SE). Rates were similar at ~ 8.5 -9.0 mg m⁻² d⁻¹ for sediment cores collected from Big Traverse East, Muskeg Bay, and 4-Mile Bay.

Under aerobic conditions, P mass increases in the overlying water column were much less compared to sediment cores incubated under anaerobic conditions (Figure 9 and 10; upper panels). In addition, P concentrations were an order of magnitude lower near the end of the incubation period under aerobic versus anaerobic conditions (Figure 9 and 10; lower panels). Nevertheless, P mass and concentrations increased linearly in the overlying water column over the first 10 days of incubation, indicating some net P diffusion out of the sediments and into the overlying water column even under aerobic conditions. P declined from relatively low initial concentrations of ~ 0.02 mg L⁻¹ to near zero by day 2 then increased linearly until \sim day 10. This initial decline in concentration

may have been due to equilibration and adsorption of P onto the sediment surface during initial aeration of the incubation systems (Penn et al. 2000). Although P increases were much lower under aerobic conditions, concentrations approached 0.05 mg L^{-1} in nearly all the systems by the end of the incubation period (Figure 9 and 10; lower panels).

Mean rates of diffusive P flux from sediments under aerobic conditions ranged between ~ 0.2 and $0.6 \text{ mg m}^{-2} \text{ d}^{-1}$ (Table 3). Lake Traverse sediment exhibited the highest aerobic diffusive P fluxes at $0.4 (\pm 0.1 \text{ SE})$ and $0.6 (\pm 0.3 \text{ SE}) \text{ mg m}^{-2} \text{ d}^{-1}$ for the East and West station, respectively. By comparison, aerobic diffusive P fluxes were only $0.2 \text{ mg m}^{-2} \text{ d}^{-1}$ for Muskeg and 4-Mile Bay. Although much lower compared to rates under anaerobic conditions, aerobic diffusive P fluxes on the order of $\sim 0.5 \text{ mg m}^{-2} \text{ d}^{-1}$ can represent an important contribution to the P budget of these lakes.

Phosphorus Equilibrium Characteristics

Overall, sediments from the Lake of the Woods exhibited undetectable P desorption when subjected to low aqueous P concentrations (Figure 11). As aqueous P concentration increased, sediments strongly adsorbed P from solution. This pattern suggested that resuspended sediments are mostly likely a sink for phosphate and sequester P rather than desorb it under conditions of P disequilibrium. The EPC (equilibrium P concentration) was $\sim 0.01 \text{ mg L}^{-1}$ for Big Traverse Lake (Table 4) and similar to the measured SRP concentration in the lake at the time of sediment collection in September. The equilibrium P concentration for Muskeg and 4-Mile Bay was below detection limits (i.e., 0.002 mg L^{-1}). Similarly, water-extractable P concentrations were relatively low at $\sim 0.010 \text{ mg L}^{-1}$ (Table 4). The linear adsorption coefficient reflects the phosphate concentration required to change the equilibrium P concentration by 1 mol L^{-1} (Froelich 1988). It was near 1000 L kg^{-1} or higher for all stations, suggesting that sediment can rapidly adsorb aqueous phosphate in the water column with little change in the equilibrium P concentration (i.e., well buffered with respect to equilibrium P).

Patterns of P sorption by sediment did not appear to follow a linearized Langmuir model that would indicate a P saturation maximum (i.e., a point at which all binding sites are filled with P; Figure 12). Instead, P sorption tended to follow a Langmuir multi-surface layer, a Langmuir-Freundlich, or Freundlich model in which binding is regulated by P concentration in solution and by diffusion of P to interior sites on particles and polymers (Figure 12). Assuming that the combined loosely-bound and iron-bound P fraction approximated the exchangeable P pool of the sediment, the degree of P saturation ranged from ~ 16 to 26% for the two-surface layer model (i.e., 224 mg/kg / 857 mg/kg for Big Traverse West) to ~ 2 to 7% for the Langmuir-Freundlich model. These ranges suggested that P saturation of binding sites on the sediments of the Lake of the Woods was currently modest (Table 4).

Phosphorus Dynamics during Simulated Sediment Resuspension

Turbidity and TSS concentrations were relatively low at shear stresses $< \sim 1.5$ dynes cm^{-2} and increased substantially above this value for all sediments (Figure 13 and 14). Big Traverse East sediment exhibited the lowest critical shear stress at 1.3 dynes cm^{-2} while the other stations ranged from ~ 2.1 to 2.3 dynes cm^{-2} (Table 5). Reasons for the lower critical shear stress at Big Traverse East are not precisely known and variations in sediment textural characteristics and particle size distribution did not appear to explain the differences in critical shear stress. Perhaps differences in critical shear stresses were due to variations in particle sorting and fine-scale (mm scale) gradients in sediment properties at the sediment-water interface that were not captured from the composite 10-cm sediment section used for analysis. Critical shear stresses for the Lake of the Woods sediments also fell within ranges measured for some other nearby lakes and impoundments that exhibit frequent sediment resuspension (Table 5).

SRP concentrations in the overlying water column of sediment systems ranged between ~ 0.015 and 0.020 mg L^{-1} before initiation of shear stress turbulence (Figures 15 and 16). The concentration generally declined as a function of sediment resuspension for the Big Traverse West, Muskeg, and 4-Mile sediment systems. Net declines in SRP

concentration ranged between 0.002 and 0.005 mg L⁻¹ in these systems. Notably, SRP concentrations increased slightly during resuspension in the Big Traverse East sediment system and the net increase in SRP concentration was ~ 0.004 mg L⁻¹ at shear stresses of 2 to 3 dynes cm⁻². SRP concentrations also increased at the greatest shear stress in the Muskeg and 4-Mile Bay sediment systems. Overall, mean net SRP concentrations during resuspension estimated over all shear stresses were 0.017 to 0.020 mg L⁻¹ with negligible net change in concentration from the initial 0.019 mg L⁻¹ (Table 6). These general patterns corroborated findings from the P equilibrium experiments and water-extractable P determinations; namely, that the EPC achieved between resuspended sediment and the surrounding water was relatively low.

DISCUSSION

Diffusive P fluxes were relatively high under anaerobic conditions and coincided with moderately high concentrations of redox-sensitive sediment P. In contrast, aerobic diffusive P fluxes were over 20 times lower. Sediment total Fe concentrations were high, falling within the upper range of concentrations reported in Barko and Smart (1986), and the sediment Fe:P ratio exceeded 25. These patterns suggested that diffusive P flux from sediments in the Lake of the Woods was probably coupled with Fe cycling. Under oxygenated conditions, Fe is in an oxidized state (Fe⁺³) as an Fe-oxyhydroxide (Fe(OOH); solid precipitate) and strongly adsorbs phosphate, resulting in low diffusive P flux from sediments (Mortimer 1971). Fe(OOH) becomes reduced to Fe⁺² in conjunction with bacterial metabolism under anaerobic conditions, resulting in desorption of phosphate and much higher rates of diffusive P flux, as observed for the Lake of the Woods sediments incubated under anaerobic conditions.

The high Fe:P ratio in the sediment also indicated that binding sites for P on Fe(OOH) complexes were well below saturation and excess Fe(OOH) was available to efficiently bind P in the oxidized microzone. Jensen et al. (1992) found a negative relationship between diffusive P fluxes under aerobic conditions and the sediment Fe:P ratio (i.e., aerobic P fluxes decreased with increasing Fe:P ratio in the sediment) for a variety of

Danish lake sediments, suggesting that the sediment Fe:P ratio could be used as an indicator to evaluate the binding capability for P under aerobic conditions. They suggested that a higher Fe:P ratio reflected greater free sorption sites for P binding and that a sediment Fe:P ratio of 10 to 15 was associated with regulation of diffusive P flux from sediments under aerobic conditions.

Because the Lake of the Woods system is very large and shallow, frequent wind-generated mixing probably resulted in oxygenated conditions in the bottom waters and maintenance of an oxidized microzone at the sediment interface throughout the summer, driving diffusive P flux primarily under aerobic conditions. Although aerobic P fluxes were much lower versus those under anaerobic conditions, this source may, nevertheless, be important in the P economy and should be considered in an overall P budget of the system. A basin- or embayment-wide aerobic P flux for different areas of the system could be estimated by multiplying the measured laboratory-derived P flux by sediment areas characterized by fine-grained particle accumulation. These accumulation zones could be characterized by moisture content, density, or grain-size compositional characteristics (i.e., moisture content > 75%, sand composition < 10%, etc). Although more labor intensive, estimates for incorporation into a P budget could also be derived from distributional maps of sediment textural characteristics (moisture content, particle-size distribution, etc) and relationships between sediment textural characteristics versus diffusive P flux. A similar analysis was conducted by James and Larson (2008) for the lower Minnesota River system. More data collection would be needed for this approach.

Water temperature, not considered in this research, probably also played an important role in regulating sediment bacterial transformations and, thus, aerobic diffusive P fluxes. For instance, rates would be expected to increase as bottom water temperature increases. James and Barko (2004) found that rates increased exponentially as a function of temperature for sediment collected in Lake Pepin, Upper Mississippi River. Future research on diffusive P fluxes from sediment in the Lake of the Woods should address temperature effects on rates.

