

Internal Phosphorus Loading and Sediment
Phosphorus Fractionation Analysis for
Potato and Sand Lakes, Wisconsin

1 September, 2012

William F. James
University of Wisconsin - Stout
Sustainability Sciences Institute
Menomonie, Wisconsin 54751

OBJECTIVES

The objectives of this investigation were to determine rates of phosphorus (P) release from sediments under laboratory-controlled oxic (i.e., aerobic) and anoxic (i.e., anaerobic) conditions and to quantify biologically-labile (i.e., subject to recycling and P flux to the water column) P fractions for sediments collected in Potato and Sand Lakes, Wisconsin.

APPROACH

Laboratory-derived rates of P release from sediment under oxic and anoxic conditions: Duplicate sediment cores were collected from the north, central, and south basins of Sand Lake and the central basin of Potato Lake in early July, 2012, for determination of rates of P release from sediment under controlled laboratory conditions (Table 1). Phosphorus release rates were determined under anoxic (i.e., anaerobic) conditions for sediment cores collected at all sites. Additionally, oxic (i.e., aerobic) P release rates were determined for sediment cores collected in Potato Lake. In the laboratory, all cores were 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 remover tool. Surface water collected from each lake was filtered through a glass fiber filter (Gelman A-E), with 300 mL then siphoned onto the sediment contained in the small acrylic core liner without causing sediment resuspension. Sediment incubation systems consisted of the upper 10-cm of sediment and filtered overlying water contained in acrylic core liners that were sealed with rubber stoppers. They were placed in a darkened environmental chamber and incubated at a constant temperature of ~20 °C to reflect summer conditions. The oxidation-reduction environment in the overlying water was controlled by gently bubbling air (oxic) or nitrogen (anoxic) through an air stone placed just above the sediment surface in each system. Bubbling action insured complete mixing of the water column but did not disrupt the sediment. Anoxic conditions were verified using a dissolved oxygen electrode.

Water samples for soluble reactive P were collected from the center of each system using an acid-washed syringe and filtered through a 0.45 μm membrane syringe filter (Nalge). The water volume removed from each system during sampling was replaced by addition of filtered lake water preadjusted to the proper oxidation-reduction condition. These volumes were accurately measured for determination of dilution effects. Soluble reactive P was measured colorimetrically using the ascorbic acid method (APHA 2005). Rates of P release from the sediment ($\text{mg m}^{-2} \text{d}^{-1}$) were calculated as the linear change in mass in the overlying water divided by time (days) and the area (m^2) of the incubation core liner. Regression analysis was used to estimate rates over the linear portion of the data.

Sediment chemistry: The upper 10 cm of an additional core collected from each lake station was sectioned for analysis of moisture content (%), sediment density (g/mL), loss on ignition (i.e., organic matter content, %), loosely-bound P, iron-bound P, and labile organic P (all expressed at mg/g). A known volume of sediment was dried at 105 $^{\circ}\text{C}$ for determination of moisture content and sediment density and burned at 500 $^{\circ}\text{C}$ for determination of loss-on-ignition organic matter content (Håkanson and Jansson 2002).

Phosphorus fractionation was conducted according to Hieltjes and Lijklema (1980), Psenner and Puckso (1988), and Nürnberg (1988) for the determination of ammonium-chloride-extractable P (loosely-bound P), bicarbonate-dithionite-extractable P (i.e., iron-bound P), and sodium hydroxide-extractable P (i.e., aluminum-bound P). A subsample of the sodium hydroxide extract was digested with potassium persulfate to determine nonreactive sodium hydroxide-extractable P (Psenner and Puckso 1988). Labile organic P was calculated as the difference between reactive and nonreactive sodium hydroxide-extractable P.

The loosely-bound and iron-bound P fractions are readily mobilized at the sediment-water interface as a result of anaerobic conditions that result in desorption of P from 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 are 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 are 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 P is more chemically inert and subject to burial rather than recycling.

RESULTS AND INTERPRETATION

Rates of Phosphorus Release from Sediment

Phosphorus mass and concentration increased in the overlying water column of Sand Lake sediment systems maintained under anoxic conditions (Figure 1). Rates of P mass and concentration increase were generally linear over the first 5 days of incubation; concentrations tended to a lesser extent thereafter. This pattern was probably due to diminishment of P concentration gradients at the sediment-water interface over time, which drive P diffusion out of sediment and into the overlying water column. The mean P concentration in the overlying water column of sediment systems at the end of the incubation period was relatively high for sediment cores collected in the north and south basins of Sand Lake at 1.746 mg/L (± 0.154 standard error; SE) and 1.733 mg/L (± 0.304 SE), respectively, suggesting the potential for the buildup of high concentrations of P in the hypolimnion during the summer stratified period. The mean P concentration was lower for the central basin sediments of Sand Lake (0.698 mg/L ± 0.00 SE), compared to the other basins. Nevertheless, the mean concentration was high and typical of concentrations observed in the hypolimnion of eutrophic lakes. In marked contrast, P mass and concentrations did not increase in the overlying water column of sediment systems incubated under anoxic conditions for Potato Lake sediments (Figure 2). This

pattern was very unusual given the concentration of biologically-labile P in the sediment (see below).

