Alum Dosage Considerations for Lake Desair, Wisconsin

Summer algal bloom in progress (2012), Lake Desair, WI

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OBJECTIVES

The objectives of these investigations were several-fold for Lake Desair:

1. determine spatial variations in diffusive phosphorus flux from sediments under anoxic conditions,
2. examine spatial and vertical variations in phosphorus fractions that are active and mobile in anoxic P release from sediment (i.e., redox-sensitive P and labile organic P),
3. quantify the thickness of the sediment layer potentially active in anoxic P release,
4. estimate the dosage of alum (as aluminum) required to bind redox-sensitive P fractions in the active sediment layer, and
5. provide cost estimates for alum application based on treatment areas in the lake.

APPROACH

Sediment diffusive phosphorus flux under anoxic conditions: Duplicate sediment cores were collected from three stations located in the deep basin of Lake Desair in early July, 2012, for determination of rates of P release from sediment under anoxic conditions (***Figure 1 and Table 1***). 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 the lake was filtered through a glass fiber filter (Gelman A-E), with 300 mL then siphoned onto the sediment contained in the small acrylic core liner without causing sediment resuspension. Sediment incubation systems consisted of the upper 10-cm of sediment and filtered overlying water contained in acrylic core liners that were sealed with rubber stoppers. They were placed in a darkened environmental chamber and incubated at a constant temperature (20 ^{o}C). The oxidation-reduction environment in the overlying water was controlled by gently bubbling 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 (mg m^{-2} 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.

Phosphorus profiles in the sediment: An additional core collected from each station was sectioned at 2-cm intervals over the upper 12 cm for analysis of moisture content (%), sediment and bulk density (g/mL), loss on ignition (i.e., organic matter content, %), loosely-bound P, iron-bound P, aluminum-bound P, and labile organic P (all expressed at mg/g). A known volume of sediment was dried at 105 ^{o}C for determination of moisture content, sediment, and bulk density and burned at 500 ^{o}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 lead to 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 fraction 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 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.

Alum dosage determination: Sediment collected from each sampling station in the lake (***Figure 1***) was subjected to a range of aluminum sulfate (as Al) concentrations to determine the dosage required to inactivate the redox-P fraction (Rydin and Welch 1999). Alum (as aluminum sulfate; $Al_2(SO_4)_3 \cdot 18\ H_2O$) was combined with 0.1 M sodium bicarbonate ($NaHCO_3$) to a concentration of 0.7 to 1.4 g Al L^{-1} to form an aluminum hydroxide ($Al(OH)_3$) floc. Aliquots of this solution, diluted to a final volume of 10 mL with distilled water, were added to centrifuge tubes containing the equivalent of 0.025 g dry weight (DW) of fresh sediment to obtain Al concentrations ranging from 0 (i.e., control) to greater than 100 mg Al g^{-1} DW sediment or higher. The assay tubes were shaken for a minimum of 2 hours at 20 ^{o}C in a darkened environmental chamber, centrifuged at 500 g to concentrate the sediment, and decanted for redox-P determination.

Al dosage was estimated as the concentration ($g \cdot m^{-2}$) required to bind at least 90% of the redox-P. The dry mass concentration of redox-P ($mg \cdot g^{-1}$) was converted to an areal concentration ($g \cdot m^{-2}$) as,

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

where, ρ is sediment bulk density ($\text{g}\cdot\text{cm}^{-3}$), θ is sediment porosity (100 – percent moisture content; dimensionless), and h is sediment thickness (m). The Al concentration ($\text{g}\cdot\text{m}^{-2}$) was estimated as,

$$\text{Al } (\text{g}\cdot\text{m}^{-2}) = \text{Redox-P } (\text{g}\cdot\text{m}^{-2}) \cdot \text{Al:P}_{90\%} \quad 2)$$

where, $\text{Al:P}_{90\%}$ is the binding ratio required to adsorb at least 90% of the redox- P in the sediment.

Maximum allowable Al dosage based on alkalinity and pH in the lake: Addition of aluminum sulfate to a lake leads to hydrolysis and the liberation of hydrogen ions which lowers the pH of the water column. Since Al toxicity to the biota can occur if the pH falls below 6, maintaining a pH > 6.0 must also be considered in dose determination. For situations where alkalinity is low or the required dosage exceeds the maximum allowable dosage to maintain pH > 6.0, buffered aluminum sulfate-sodium aluminate treatment will be needed to maintain pH near neutrality. Surface water collected from the lake was analyzed for total alkalinity and pH according to APHA (2005). These results were used in conjunction with the Al dosage nomograph presented in Cooke et al. (2005) to estimate a maximum volumetric Al dosage based on the alkalinity and pH of the lake for comparison with the sediment P-based dosage. If the latter estimate exceeded the maximum allowable dosage, other strategies such as use of buffered aluminum sulfate-sodium aluminate or application of multiple lower aluminum sulfate dosages over a period of years should be used.