Surficial sediments collected from stations in the Lake of the Woods were composed primarily of silts and clays and exhibited a moderately low critical shear stress, suggesting strong susceptibility to wind-generated resuspension. Indeed, Big Traverse Lake, Muskeg, and 4-Mile Bays were very turbid during the September sampling period in conjunction with very windy conditions and wave activity. Equilibrium studies indicated that sediments probably act as a sink for phosphate and bind P during resuspension events when aqueous concentrations exceed ~ 0.01 to 0.02 mg/L as soluble P. This finding was supported by several factors: the Fe concentration and the Fe:P ratio of the sediment was high, implying binding of soluble P onto Fe(OOH) complexes; P binding sites were undersaturated with respect to an estimated S_{\max} ; the k_d was high, suggesting high buffering capability by resuspended sediment for soluble P; the equilibrium P concentration was low compared to other systems that drain agriculturally-managed watersheds (Table 7); and SRP tended to decline or exhibit minor net change as a function of resuspended sediment concentrations and applied shear stress in laboratory sediment systems. In particular, these patterns indicated that periods of sediment resuspension in the Lake of the Woods probably control a relatively low aqueous soluble P concentration. However, equilibrium P flux during resuspension represents a potential P source for algal uptake and growth and could be significant when ambient SRP concentrations fall below the EPC. For instance, P desorption from resuspended sediment might occur during a wind event that was preceded by periods where ambient SRP was near zero due to an algal bloom.

Future P budgetary and modeling analyses probably need to consider the role of sediment resuspension in regulating total P concentrations in the water column of the Lake of the Woods and potential availability for algal uptake. Sediment critical shear stresses determined in this study could be combined with bathymetric information on fetch and wind speed and direction monitoring data to estimate sediment resuspension and resulting total P concentrations using empirical or mechanistic models (Hamilton and Mitchell 1996, Bailey and Hamilton 1997, CHL-ERDC 2011). Concentrations of sediment P (mg kg^{-1}) as a function of particle size distribution are not currently known and might be important in accurately predicting resuspended total P concentrations. For

instance, finer-grained particles (i.e., fine silts and clays) are most susceptible to resuspension and binding sites can be enriched with P due to greater surface areas per unit particle volume. James (2010) found that sediment particles $< 0.4 \mu$ exhibited four times higher concentrations of exchangeable P than coarse silts in the range of 16 to 63 μ for sediments in the Lower Minnesota River system. Because wind-generated bottom shear stresses probably frequently drive resuspension in areas with long fetches, particle sorting has likely resulted in the establishment of a sediment surficial layer composed of very fine-grained P-enriched silts and clays.

Preliminary total P budgets for the Lake of the Woods have suggested that tributary P loadings do not account for total P concentration and mass balance, implying that internal P loading sources to the system that may be driving algal productivity. The present research provides findings and insights on internally-derived P sources to the system via diffusive fluxes from bottom sediments and equilibrium fluxes from resuspended sediment. A portion of the P imbalance may likely be due to frequent resuspension that contributes to high total P concentrations in the water column and the total P composition is probably dominated at times by resuspended inorganic sediment P as well as P in algal cells. Thus, future P budgetary and modeling analysis perhaps needs to consider the *availability* of both tributary loads and internally-derived P sources for algal uptake (i.e., soluble versus total P flux to the water column). The findings from the present study suggested that diffusive and equilibrium soluble P fluxes from sediments are relatively low, implying that a large portion of the total P imbalance could be due to sources that are not directly available for algal uptake (for instance, the fraction of resuspended sediment that is not a part of the exchangeable P pool). In addition, more detailed information is needed on tributary soluble P loading (versus total P) in order to better understand and target P sources that are driving algal productivity in the Lake of the Woods.

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Table 1. Operationally-defined sediment phosphorus fractions based on sequential extraction.		
Variable	Extractant	Recycling potential
Loosely-bound P	1 M ammonium chloride	Biologically-labile; recycled via eH and pH reactions and equilibrium processes
Iron-bound P	0.11 M sodium bicarbonate-dithionate	Biologically-labile; recycled via eH and pH reactions and equilibrium processes
Labile organic P	persulfate digestion of the sodium hydroxide extract	Biologically-labile; recycled via bacterial mineralization of organic P and mobilization of polyphosphates stored in bacterial cells
Aluminum-bound P	0.1 N sodium hydroxide	Biologically-refractory and subject to burial
Calcium-bound P	0.5 N hydrochloric acid	Biologically-refractory and subject to burial
Refractory organic P	calculated as the difference between sediment total P and the sum of the other fractions	Biologically-refractory and subject to burial

Table 2. Textural characteristics for sediments collected in Lake of the Woods.							
Station	Moisture Content (%)	Bulk Density (g/cm ³)	Sediment Density (g/cm ³)	Loss-on-ignition (%)	Sand (%)	Silt (%)	Clay (%)
Big Traverse West	83.9	1.093	0.187	14.0	1.0	46.7	52.3
Big Traverse East	81.7	1.110	0.227	12.4	1.3	50.0	48.6
Muskeg Bay	75.5	1.146	0.314	15.8	5.4	70.0	24.7
4-Mile Bay	59.9	1.282	0.516	10.8	6.5	79.7	13.8

Table 3. Mean (1 standard error in parentheses; n=3) rates of phosphorus (P) release and concentrations of biologically labile (i.e., subject to recycling) and refractory (i.e., relatively inert and subject to burial) P for sediments collected in Lake of the Woods. DW = dry mass, FW = fresh mass.

Station	Diffusive P Flux		Redox-sensitive and biologically labile P				Refractory P		
	Oxic (mg m ⁻² d ⁻¹)	Anoxic (mg m ⁻² d ⁻¹)	Loosely-bound P (mg/g DW)	Iron-bound P (mg/g DW)	Iron-bound P (mg/g FW)	Labile organic P (mg/g DW)	Aluminum-bound P (mg/g DW)	Calcium-bound P (mg/g DW)	Refractory organic P (mg/g DW)
Big Traverse West	0.6 (0.3)	12.5 (0.9)	0.010	0.214	35	0.124	0.084	0.122	0.207
Big Traverse East	0.4 (0.1)	8.6 (2.9)	0.016	0.224	41	0.115	0.095	0.154	0.117
Muskeg Bay	0.2 (<0.1)	9.2 (2.6)	0.016	0.121	30	0.130	0.069	0.149	0.207
4-Mile Bay	0.2 (<0.1)	8.3 (2.6)	0.016	0.101	40	0.058	0.072	0.163	0.232

Station	Total P (mg/g DW)	Redox P		Bio-labile P		Refractory P	
	(mg/g DW)	(mg/g DW)	(%)	(mg/g DW)	(%)	(mg/g DW)	(%)
Big Traverse West	0.761	0.224	29.4%	0.348	45.7%	0.413	54.3%
Big Traverse East	0.721	0.240	33.3%	0.355	49.2%	0.366	50.8%
Muskeg Bay	0.692	0.137	19.8%	0.267	38.6%	0.425	61.4%
4-Mile Bay	0.642	0.117	18.2%	0.175	27.3%	0.467	72.7%

Station	Total Fe (mg/g DW)	Total Mn (mg/g DW)	Total Ca (mg/g DW)	Fe:P
Big Traverse West	32.53	1.02	7.26	42.7
Big Traverse East	28.37	0.88	6.93	39.3
Muskeg Bay	19.62	0.50	11.12	28.4
4-Mile Bay	16.94	0.41	25.87	26.4

Table 4. Equilibrium phosphorus (P) characteristics, estimated P sorption capacity, and percent P saturation characteristics for surface sediment in the Lake of the Woods.

Station	Water-extractable P (mg/L)	Equilibrium P Concentration (mg/L)	Linear Partition Coefficient (L/kg)	Loosely-bound and Iron-bound P (mg/kg)	P Sorption Capacity		P Saturation	
					Two-Surface layer Model (mg/kg)	Langmuir-Freundlich Model (mg/kg)	Two-Surface layer Model (%)	Langmuir-Freundlich Model (%)
Big Traverse West	0.011	0.007	3,255	224	857	3,554	26.1%	6.3%
Big Traverse East	0.011	0.013	1,954	240	952	3,606	25.2%	6.7%
Muskeg Bay	0.007	near zero	1,380	137	857	3,554	16.0%	3.9%
4-Mile Bay	0.012	near zero	706	117	476	7,410	24.6%	1.6%

Table 5. A comparison of sediment critical shear stresses measured for stations in the Lake of the Woods versus some other lakes in the upper mid-west.	
Station	Critical Shear Stress (dynes/cm ²)
Big Traverse West	2.08
Big Traverse East	1.30
Muskeg Bay	2.33
4-Mile Bay	2.15
Peoria Lake (IL) ¹	2.30
Marsh Lake (MN) ²	2.30
Lake Christina (MN) ³	1.40

Table 6. Mean (1 standard error; n = 5 to 8) soluble reactive phosphorus (SRP) concentration and mean change in SRP during resuspension for various sediments. The mean initial SRP concentration (i.e., prior to sediment resuspension) was 0.019 mg/L. Plus and minus signs indicate a net increase (+) or decrease (-) in SRP versus the initial concentration.

Station	Average SRP during resuspension (mg/L)	Average change in SRP during resuspension (mg/L)
Big Traverse West	0.017 (< 0.001)	+ 0.002 (< 0.001)
Big Traverse East	0.018 (< 0.001)	- 0.001 (< 0.001)
Muskeg	0.020 (< 0.001)	0.000 (< 0.001)
4-Mile	0.020 (< 0.001)	- 0.001 (< 0.001)

Table 7. Comparison of the equilibrium phosphorus concentration (EPC) for suspended and despoited sediments in various river systems.