Overall, mean rates of P release under controlled laboratory conditions at ~ 20 °C were high for Sand Lake sediments, ranging between 6.2 and 14.9 mg m⁻² d⁻¹ (Table 2). Mean anoxic P release rates were greatest for north and south basin sediments, versus the central basin of the lake. This pattern may be related to bathymetric patterns and possible variations in the deposition of P-rich sediments in the deep basins of the lake. The north and south Sand Lake stations were located deep depressions versus the central station, which was located in a shallower region that spanned the north and south basins. The north and south basins would tend to function as zones of sediment accumulation as a result of focusing of P-rich fine-grained sediments with higher concentrations of redox-sensitive P (see below and Table 3). Indeed, patterns of higher anoxic P release rates correlated well with higher concentrations of loosely-bound and iron-bound P fractions in the north and south basin versus lower anoxic P release rates and lower concentrations of redox-sensitive P at the central station.

Anoxic P release rates in the north and south basins of Sand Lake exceeded the upper 25% quartile for regional lakes in west-central Wisconsin (Figure 3). Rates determined for the central station in Sand Lake fell within the lower 25% quartile while those measured for Potato Lake were very low relative to other lakes in the region.

In addition to negligible P release under anoxic conditions, the mean rate of P release from sediment was also negligible under oxic conditions for Potato Lake sediments. These results were very surprising and reasons for this pattern are not entirely known. Rates are typically low or negligible under aerobic conditions if iron oxyhydroxides play a role in binding phosphate at the sediment oxygenated microzone (i.e., the thin layer of surface sediment exposed to oxygenated conditions). However, P release rates usually increase under anoxic conditions when iron becomes reduced during anaerobic bacterial metabolism and loses its binding efficiency for phosphate. The surface sediments in Potato Lake were very flocculent and exhibited a high moisture content of 97%,

indicating that the sediment was composed primarily of interstitial water (i.e., porewater) with very little sediment iron-bound P mass per unit volume of sediment (i.e., expressed on a m^3 or $\text{m}^2\text{-cm}$, basis). The concentration of iron-bound P per fresh mass of sediment (i.e., including porewater as well as sediment mass) was minor at $6 \mu\text{g P/g}$ sediment fresh mass and $0.06 \text{ g P/m}^2\text{-cm}$ (see Table 3), which might explain the negligible rates of P release under anoxic conditions. Using the regression relationship between iron-bound P and the anoxic P release rate developed by Nürnberg (1988), the predicted anoxic P release rate for an iron-bound P concentration of $6 \mu\text{g P/g}$ fresh mass sediment was $0.3 \text{ mg m}^{-2} \text{ d}^{-1}$ (i.e., predicted anoxic P release rate = $(6 \mu\text{g/g} * 0.285) - 1.38$), which is low and compares with the actual undetectable rate measured for Potato Lake sediments.

Sediment Textural and Chemical Characteristics

Sediments from Potato and Sand Lake stations generally exhibited very high moisture content and low bulk density, indicating very fine-grained flocculent sediment (Table 2). Organic matter content was nominal for Sand Lake sediments compared to other lakes in the region (Table 2 and Figure 4). In contrast, Potato Lake sediments exhibited very high organic matter content at $\sim 56\%$, relative to some other lakes in Wisconsin (Figure 4).

Iron-bound P (expressed on a sediment dry mass basis; mg P/g DW sediment) accounted for greater than 50% of the biologically-labile P for the north and south basin stations of Sand Lake (Figure 5 and 6). Loosely-bound and iron-bound P concentrations were also very high at these stations versus the central station of Sand Lake (Figure 6) and they fell above the 25% quartile compared to other regional Wisconsin lakes (Figure 7). Expressed on a fresh sediment mass basis ($\mu\text{g P/g}$ fresh mass sediment), concentrations of iron-bound P were relatively high for the north and south basin sediments of Sand Lake, reflecting higher rates of P release under anoxic conditions at these same stations.

In contrast, labile organic P (expressed on a sediment dry mass basis; mg P/g DW sediment) represented most of the biologically-labile P at the central station sediments of Sand Lake (Figure 5). However, concentrations of this fraction fell near the median concentration for regional Wisconsin lakes (Figure 7). The central station sediments of Sand Lake also exhibited a relatively low loosely-bound P and iron-bound P concentration versus other Sand Lake stations (Figure 6), reflecting a lower rates of P release under anoxic conditions. Overall, sediments from the north basin exhibited the greatest concentration of biologically-labile P followed by the south basin (Figure 6). The central station exhibited the lowest concentration of biologically-labile P.

The biologically-labile P fraction (expressed on a sediment dry mass basis; mg P/g DW sediment) for sediment collected in the central basin of Potato Lake was dominated by the labile organic P fraction at 66% (Figure 5). Loosely-bound P represented 21% and iron-bound P accounted for 13% of the biologically-labile P (Figure 5). The loosely-bound P and labile organic P concentrations for Potato Lake sediments were higher and fell above the upper 25% quartile compared to other lakes on the regional area (Figure 7). Iron-bound P fell near the median for lakes in west-central Wisconsin. However, as mentioned above, the very high moisture content of sediments in Potato Lake translated into very low concentrations when expressed on a sediment volumetric or wet mass basis.