RESULTS AND INTERPRETATION

Anoxic diffusive P flux and sediment characteristics

Soluble P mass and concentration increased rapidly in the overlying water column of sediment systems maintained under anoxic conditions (***Figure 2***). Rates of soluble P mass and concentration increase were most rapid during the first two days and then exhibited a less rapid linear increase thereafter. The mean soluble P concentration maximum at the end of the incubation period was also high at 1.152 mg/L (± 0.071 SE), 1.038 mg/L (± 0.174), and 0.715 mg/L (± 0.174 SE) for the north, central, and south station sediment incubation systems, respectively, and similar to P concentrations observed in the hypolimnion of the lake (Cedar Corporation 2006). Mean anoxic diffusive flux rates varied between 8.4 mg m^{-2} d^{-1} at the north station to 14.7 mg m^{-2} d^{-1} at the deeper central station (***Table 2***). In general, these rates were high and indicative of phosphorus-rich sediments found in eutrophic lake systems.

For the upper 10-cm sediment layer, average moisture content was relatively low, while sediment and bulk density were high, suggesting that sediments were densely packed with fine particles (***Table 3***). In contrast, many lakes in the west-central region of Wisconsin exhibit very flocculent sediments with much higher moisture content (***Figure 3***). Loss-on-ignition organic matter content was relatively low at only 13 to 16%, indicating that sediments were composed primarily of inorganic silts and clays derived from the watershed.

The biologically-labile P fraction in the upper 10-cm sediment layer was overwhelmingly composed of iron-bound P (56% to 82% of the biologically-labile P; ***Figure 4 and Table 2***). In addition, the iron-bound P concentration was very high, ranging between 0.58 and 1.43 mg/g DW, further suggesting the potential for high internal P loading from lake sediment. Labile organic P represented between 10% and 40% while the loosely-bound P fraction accounted for less than 10% of the biologically-labile P (***Figure 5***).

Sediment vertical profiles

Sediment moisture content was generally highest in the upper 2-cm sediment layer at each station and declined with increasing sediment depth (***Figure 6***). This vertical pattern is typically observed in lake sediments and due to compaction as sediments become buried with new sediment layers over time. However, there were exceptions to this pattern for the central and south station vertical profiles. For instance, a minimum in percent moisture content was observed at the 3-cm sediment layer of the south core vertical profile. As discussed below, these unusual patterns may be related to variations in the composition of deposited sediment over time. Organic matter content exhibited a similar vertical pattern to that of moisture content, generally declining in concentration with increasing depth of sediment.

The iron-bound P fraction accounted for much of the biologically-labile P over the upper 10-cm sediment layer while labile organic P represented the second highest concentration for all cores (***Figure 6***). However, distinct vertical patterns in concentration were not clearly evident. For instance, iron-bound P gradually increased in concentration between the sediment surface and the 8-cm depth, then declined below 8-cm at the central station. But, iron-bound P concentrations were more variable vertically at the other stations. Typically, sediment P concentrations are elevated in the upper 4 to 6-cm layer versus deeper layers of eutrophic lake sediments due to accumulation of sediment P that is recycled in excess of burial and diagenesis (Carey and Rydin 2011). However, Lake Desair sediment may be unusual in that it receives considerable agricultural runoff and probably exhibits a relatively high and variable annual sedimentation rate, depending on interannual precipitation patterns. Variable sedimentation patterns would likely result in concentration maxima and minima throughout a vertical profile versus patterns described by Carey and Rydin (2011).

Aluminum sulfate dosage requirements

The alum (as Al) dosage required to bind at least 90% of the redox-sensitive P (i.e., the sum of the loosely-bound and iron-bound P fraction) varied between ~ 25 and 28 mg Al/g DW sediment, while the Al:P ratio (i.e., parts of Al required to bind one part of redox-sensitive P) varied between ~ 18:1 and 54:1 (***Figure 7***). Conversion to an areal dosage (i.e., g Al/m^2) is shown in ***Table 4***. Because Lake Desair sediments exhibited a relatively high sediment and bulk density, there was also a relatively high mass of redox-sensitive P per unit area to be inactivated for each sediment layer, resulting in high Al dosages to bind redox-sensitive P. For instance, the Al dosage required to bind redox-sensitive P in the upper 6-cm layer of Lake Desair sediment varied between 263 g/m^2 and 437 g/m^2 (***Table 4***). In contrast, dosage estimates that resulted in successful sediment P control have ranged between 40 and 137 g/m^2 (***Table 5***).