System	EPC (mg/L)	Reference
Lower Minnesota River (USA)	0.117	James and Larson (2008)
Lake Pepin (USA)	0.115	James and Barko (2004)
Redwood River (USA)	0.070	James et al. (2002)
Eau Galle River (USA)	0.129	James and Barko (2005)
Colorado River (USA)	0.040	Mayer and Gloss (1980)
Bermejo River (Argentina)	0.060	Carignan and Vaithyanathan (1999)
Paraguay River (Argentina)	0.020-0.090	Carignan and Vaithyanathan (1999)
Parana River (Argentina)	0.005-0.021	Carignan and Vaithyanathan (1999)
Bear Brook (USA)	0.002	Meyer (1979)
NY wooded streams (USA)	<0.002	Klotz (1985)
Lower Mississippi River (USA)	0.108	Wauchope and McDowell (1984)
Xiangxi River (China)	0.100	Chang-Ying et al. (2006)

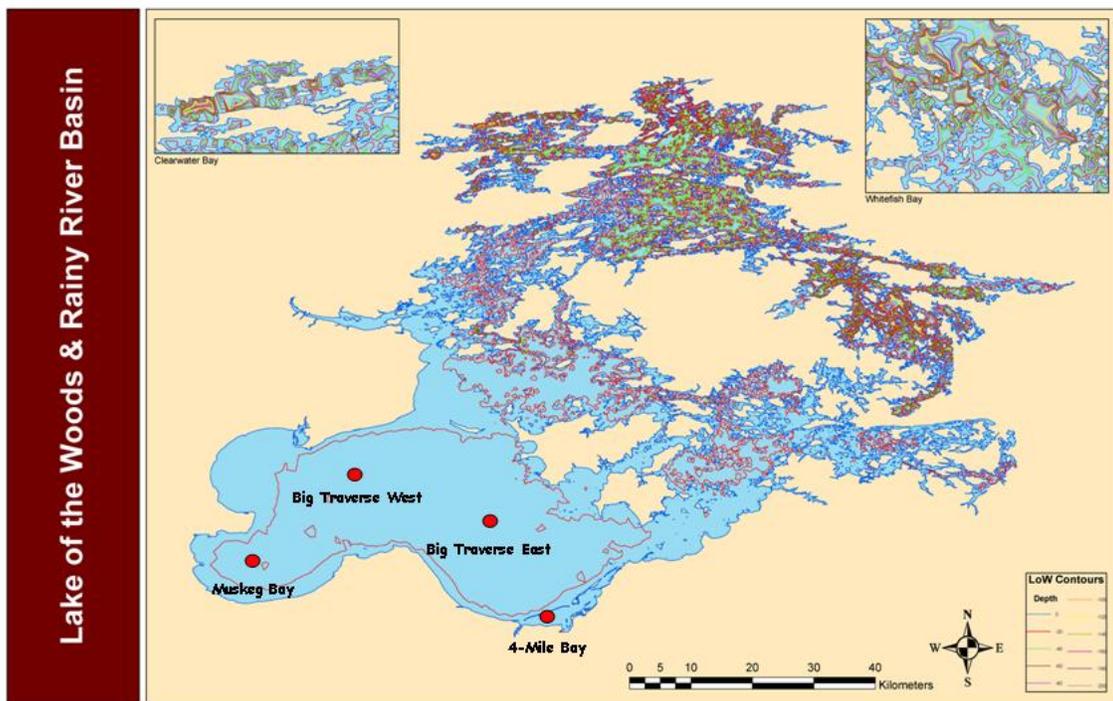


Figure 1. Sediment sampling station locations in the Lake of the Woods system.

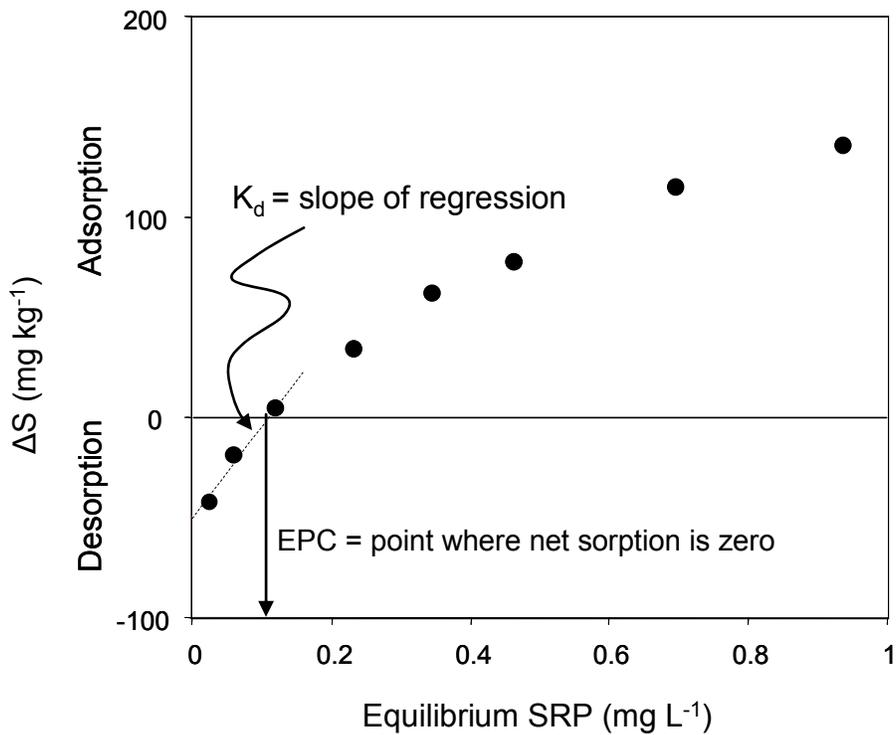


Figure 2. An example showing the estimation of the equilibrium phosphorus (P) concentration (EPC) and the linear adsorption coefficient (k_d). The final equilibrium soluble reactive P (SRP) concentration is plotted against the change in SRP in solution after 24 hours of exposure to sediment. The net change in SRP concentration is divided by the mass of sediment (dry mass) to estimate the exchangeable sediment P (ΔS). Negative S indicates desorption of P from the sediment to the surrounding water while a positive S represents adsorption of soluble P from the surrounding water to the sediment. The slope of the regression between equilibrium SRP and ΔS near the EPC represents k_d . The EPC is the concentration where there is no net adsorption or desorption of P.

Particle Entrainment Simulator

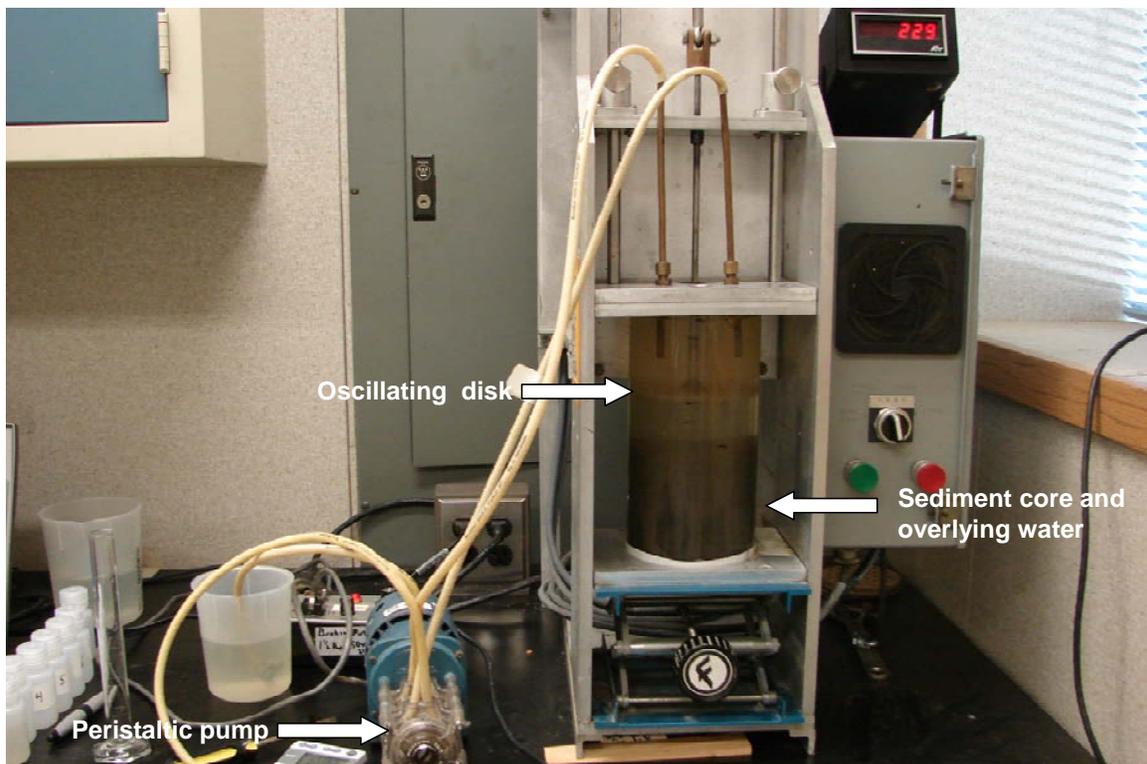


Figure 3. Schematic of the particle entrainment simulator used to estimate sediment critical shear stress and examine soluble reactive phosphorus concentrations during simulated resuspension.