Summary

Rates of P release from sediment under laboratory-controlled conditions at 20 °C were relatively high in Sand Lake and suggested the potential for internal P loading, particularly for the north and south basin sediments,. High sediment dry mass concentrations of loosely-bound and iron-bound P (collectively referred to as redox-sensitive P), which have been positively correlated with anoxic P release rates (Nürnberg 1988), tended to correlate with anoxic P release rates in Sand Lake, suggesting that iron-bound P in sediment is an important source for diffusive P flux under anoxic conditions. These rates represented a potential maximum internal P loading rate for Sand Lake and are likely higher compared to P mass balance because factors like variation in

temperature and hypolimnetic anoxia were not factored into the laboratory rate calculation.

In contrast, rates of P release from sediments collected in Potato Lake were negligible under both oxic and anoxic conditions. On a sediment dry mass basis, iron-bound P concentrations were near the median compared to other lakes in west-central Wisconsin. However, very high sediment moisture content implied that sediment was very fluid in Potato Lake and composed almost entirely of porewater. Thus, the iron-bound P concentration was much lower per unit volume of sediment, which likely explains the very low potential for sediment internal P loading in the lake.

REFERENCES

- APHA (American Public Health Association). 2005. Standard Methods for the Examination of Water and Wastewater. 21th ed. American Public Health Association, American Water Works Association, Water Environment Federation.
- Boström B. 1984. Potential mobility of phosphorus in different types of lake sediments. *Int. Revue. Ges. Hydrobiol.* 69:457-474.
- 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.
- Håkanson L, Jansson M. 2002. Principles of lake sedimentology. The Blackburn Press, Caldwell, NJ USA.

Hjieltjes AH, Lijklema L. 1980. Fractionation of inorganic phosphorus in calcareous sediments. *J. Environ. Qual.* 8: 130-132.

Hupfer M, Gächter R., Giovanoli R. 1995. Transformation of phosphorus species in settling seston and during early sediment diagenesis. *Aquat. Sci.* 57:305-324.

Jensen HS, Kristensen P, Jeppesen E, Skytthe A. 1992. Iron:phosphorus ratio in surface sediment as an indicator of phosphate release from aerobic sediments in shallow lakes. *Hydrobiol.* 235/236:731-743.

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.* 45:453-462.

Plumb RH. 1981. Procedures for handling and chemical analysis of sediment and water samples. Technical Report EPA/CE-81-1. US Army Engineer Waterways Experiment Station, Vicksburg, MS.

Psenner R, Puckso R. 1988. Phosphorus fractionation: Advantages and limits of the method for the study of sediment P origins and interactions. *Arch. Hydrobiol. Biel. Erg. Limnol.* 30:43-59.

Table 1. Redox (i.e., oxic and/or anoxic) conditions used for determination of rates of phosphorus release from sediment for various stations.			
Lake	Station	Redox Condition	
		Oxic	Anoxic
Sand	North Basin		X
Sand	Central Basin		X
Sand	South Basin		X
Potato	Central Basin	X	X

Table 2. Textural characteristics for sediments collected in Sand and Potato Lakes.					
Lake	Station	Moisture Content (%)	Bulk Density (g/cm ³)	Sediment Density (g/cm ³)	Loss-on-ignition (%)
Sand	North Basin	93.1	1.033	0.072	23.4
	Central Basin	94.2	1.028	0.062	23.6
	South Basin	95.1	1.024	0.054	22.1
Potato	Central Basin	97.3	1.007	0.031	56.5

Table 3. Mean (1 standard error in parentheses; n=2) rates of phosphorus (P) release and concentrations of biologically-labile (i.e., subject to recycling and flux to the hypolimnion) P for sediments collected in Sand and Potato Lakes. DW = dry mass, FW = fresh mass).

Lake	Station	Diffusive P flux		Biologically labile P						Refractory P
		Oxic (mg m ⁻² d ⁻¹)	Anoxic (mg m ⁻² d ⁻¹)	Loosely-bound P (mg/g DW)	(mg/g DW)	Iron-bound P (ug/g FW)	(g/m ² -cm)	Redox-sensitive P (mg/g DW)	Labile organic P (mg/g DW)	Aluminum-bound P (mg/g DW)
Sand	North Basin		13.1 (0.9)	0.319	2.911	199	2.075	3.230	0.303	1.430
	Central Basin		6.2 (0.1)	0.020	0.216	12	0.129	0.236	0.354	0.125
	South Basin		14.9 (3.0)	0.325	1.195	72	0.600	1.520	0.879	1.195
Potato	Central Basin	<0.1	<0.1	0.369	0.216	6	0.059	0.585	1.136	0.320