Typically, Al dosage is based on binding peak redox-sensitive P concentrations in the upper 4- to 10-cm layer. However, Lake Desair sediment does not exhibit a distinct peak in redox-sensitive P near the sediment surface, necessitating additional evaluation for dosage estimation. Because the alum floc is dense relative to flocculent sediment with high moisture content, it can sink several cm over time and a distinct alum floc layer may be found between 4 to 10 cm below the sediment surface several years after treatment. Since sediment density is relatively high for Lake Desair sediments, however, it is likely that the alum floc will be confined to the upper 2 to 4 cm. I estimated that a dosage of ~ 80 g Al /m^2 would be required to treat the upper 2-cm sediment layer and a dosage of ~ 245 g Al /m^2 would be needed to treat the upper 4-cm sediment layer (i.e., the average for the central and south stations; ***Table 4***).

Because Lake Desair exhibited low total alkalinity (24 mg/L) and poor buffering capacity against pH for alum, the equivalent volumetric Al dosage was calculated for comparison with an estimated maximum allowable dosage to maintain pH above 6.0 and prevent Al toxicity (***Table 6***). The estimated maximum allowable dosage based on measured alkalinity and pH (9.58) in July was < 5 mg Al/L (Cooke et al. 2005; Figure

8.2). The calculated volumetric dosages equivalent to areal Al dosages of 80 and 245 g/m^2 exceeded the estimated maximum allowable dosage (***Table 6***). There are two options to prevent a pH decrease below 6.0 during alum treatment. The first option is to use a buffered aluminum sulfate-sodium aluminate application to maintain pH at ~7.0. A buffered alum treatment costs more than an alum treatment (see below). A second option is to add multiple lower doses of aluminum sulfate that are equivalent to ~ 4 mg Al/L over a period of years until the areal Al dosage concentration goal is met.

Total estimated costs to apply aluminum sulfate or aluminum sulfate-sodium aluminate to Lake Desair depend on treatment area in the lake. Usually, sediment treatment area is based on the vertical extent of hypolimnetic anoxia in the summer or the position of the thermocline. ***Table 7*** shows alum application cost estimate scenarios for sediments confined to the 15, 20, and 25 ft depth contour in the lake. If a 2-cm sediment layer is chosen for P inactivation, estimated costs (including setup cost) could range from ~ $46,000 to $109,000 for aluminum sulfate application and between ~$50,000 and $118,000 for a buffered aluminum sulfate-sodium aluminate application. Treatment costs will increase substantially if the upper 4-cm sediment layer is considered for treatment.

I did not factor the concentration of labile organic P into the dosage calculation and cost estimate. Labile organic P may be mineralized by bacteria and become a source of internal P loading and it may also represent polyphosphate stored in bacterial cells that becomes released during anaerobic conditions. The former mechanism represents a slow rate while the latter mechanism can be a fast rate. Labile organic P represented a significant fraction in Lake Desair sediment but it is difficult to differentiate its rate of breakdown. Recent research has suggested that alum dosage should be targeted toward complete saturation of binding sites with sediment P within the first month of application in order to maximize efficiency. If the Al floc does not immediately bind P, binding efficiency appears to decline significantly over time (at least during the first year of treatment). I recommend targeting the redox-sensitive P fraction in the upper 2-cm layer at a minimum in order to maximize P binding efficiency and to monitor anoxic diffusive P flux and changes in sediment P fractions within the sediment over time in order to evaluate Al dosage effectiveness in controlling internal P loading. Post monitoring will be important in making informed decisions regarding treatment effectiveness and the need for adjustments in future dosage and application.

Also not factored into the calculation is binding of P in the water column as the Al floc settles to the sediment surface. For instance, if alum is applied early in the growing season before hypolimnetic accumulation of internal P loads, additional P in the water column might be minimal. Similarly, alum treatments have been conducted after fall turnover when hypolimnetic P is adsorbed by oxided Fe. If alum is applied in late August when P concentrations are high in the anoxic hypolimnion, the additional P in the water column should be considered in the dosage estimate. I tend to recommend a late spring alum application at the onset of stratification (~ May).

Another factor to consider is multiple lower Al dose applications over a period of years versus a one-time high Al dosage application. Application of lower doses at two to three year intervals would ensure saturation of binding sites with P and ultimately more effective control of internal P loading. The less expensive aluminum sulfate application could be considered under this scenario if dosage is below the maximum allowable to prevent pH < 6.0. However, cost savings incurred from use of aluminum sulfate only would probably be offset by additional setup fees (i.e., costs to ship alum from commercial manufacturers and to setup up the application operation) for each treatment. Since sedimentation of new P from agricultural sources may exacerbate burial the Al floc and it effectiveness in controlling internal P loading, a succession of lower dosage applications might be more successful in controlling new sources of sediment P. A potential drawback to this application scenario is that some internal P loading might occur, albeit much lower, over the first several years until all the redox-sensitive P in the active sediment layer has been bound by the Al floc.