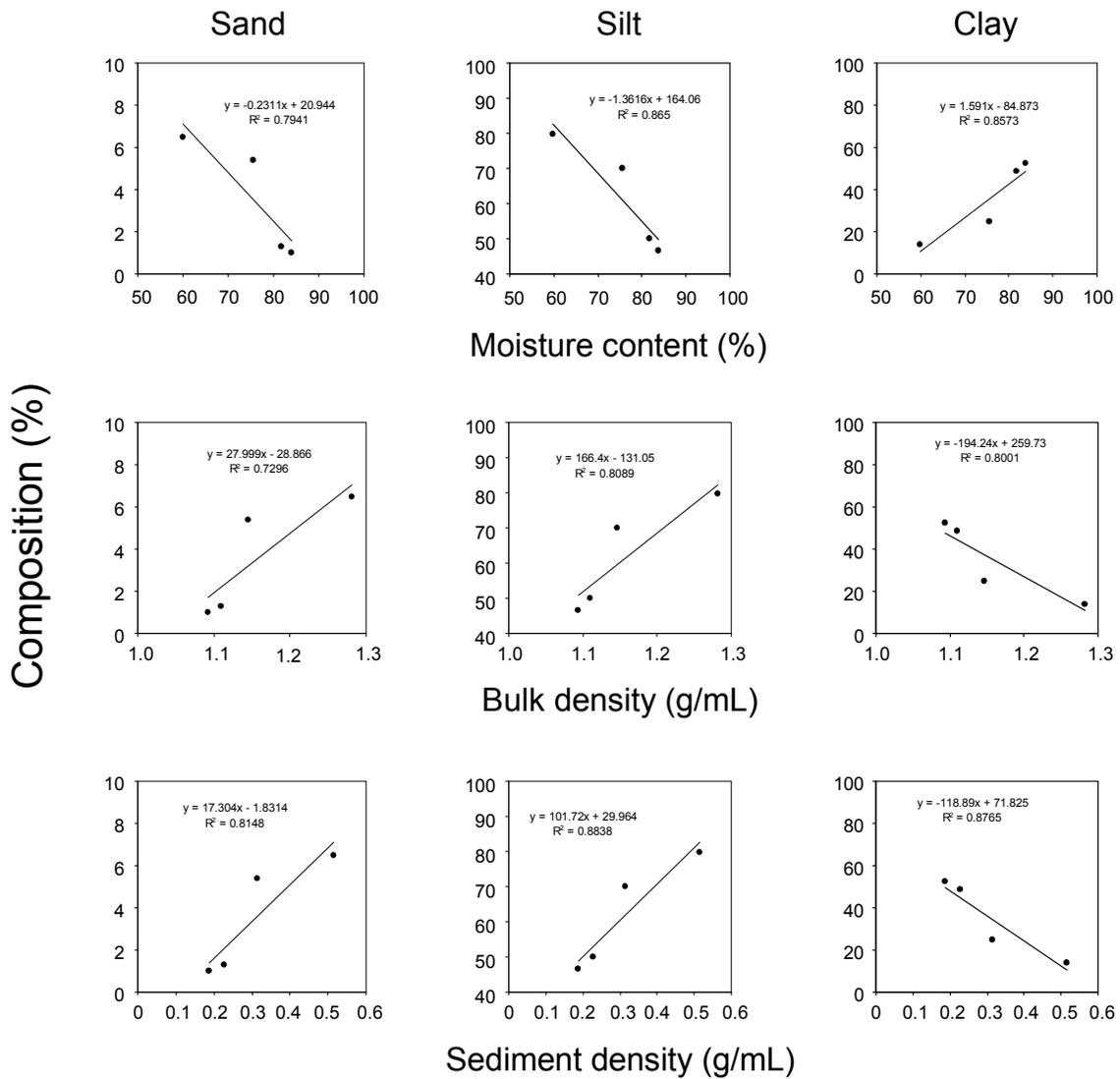


Figure 4. Relationships between sand, silt, or clay percent composition and various sediment textural characteristics.

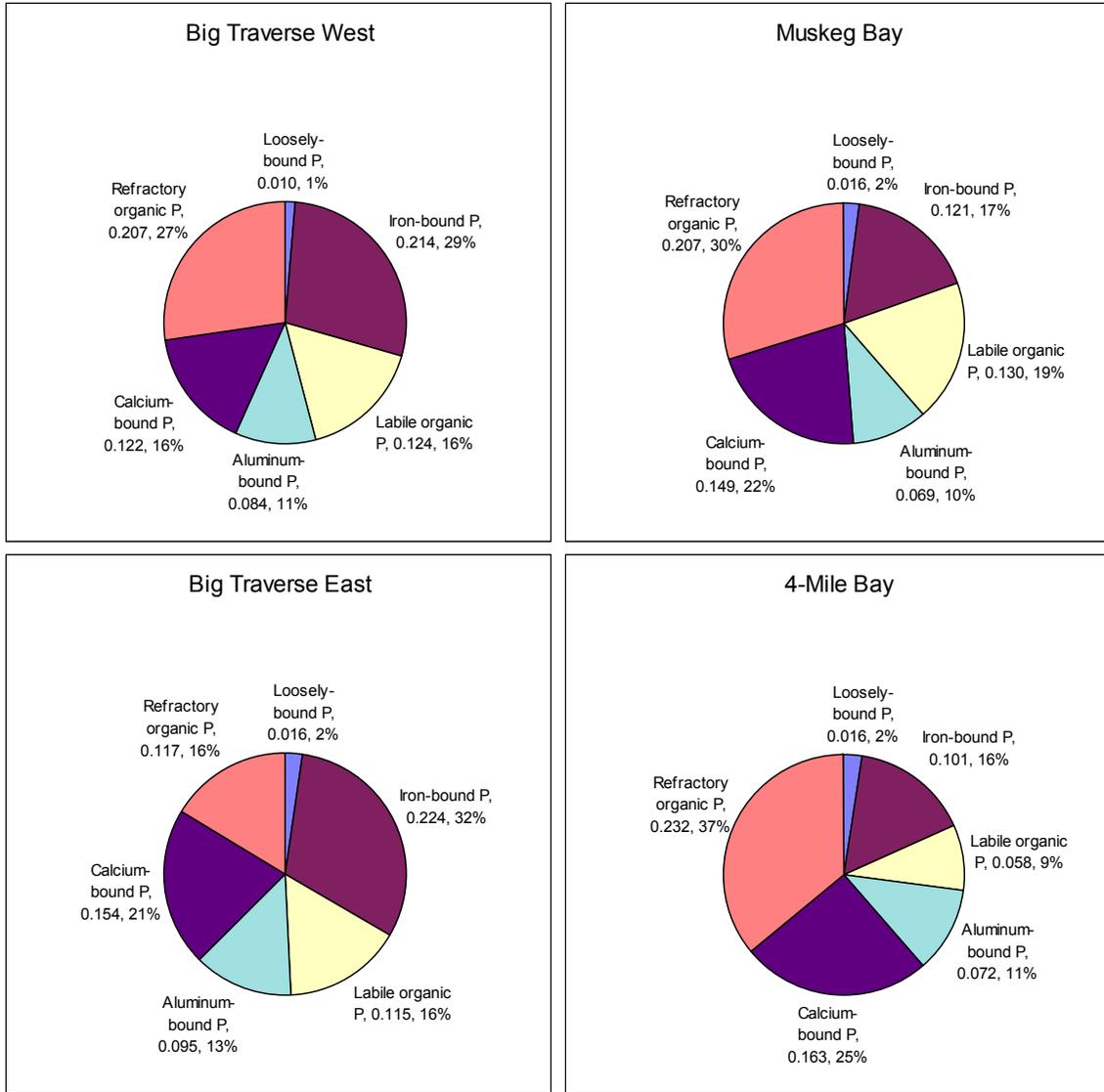


Figure 5. The composition of biologically-labile (i.e., subject to recycling and biological uptake; loosely-bound, iron-bound, labile organic phosphorus) and biologically-refractory phosphorus (P; i.e., more inert to recycling and uptake and subject to burial; aluminum-bound, calcium-bound, refractory organic P) fractions in the upper 10-cm sediment layer for various stations in the Lake of the Woods system. Numbers below each label indicate concentration (mg g⁻¹) and relative percentage of the sediment total P.