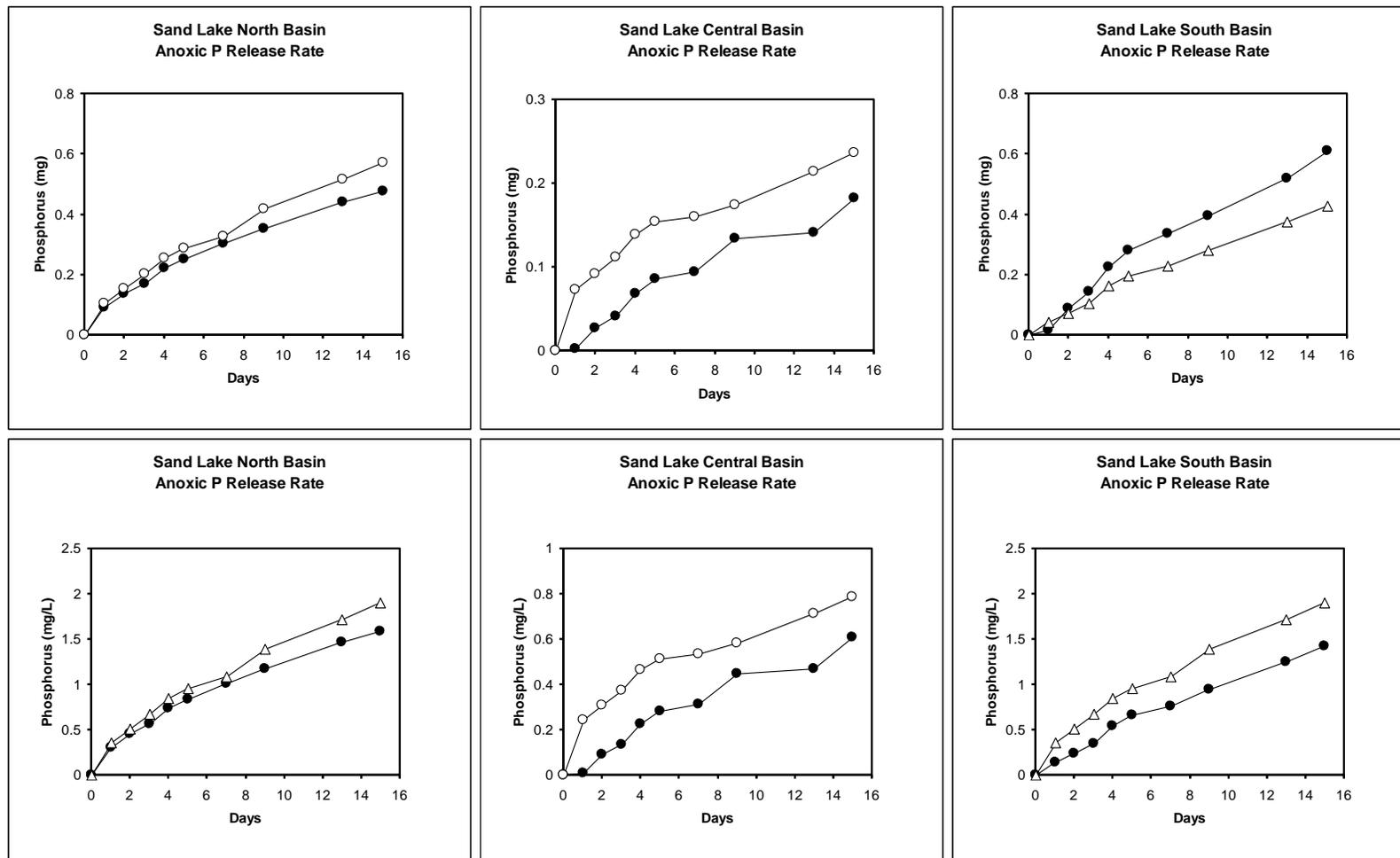


Figure 1. Changes in soluble reactive phosphorus mass (upper panel) and concentration (lower panel) in the overlying water column of sediment systems incubated under anoxic conditions versus time for sediment cores collected in Sand Lake.