Finally, cost estimates provided here represent scenarios that can be refined at a later date. For example, dosage and application rates could be based on specific areas as a possible cost-saving measure. Or the 25-ft depth contour might be treated in year one and the 15-ft depth contour treated in year 3 or 4 to provide a layered application that concentrates Al in the deepest areas of the lake where anoxic diffusive P flux is greatest and less so in the shallower areas where anoxic diffusive P flux is lower.

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Table 1. Sediment core station locations and water column depths.

Station	Depth		Coordinates (decimal degrees)	
	(ft)	(m)	East	North
North	22	6.7	45.54683	-91.77518
Central	31	9.4	45.54617	-91.77675
South	26	7.9	45.54242	-91.78059

Table 2. 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 Lake Desair. DW = dry mass, FW = fresh mass).

Station	Diffusive P flux	Biologically labile P						Refractory P
	Anoxic	Loosely-bound P	Iron-bound P			Redox-sensitive P	Labile organic P	Aluminum-bound P
	(mg m^{-2} d^{-1})	(mg/g DW)	(mg/g DW)	(ug/g FW)	(g/m^2-cm)	(mg/g DW)	(mg/g DW)	(mg/g DW)
North Basin	8.4 (0.5)	0.048	0.581	93	1.071	0.629	0.398	0.492
Central Basin	14.7 (3.2)	0.142	1.426	304	3.782	1.568	0.166	1.084
South Basin	6.4 (0.8)	0.100	1.005	229	2.693	1.105	0.634	0.821

Table 3. Textural characteristics for the upper 10-cm sediment section collected in Lake Desair.

Station	Moisture Content (%)	Bulk Density (g/cm^3)	Sediment Density (g/cm^3)	Loss-on-ignition (%)
North Basin	83.2	1.097	0.202	15.8
Central Basin	76.9	1.148	0.313	13.5
South Basin	76.6	1.145	0.276	12.9

Table 4. Aluminum (Al) dosage required to treat various sediment layers from the upper 2 cm to the upper 10 cm.

Station	Thickness of sediment layer (cm)	Al dosage requirement (g/m2)
North	0-2	54
	0-4	146
	0-6	263
	0-8	384
	0-10	526
Central	0-2	71
	0-4	211
	0-6	361
	0-8	531
	0-10	836
South	0-2	87
	0-4	277
	0-6	437
	0-8	609
	0-10	807

Table 5. Recent and proposed Al dosages for various lakes. An asterisk denotes a future treatment.

Lake	Alum Dose (g Al m^{-2})
Tiefwarensee, Germany	137
East Alaska, Wisconsin	130
Squaw, Wisconsin*	120
Half Moon, Wisconsin	115
Susser See, Germany	100
Green, Washington	94
Bald Eagle, Minnesota*	50
Burandt, Minnesota	40

Table 6. Volumetric Al dosage estimates for Lake Desair. Estimated maximum allowable doage is ~ 5 mg Al/L (Cooke et al. 2005).

Depth contour	Volumetric Al dosage equivalent (mg Al/L)	
(ft)	(80 g/m^2)	(245 g/m^2)
15	11.4	34.8
20	10.4	31.8
25	9.5	29.1

Table 7. Cost estimate scenarios to treat the upper 2-cm and the upper 4-cm sediment layers with either aluminum sulfate only or buffered aluminum sulfate-sodium aluminate for different depth contours.

		Aluminum sulfate		Aluminum sulfate-sodium aluminate	
Depth contour	Setup	Upper 2-cm layer	Upper 4-cm layer	Upper 2-cm layer	Upper 4-cm layer
15	$5,000	$104,000	$318,400	$113,000	$346,000
20	$5,000	$74,700	$229,000	$81,200	$248,600
25	$5,000	$41,300	$126,500	$44,800	$137,300