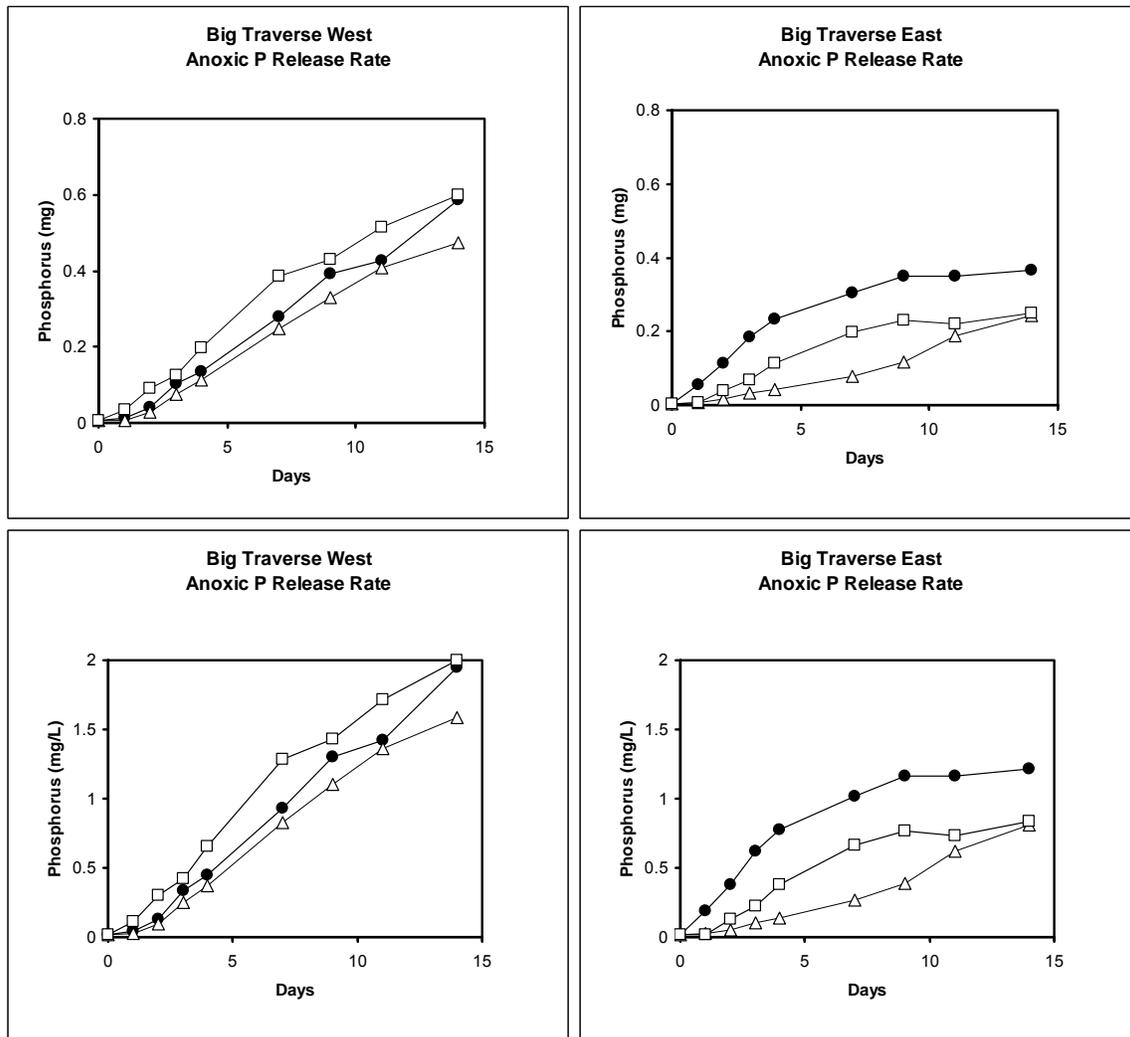


Figure 6. Soluble reactive phosphorus mass (upper panels) and concentration (lower panels) in the overlying water column versus time for sediment core systems incubated under anaerobic conditions.

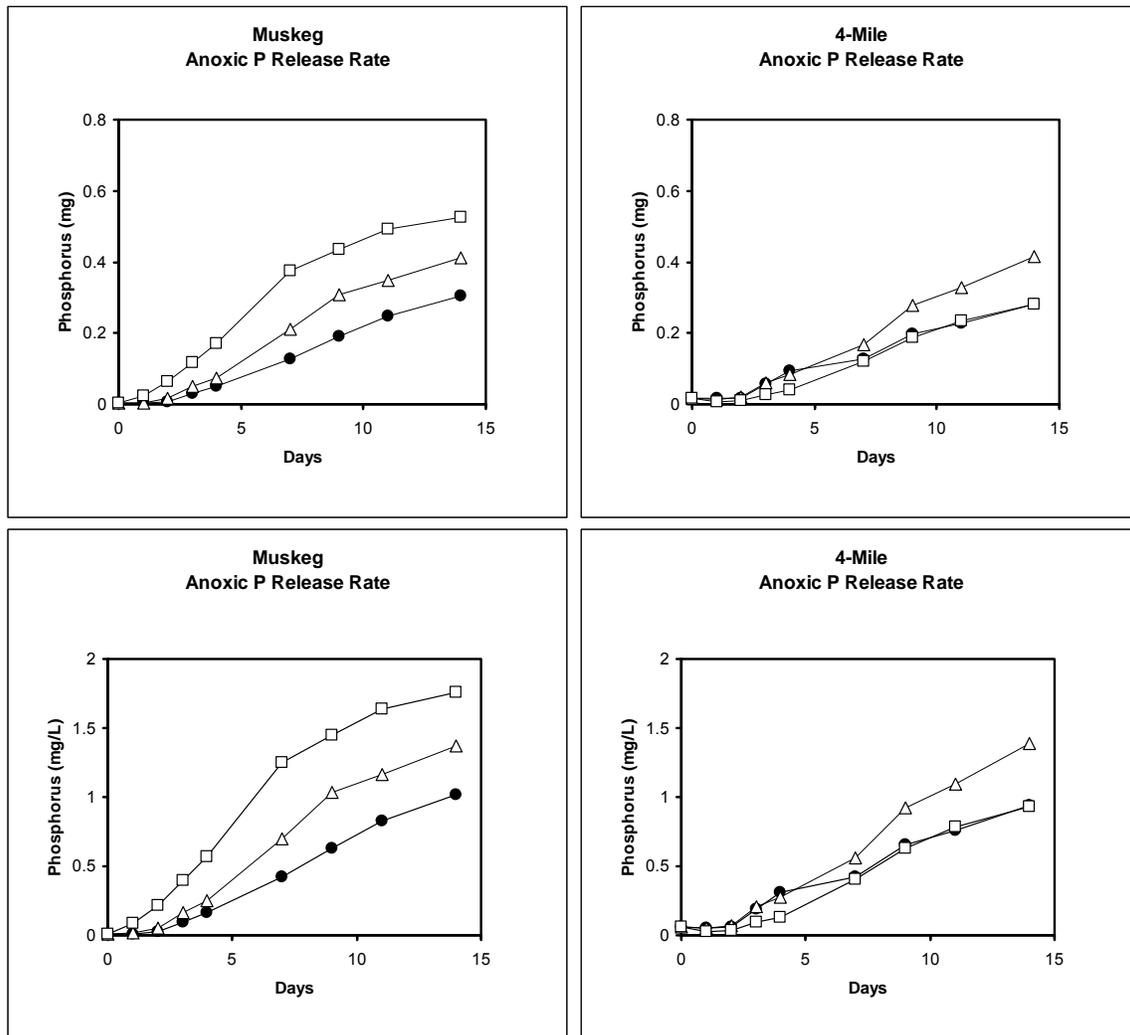


Figure 7. Soluble reactive phosphorus mass (upper panels) and concentration (lower panels) in the overlying water column versus time for sediment core systems incubated under anaerobic conditions.

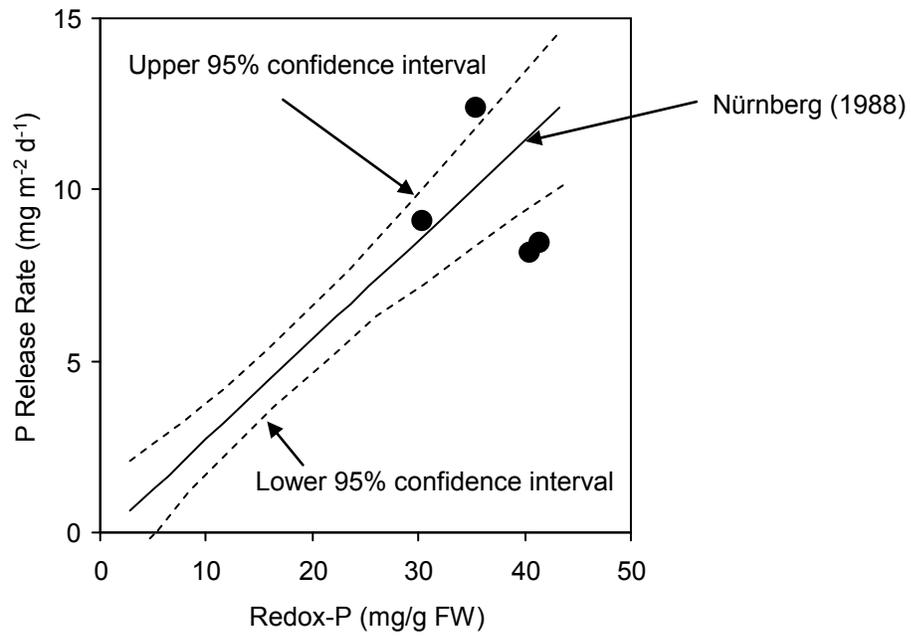


Figure 8. Anoxic diffusive flux rates versus redox-sensitive sediment phosphorus (P) measured for the Lake of the Woods. The solid regression and dashed 95% confidence limit lines are from Nürnberg (1988).