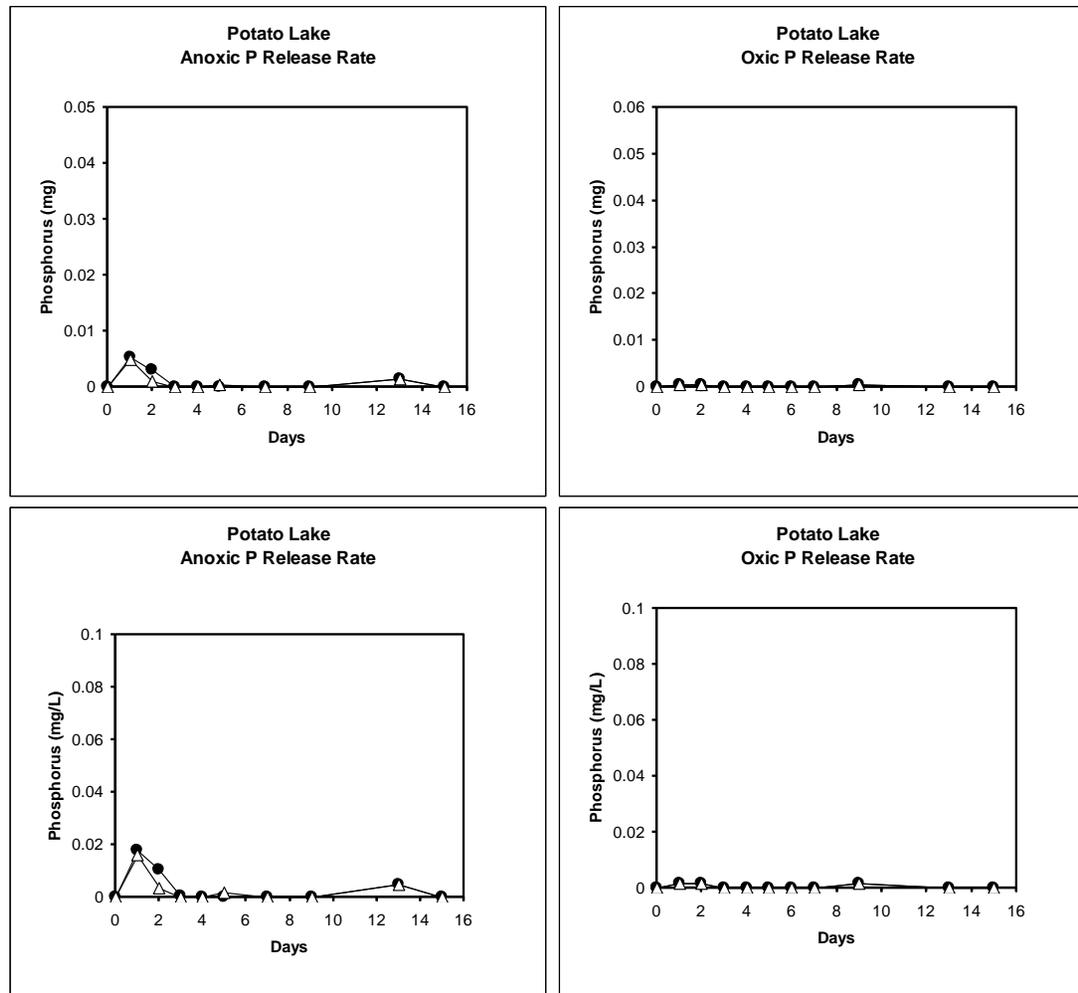


Figure 2. Changes in soluble reactive phosphorus mass (upper panel) and concentration (lower panel) in the overlying water column of sediment systems incubated under anoxic (left panels) and oxic (right panels) conditions versus time for sediment cores collected in Potato Lake.