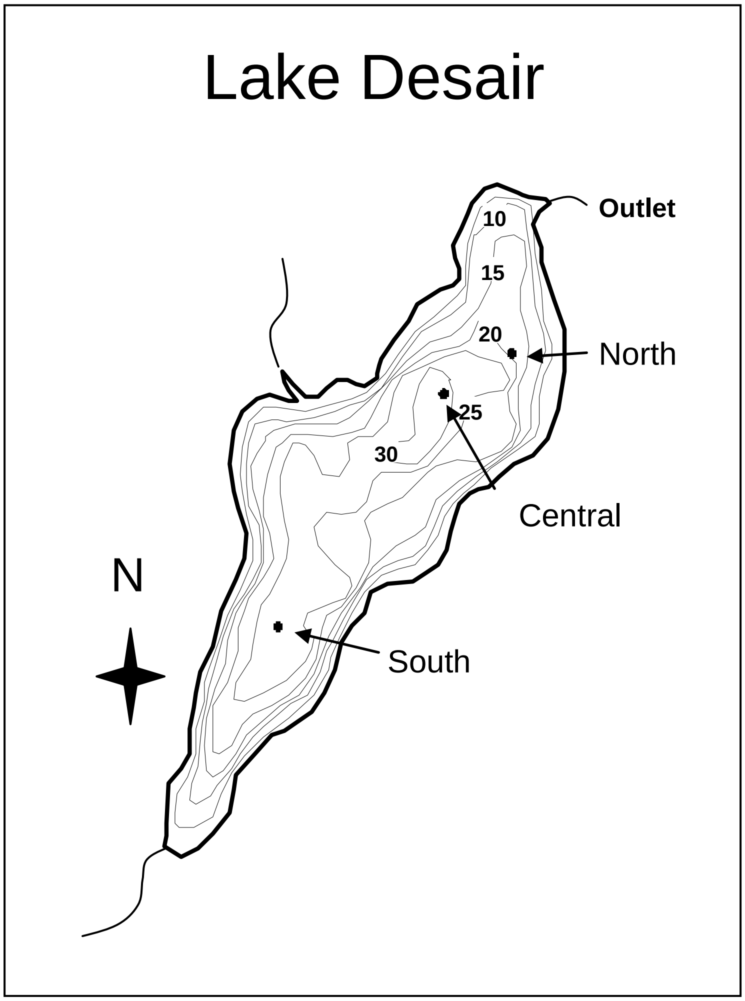

Figure 1. Sediment core station locations.

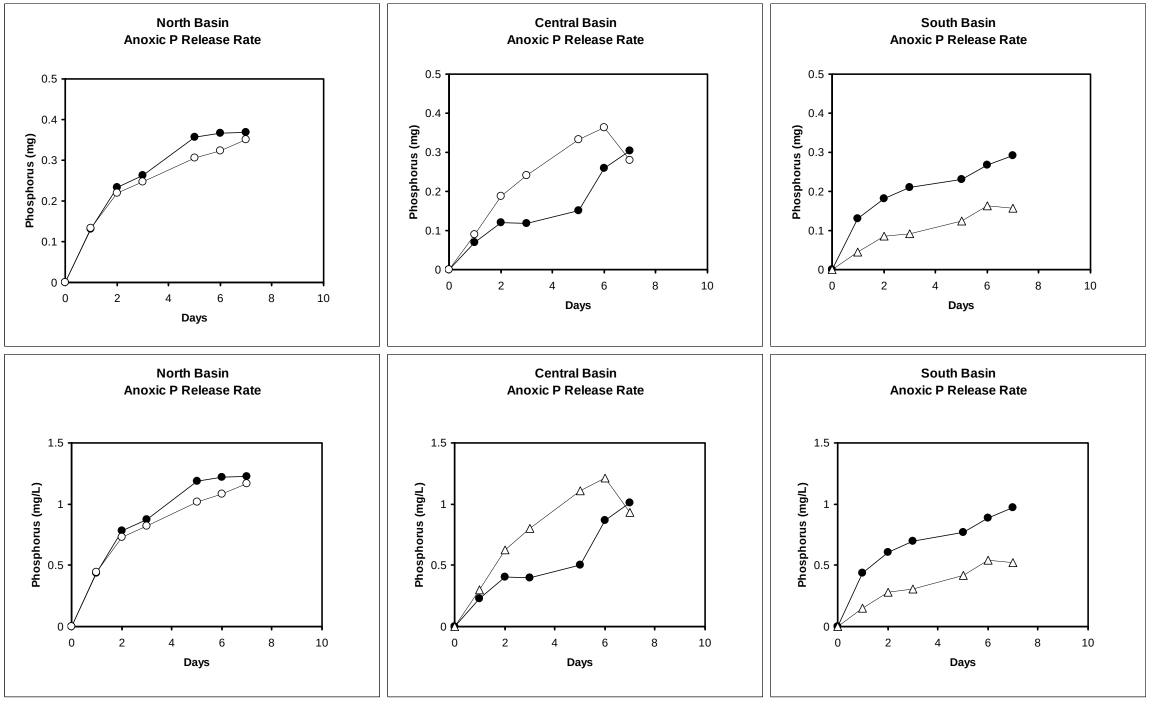

Figure 2. Changes in soluble reactive phosphorus mass (upper panel) and concentration (lower panel) in the overlying water column under anoxic conditions versus time for sediment cores collected in Lake Desair.