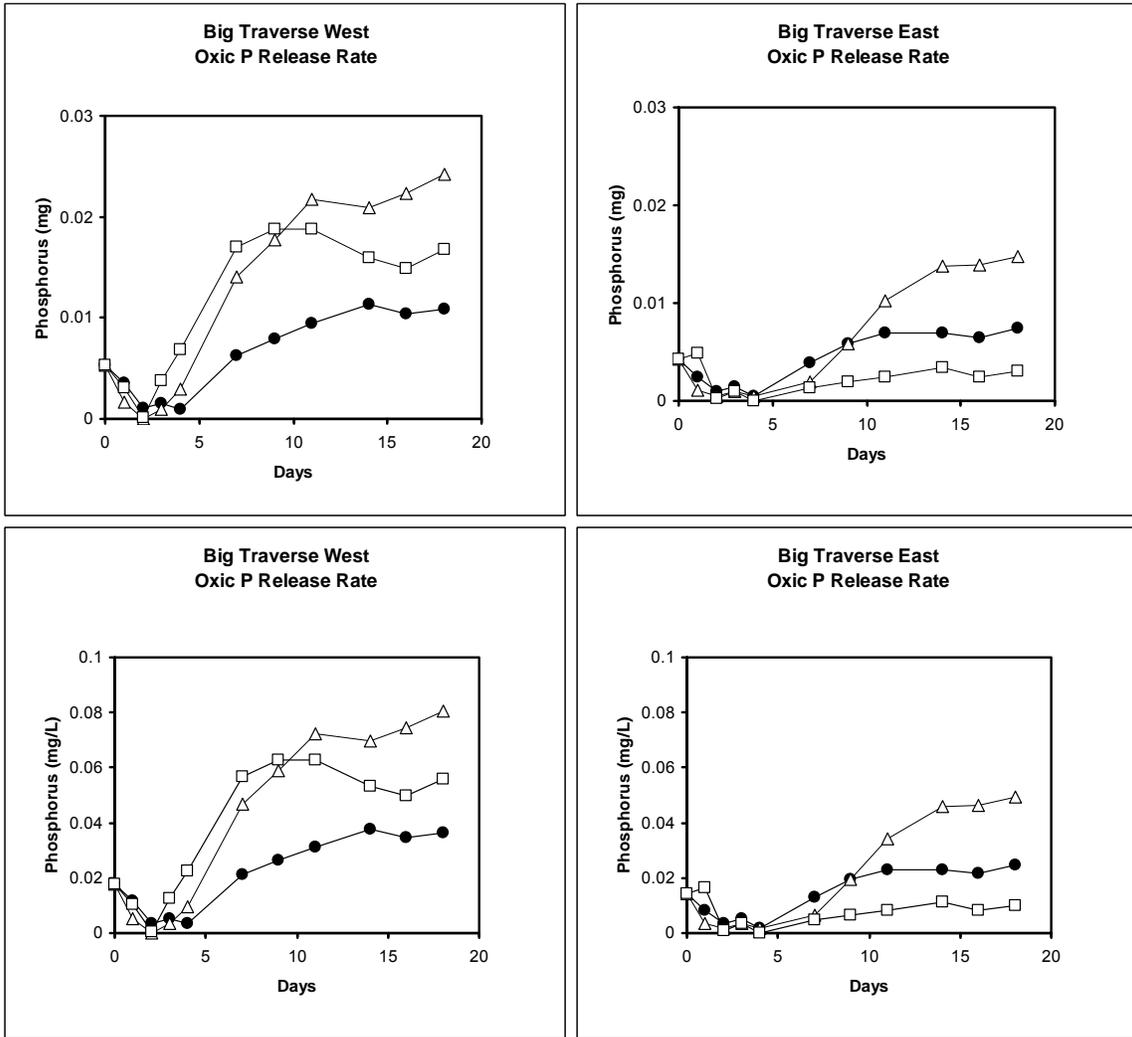


Figure 9. Soluble reactive phosphorus mass (upper panels) and concentration (lower panels) in the overlying water column versus time for sediment core systems incubated under aerobic conditions.

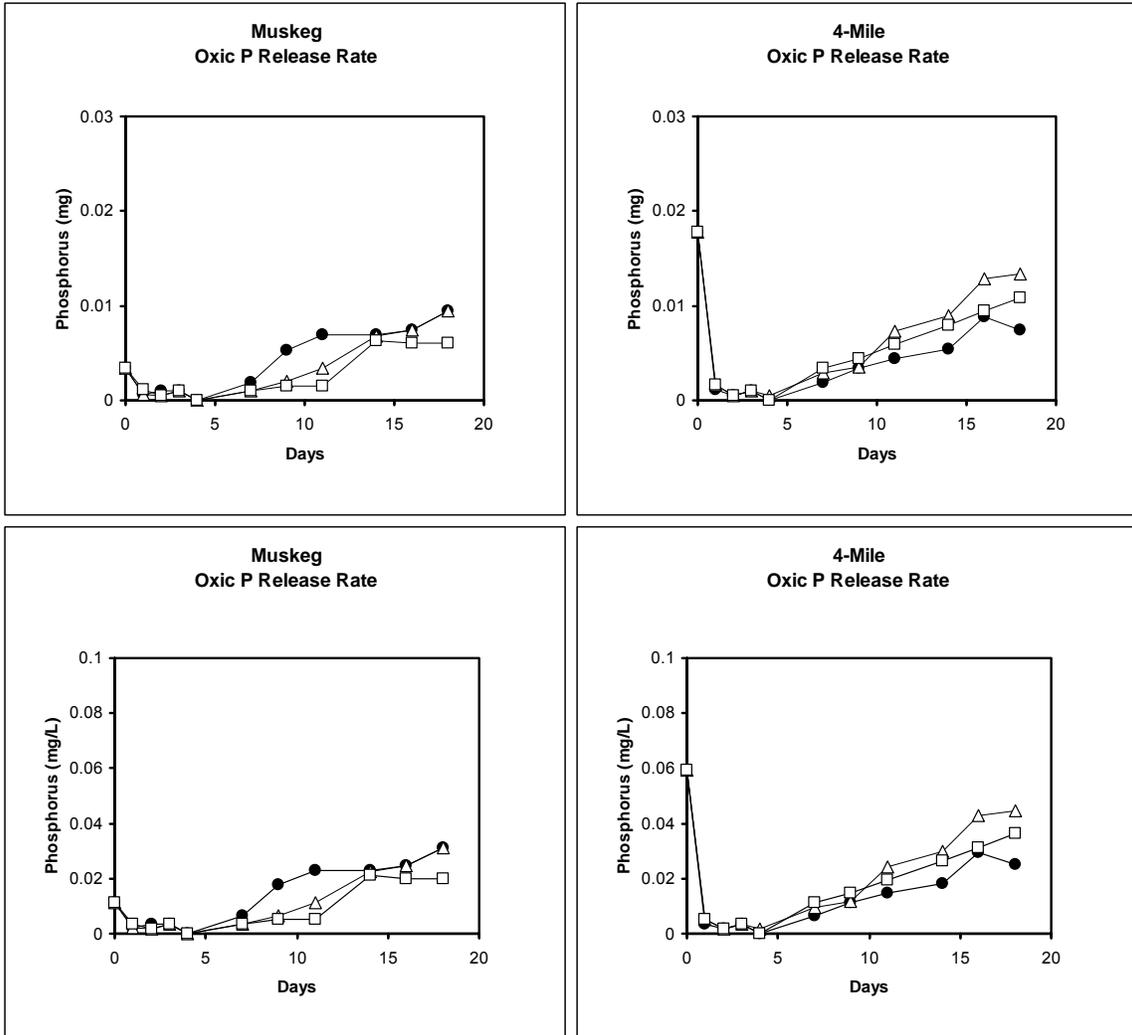


Figure 10. Soluble reactive phosphorus mass (upper panels) and concentration (lower panels) in the overlying water column versus time for sediment core systems incubated under aerobic conditions.