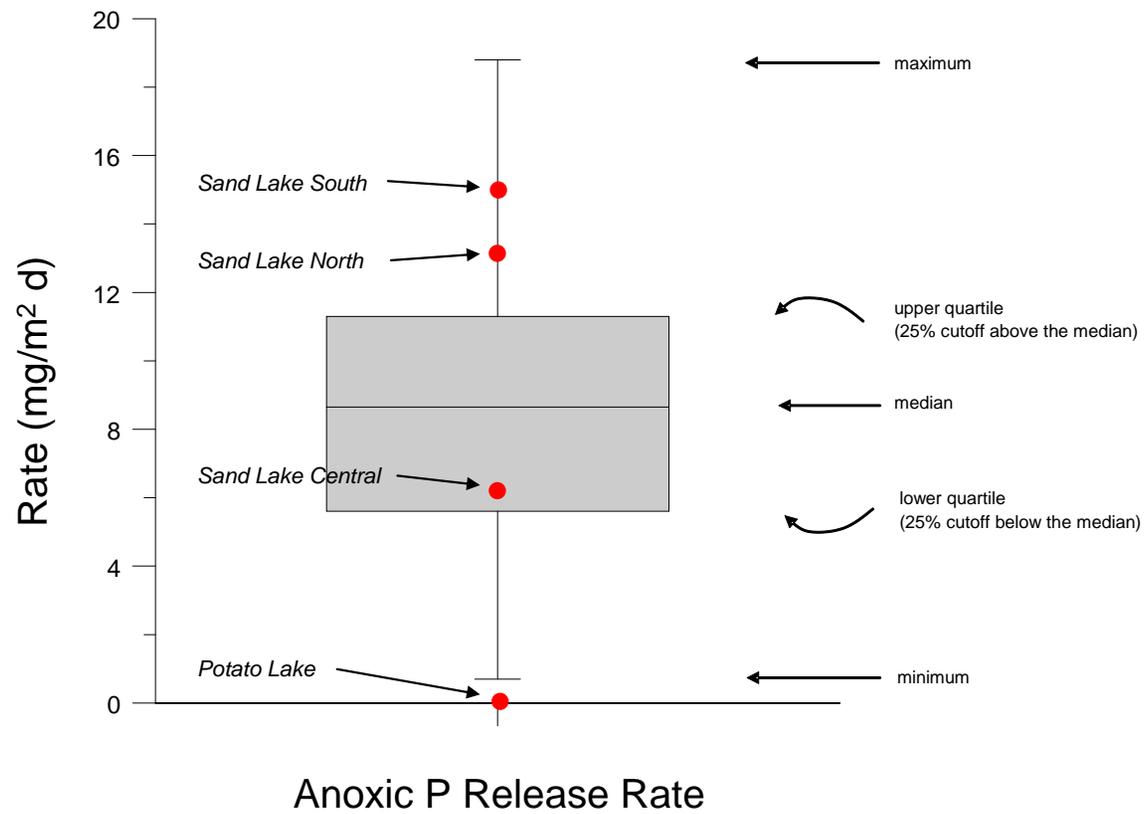


Figure 3. Box and whisker plot comparing the anoxic phosphorus (P) release rate measured Sand and Potato Lakes (red circles) with statistical ranges (7 lakes; ~ 50 stations) for lakes in west-central Wisconsin.

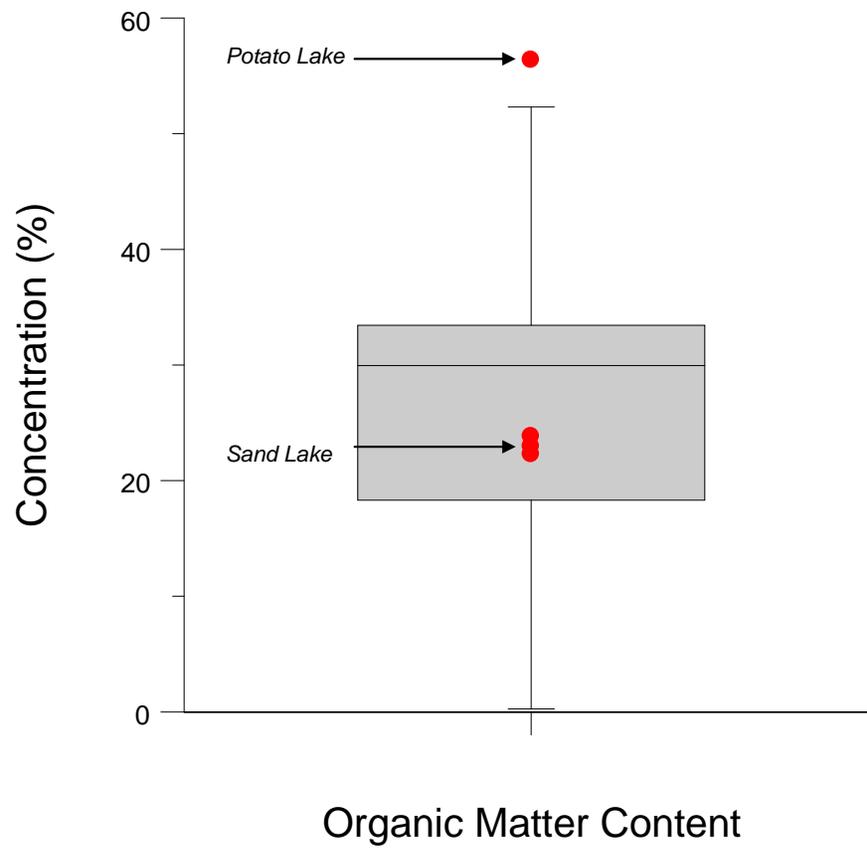


Figure 4. Box and whisker plot comparing the sediment organic matter content measured in Sand and Potato Lakes (red circles) with statistical ranges (7 lakes; ~ 50 stations) for lakes in west-central Wisconsin.