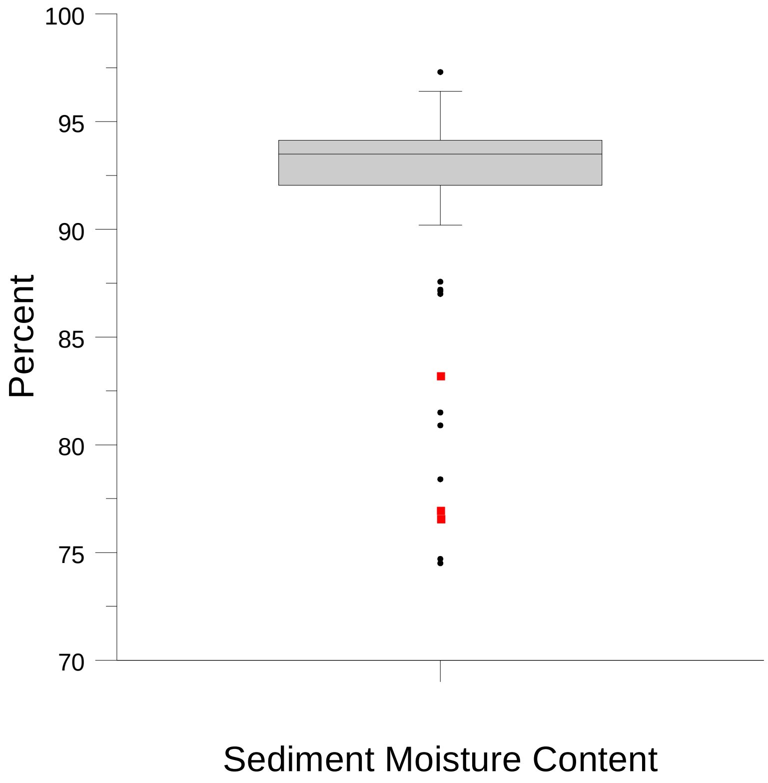

Figure 3. Box and whisker plot comparing moisture content for sediment core stations in Lake Desair (red circles) with statistical ranges (n= 8 lakes and 57 total observations) for some other lakes in west-central Wisconsin.

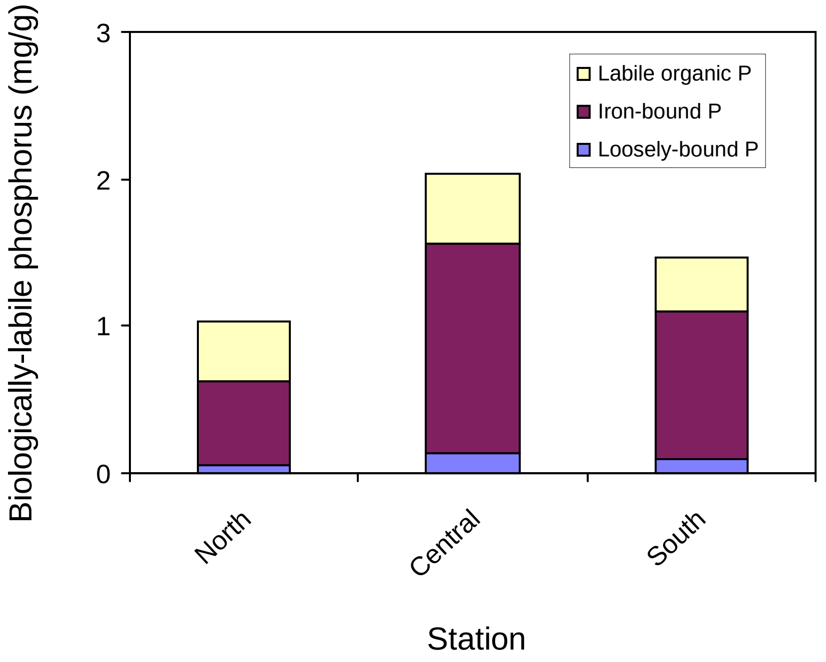

Figure 4. Variations in the loosely-bound, iron-bound, and labile organic phosphorus (P) fractions of the upper 10-cm sediment layer for various stations in Lake Desair.