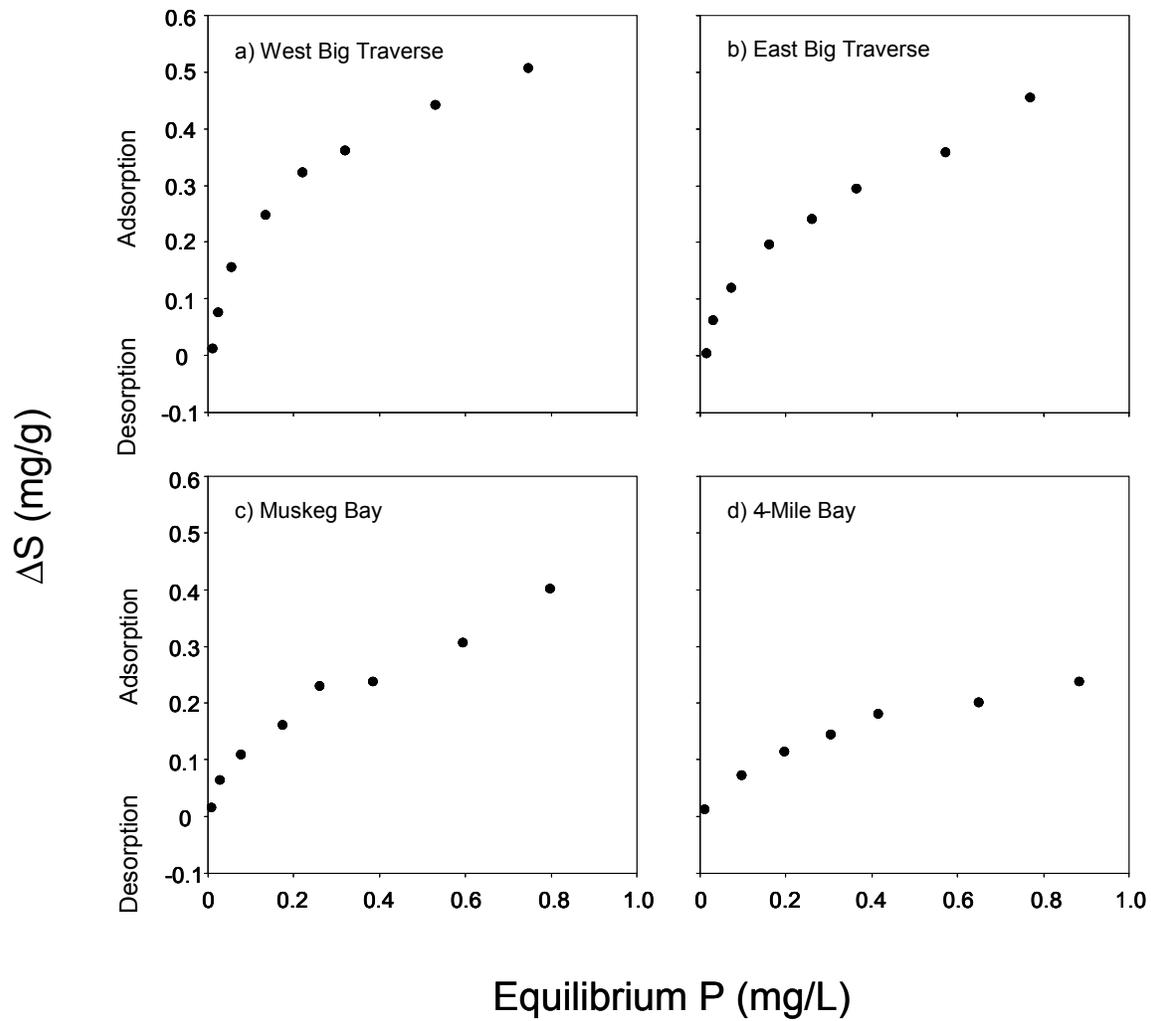


Figure 11. The change in the sediment exchangeable phosphorus (S) concentration as a function of the final (i.e., after 24-h of exposure) equilibrium soluble P concentration for sediment collected at various stations in the Lake of the Woods.

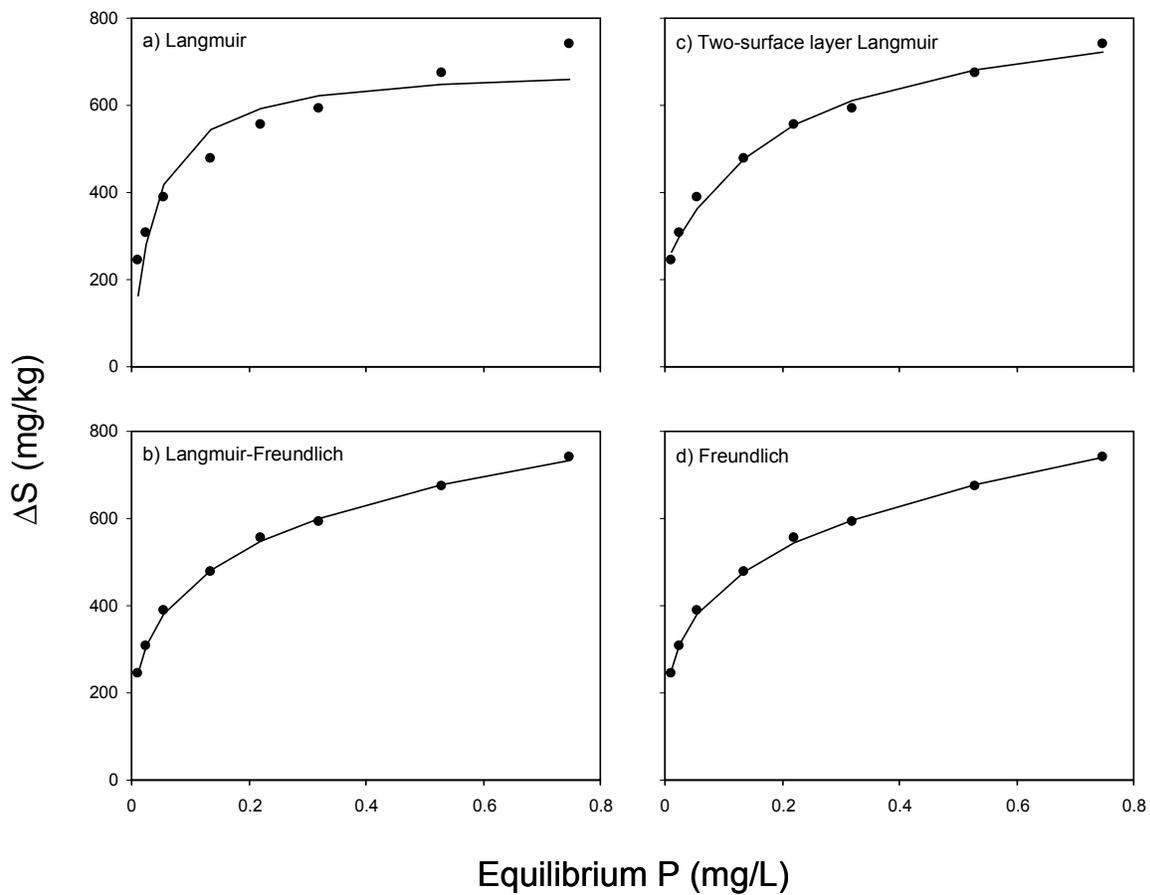


Figure 12. A comparison of different models fitted to sorption data collected from the Lake of the Woods. S represents the sum of the native exchangeable P pool and P that was adsorbed after 24-h of exposure to various soluble P concentrations. The native exchangeable P pool was defined as the sum of the loosely-bound and iron-bound P fractions.

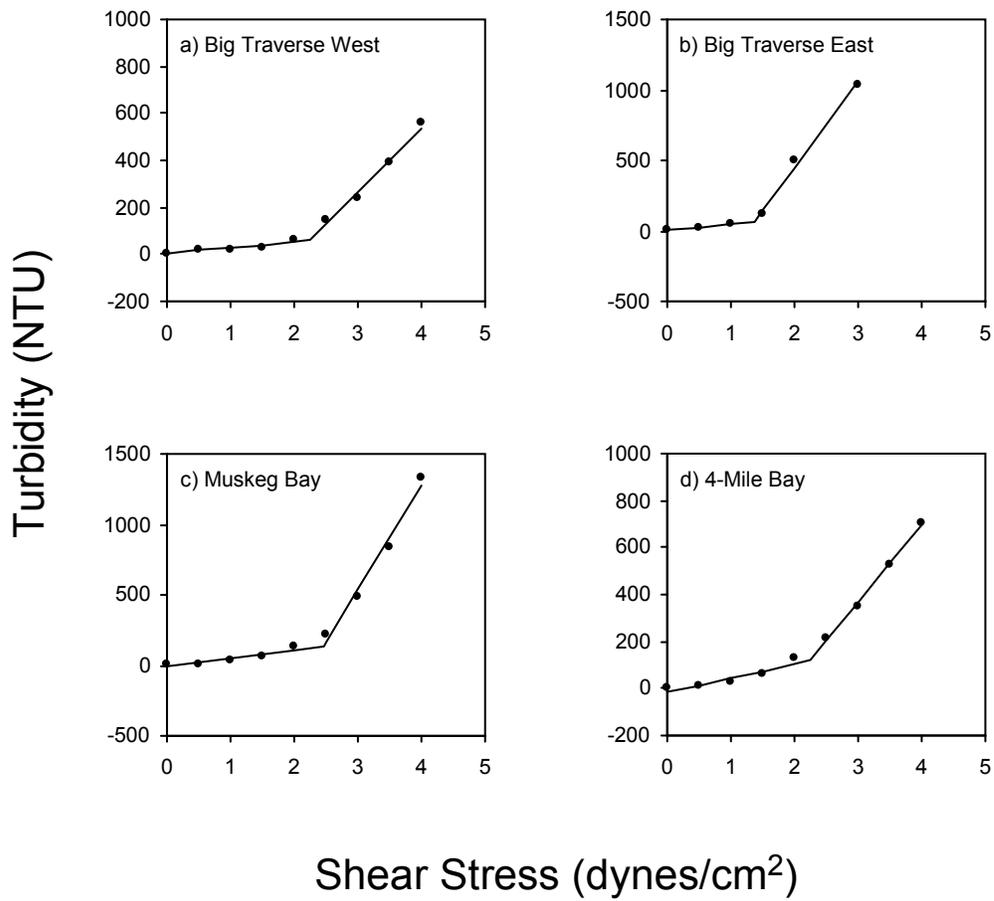


Figure 13. Changes in turbidity in the overlying water column as a function of shear stress. The inflection point approximates the critical shear stress (see Table 5).