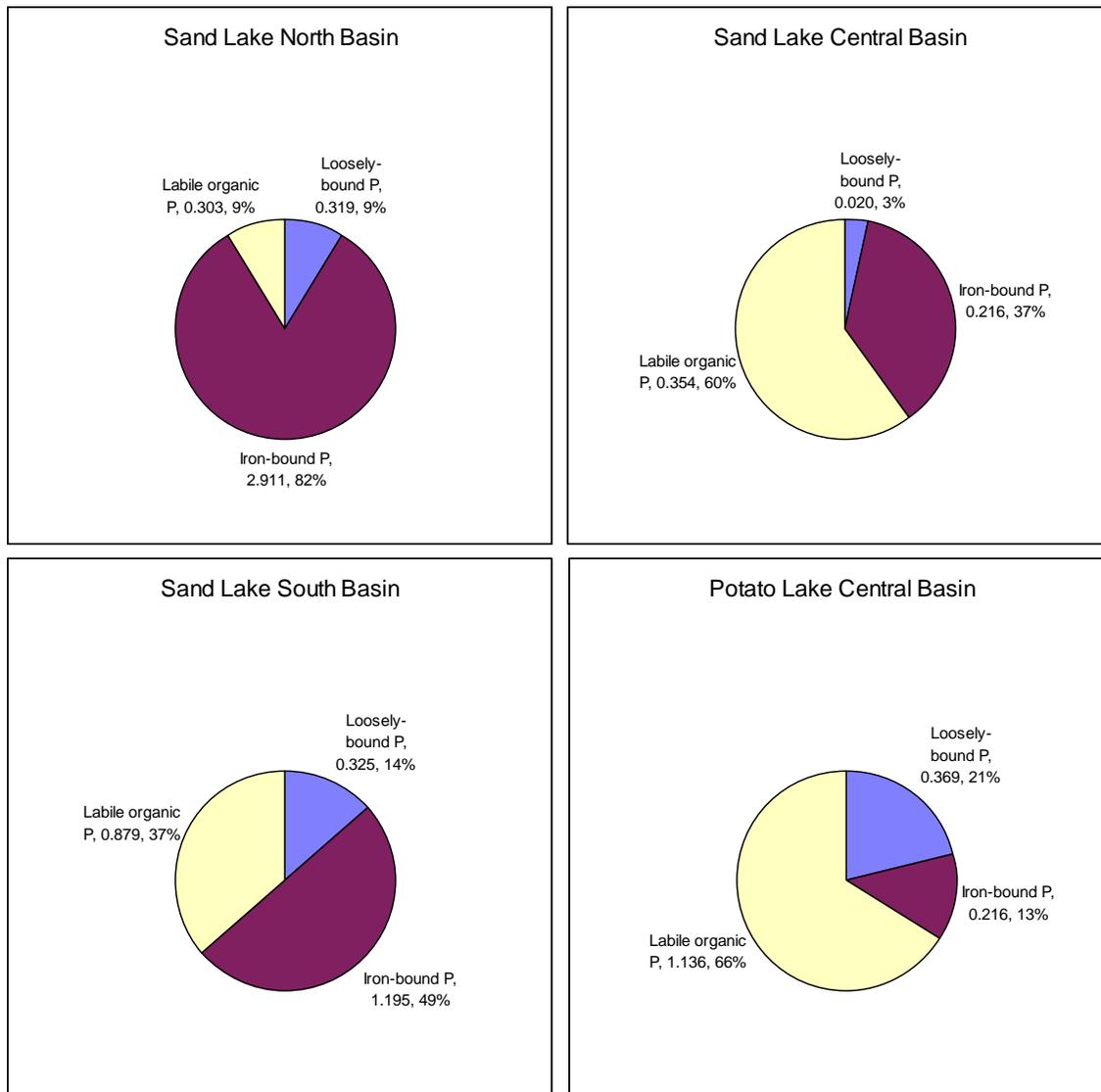


Figure 5. Biologically-labile phosphorus (P) composition for sediment collected at various stations in Sand and Potato Lakes. Loosely-bound, iron-bound, and labile organic P fractions are biologically reactive, subject to recycling, and correlated with rates of internal P loading. Values next to each label represent concentration (mg·g⁻¹ dry mass of sediment) and percent biologically-labile P, respectively.