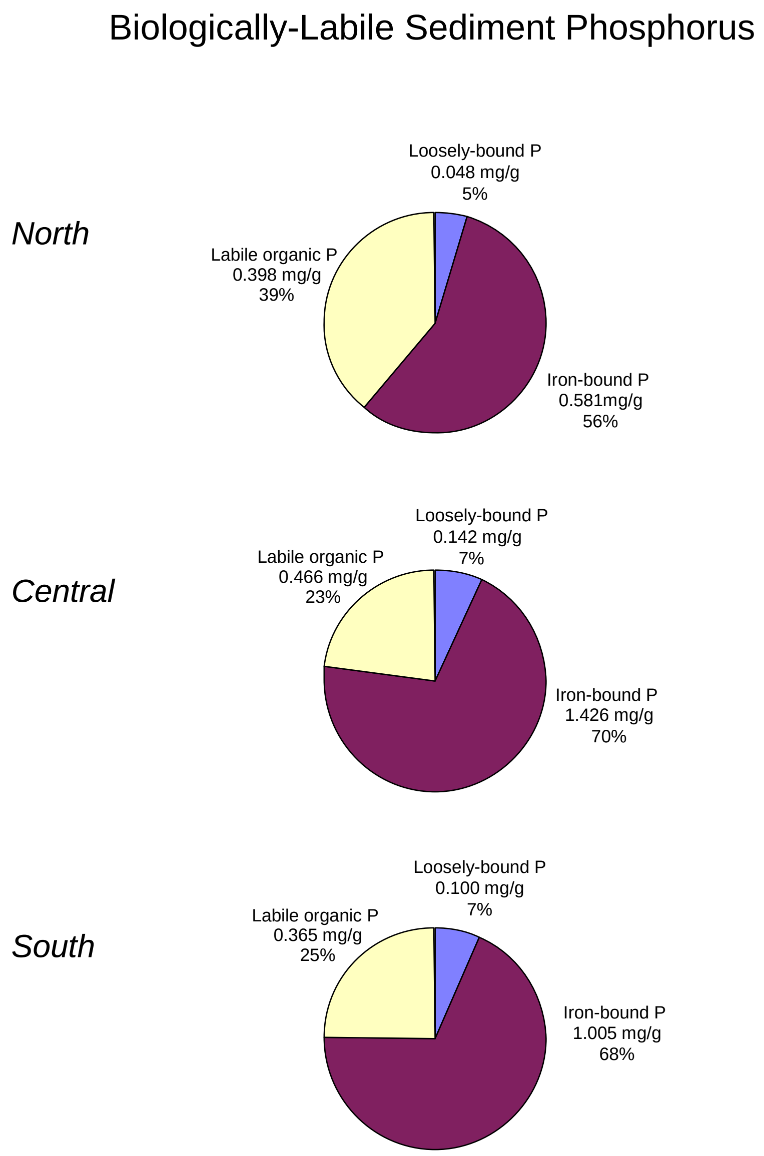

Figure 5. Pie-charts showing concentrations and proportions of loosely-bound, iron-bound, and labile organic phosphorus (P) in the upper 10-cm sediment layer for various stations in Lake Desair.