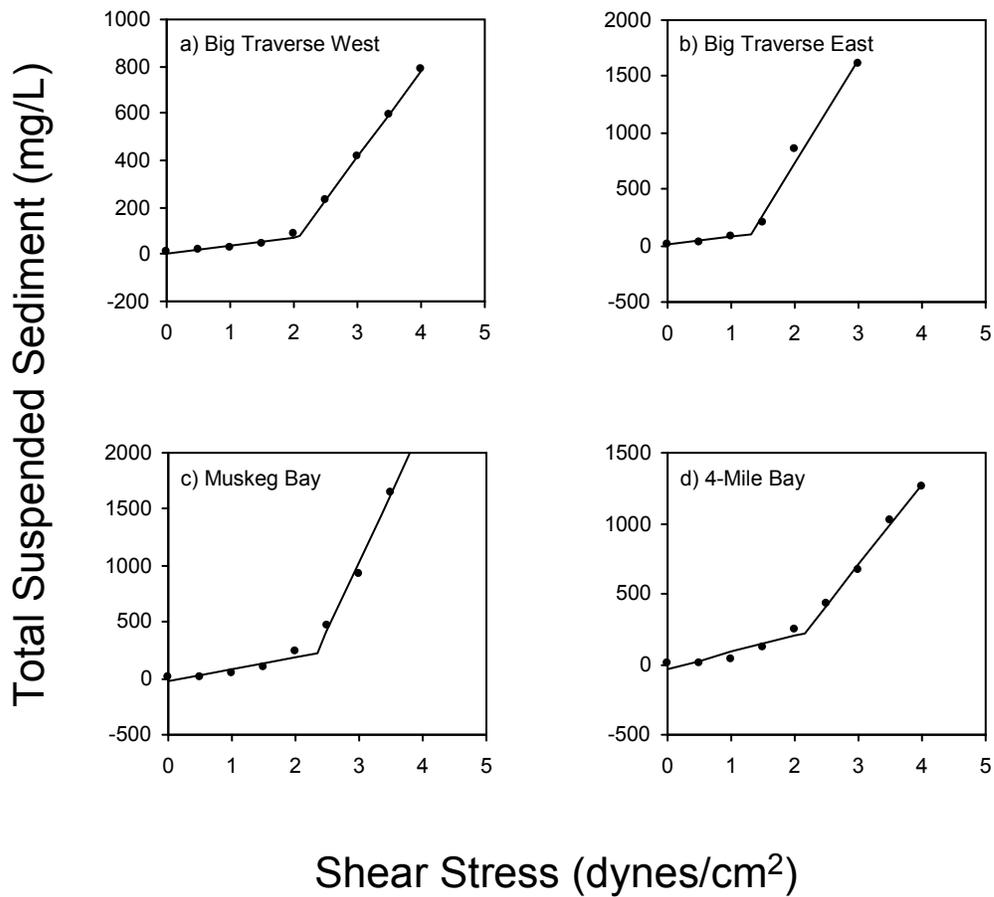


Figure 14. Changes in total suspended sediment concentration in the overlying water column as a function of shear stress. The inflection point approximates the critical shear stress (see Table 5).

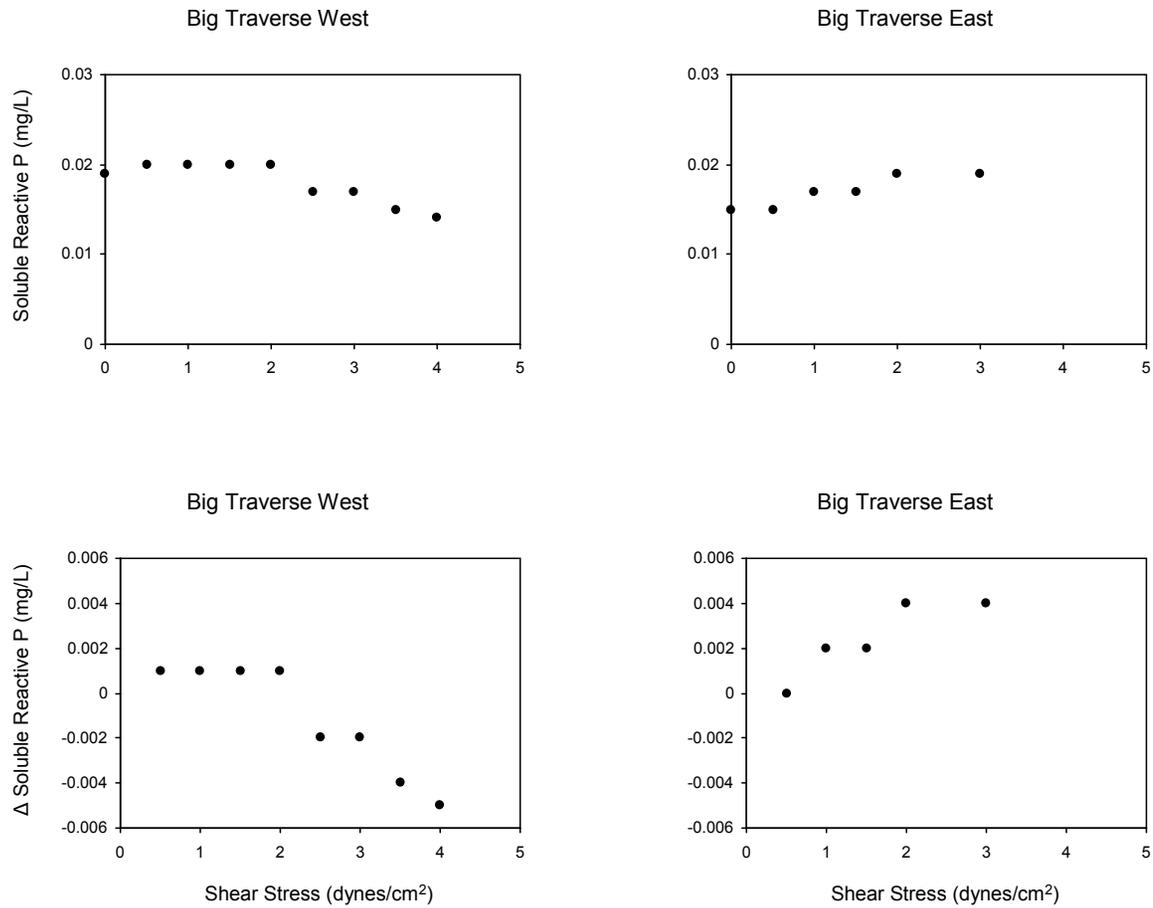


Figure 15. Variations in soluble reactive phosphorus (P) concentration (upper panels) and the net change in concentration from initial, undisturbed conditions (lower panels) as a function of applied shear stress for Big Traverse Lake sediments.

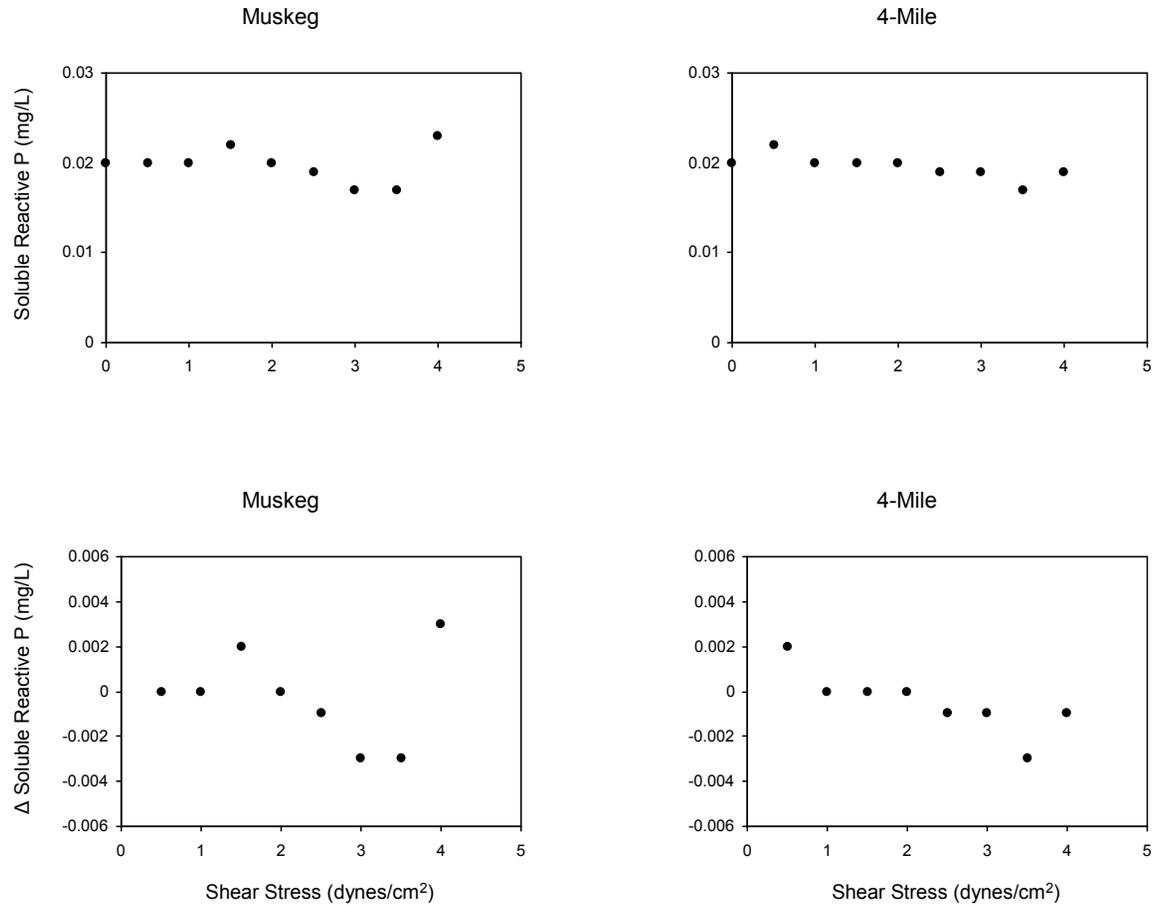


Figure 16. Variations in soluble reactive phosphorus (P) concentration (upper panels) and the net change in concentration from initial, undisturbed conditions (lower panels) as a function of applied shear stress for Muskeg and 4-Mile embayment sediments.