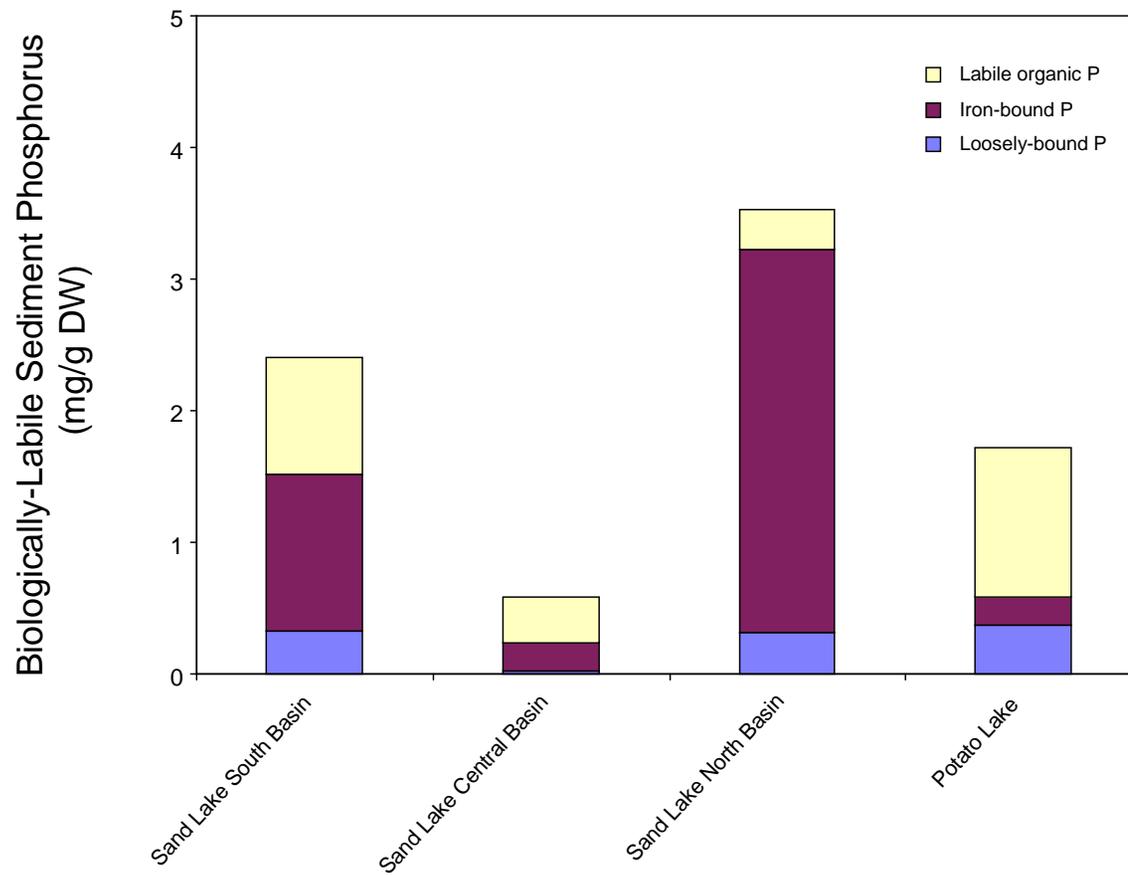


Figure 6. Comparison of biologically-labile phosphorus (loosely-bound, iron-bound, and labile organic P) concentrations in sediment for various stations in Sand and Potato Lakes.

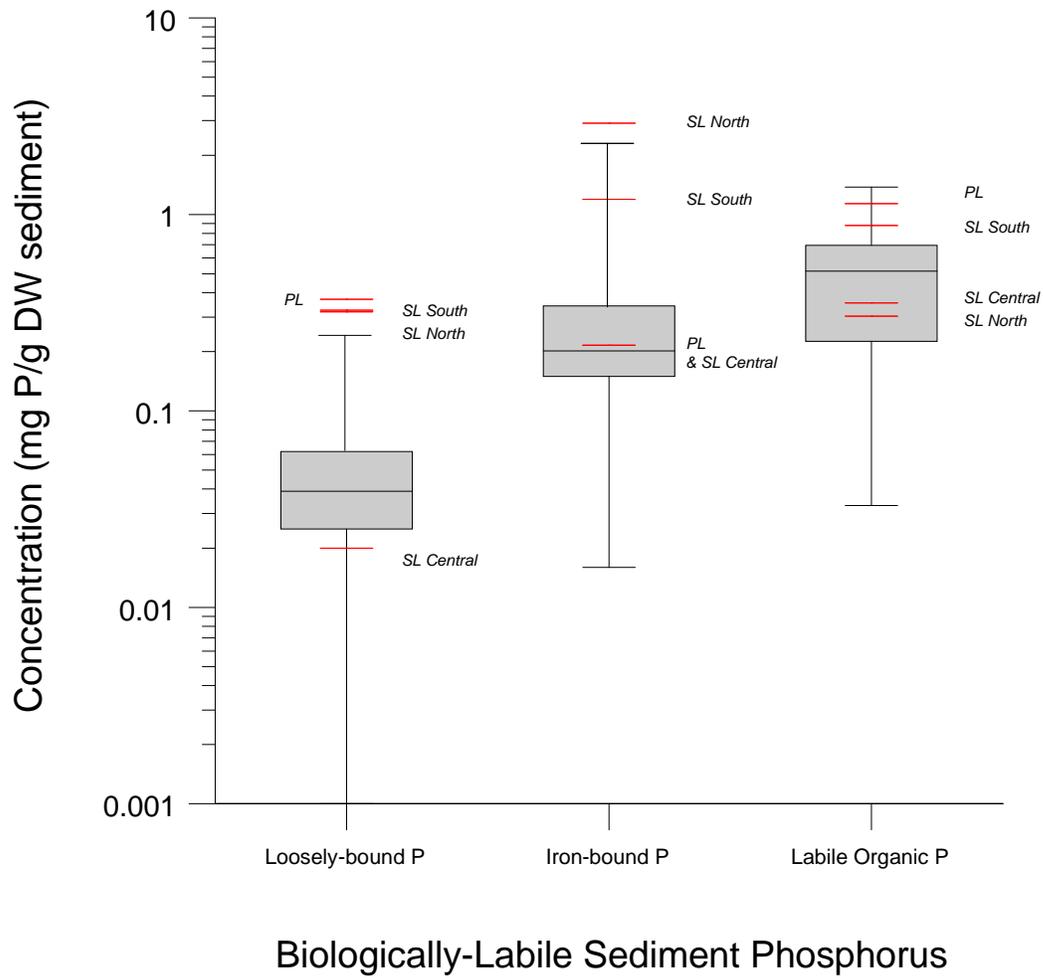


Figure 7. Box and whisker plots comparing biologically-labile sediment phosphorus (P) fractions measured for Sand (SL) and Potato Lakes (PL; red lines) with statistical ranges (7 lakes; ~ 50 stations) for lakes in west-central Wisconsin. Loosely-bound, iron-bound, and labile organic P fractions are biologically reactive, subject to recycling, and correlated with rates of internal P loading. Please note the logarithmic scale.