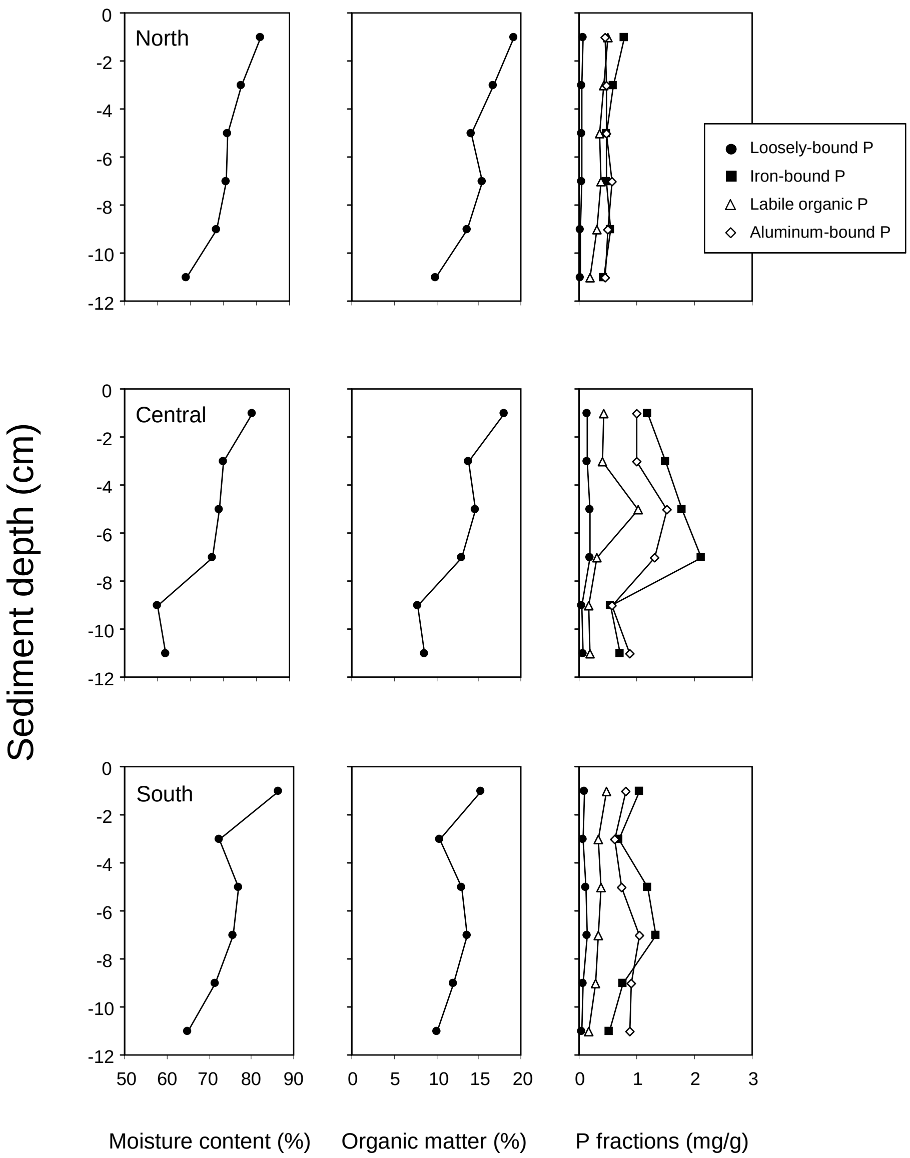

Figure 6. Vertical variations in moisture content, organic matter content, and phosphorus (P) fractions. The loosely-bound, iron-bound, and labile organic phosphorus (P) fractions represent biologically-labile P (i.e., subject to recycling) while the aluminum bound P fraction is more refractory and subject to burial.

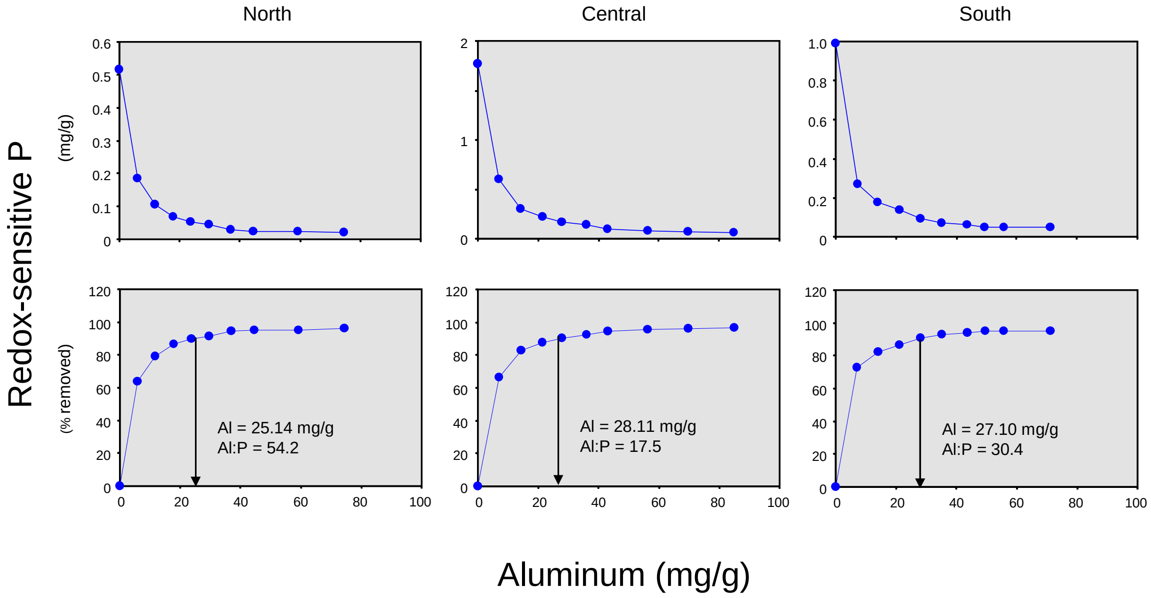

Figure 7. Variations in the concentration of redox-sensitive phosphorus (P; upper panels) and percent removed or adsorbed to the Al floc (lower panels) as a function of increasing aluminum concentration.