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# Variations in the aluminum:phosphorus binding ratio and alum dosage considerations for Half Moon Lake, Wisconsin

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## Abstract

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The aluminum:phosphorus binding ratio (Al:P) is an important variable for estimating the Al dosage required to inactivate loosely bound and iron-bound P (redox-P) in sediment for internal P loading control in lakes. For shallow Half Moon Lake, Wisconsin, the Al:P ratio varied in a negative exponential pattern as a function of increasing redox-P concentration. While more Al was needed to inactivate higher concentrations of redox-P, inactivation was more efficient at higher redox-P. The Al:P ratio needed to bind 90% of the redox-P exceeded 150:1 for redox-P concentrations <0.2 mg/g and approached 20:1 for concentrations >2.0 mg/g. Competition for binding sites by other constituents in relation to redox-P concentration may be responsible for this pattern. Although organically bound P was not important in Half Moon Lake, it may be in other cases, and lake specific assays are recommended to determine the most appropriate Al dosage. Even then, slower processes of P release from labile organic P and vertical diffusion may not be addressed by higher Al dosages, and more research is warranted. Because redox-P varied horizontally as a result of lake bathymetry, variations in the Al:P ratio were considered for lake-wide alum dose calculation for Half Moon Lake. The estimated lake-wide average dosage of 115 g Al/m<sup>2</sup> was high but similar to other recent effective treatments reported in the literature.

Key words: alum, aluminum, aluminum sulfate, fractionation, phosphorus, sediment

Lake recovery after reduction of external phosphorus (P) loading can be delayed for many years due to P flux from sediment (Jeppesen et al. 2005). One management technique used successfully to reduce this P source is application of aluminum sulfate (alum) and reaction to form amorphous aluminum hydroxide (Al(OH)<sub>3</sub>) to irreversibly bind P in the sediment (Cooke et al. 2005). Because application lowers pH during reaction to Al(OH)<sub>3</sub>, and aluminum (Al) becomes soluble and increasingly toxic to biota when pH declines below ~6, dosage in some cases has been based on the maximum concentration that can be applied and yet maintain water column pH above 6 (Kennedy and Cooke 1982). However, this dosage method does not consider binding and inactivation of sediment P or reduction of P flux from sediment. It is also problematic for softwater lakes with low alkalinity that require a buffered Al (i.e., aluminum sulfate–sodium aluminate, aluminum–lime, or other pH neutral combination) application to maintain a desirable pH.

Dosage can also be estimated by quantifying the concentration of Al needed to bind extractable sediment P forms that are active in sediment P flux (Rydin and Welch 1999, Reitzel et al. 2005, Pilgrim et al. 2007). These extractable forms include loosely bound (i.e., porewater P, loosely adsorbed P, and P associated with calcium carbonate), iron-bound (i.e., P associated with iron oxyhydroxides), and labile organic P. Loosely bound P (loose-P) and iron-bound P (Fe-P), collectively referred to as redox-sensitive P (redox-P), have been empirically related to rates of P flux from sediment under anoxic conditions (Boström et al. 1982, Nürnberg 1988, Pilgrim et al. 2007) and are believed to be functional components in oxidation–reduction and pH reactions that result in desorption of P from sediment and diffusion into the water column. Labile organic P is associated with pyrophosphates, polyphosphates, and volatile organic P forms and can be hydrolyzed or mineralized to soluble P under oxic and anoxic conditions (Hupfer et al. 2004, Hupfer and Lewandowski 2005), with a half-life on the order of 0.8 to 13 y (Ahlgren et al. 2005, Reitzel et al. 2007).

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Various studies on Al dosage requirements to inactivate sediment P have reported Al:P binding ratios ranging from 2:1 to >100:1 (Rydin and Welch 1999, Rydin et al. 2000, Lewandowski et al. 2003, Reitzel et al. 2003, 2005, James 2005, Dugopolski et al. 2008). Under controlled experimental conditions with analytical grade phosphate ( $\text{PO}_4^{-3}$ ) and alum, P can bind to precipitated  $\text{Al}(\text{OH})_3$  at a molar ratio of  $\sim 1:1$  or slightly higher at neutral pH, depending on the initial  $\text{PO}_4^{-3}$  concentration and the extent of polymer formation (Lijklema 1980). Phosphate binding efficiency can decrease over time due to changes in the crystalline structure of  $\text{Al}(\text{OH})_3$  and decreased surface area (Lijklema 1980, Berkowitz et al. 2005, 2006), particularly in the absence of sorbed  $\text{PO}_4^{-3}$  (de Vicente et al. 2008a). Also, various inorganic and organic ions in lakewater and sediment can bind with  $\text{Al}(\text{OH})_3$  in addition to  $\text{PO}_4^{-3}$ . For instance, higher humic acid (HA) concentrations can significantly reduce  $\text{PO}_4^{-3}$  binding to  $\text{Al}(\text{OH})_3$  and result in higher Al:P ratios, although this effect weakens at higher initial  $\text{PO}_4^{-3}$  concentrations (de Vicente et al. 2008b). This pattern is likely due to competition for binding sites by  $\text{PO}_4^{-3}$  at higher concentrations (Cheng et al. 2004, Guan et al. 2006), suggesting that Al:P ratios derived for natural sediment may be regulated in part by relative concentrations of redox-P versus other ions that can bind to  $\text{Al}(\text{OH})_3$ . To investigate this hypothesis, I examined Al:P ratios for sediment collected from Half Moon Lake, Wisconsin, that differed widely in redox-P concentration (i.e.,  $\sim 0.1$  to  $>2$  mg/g dry mass). I used this information and variations in redox-P concentration to estimate an Al dosage scenario for the lake.

## Site description

Half Moon Lake is a small (area =  $0.62 \text{ km}^2$ ; volume =  $12.9 \times 10^5 \text{ m}^3$ ), shallow (mean depth = 2.06 m; maximum depth = 4 m), wind-sheltered urban oxbow lake located in Eau Claire, Wisconsin (Fig. 1). External inputs occur primarily via a storm sewer system that drains residential, commercial, and industrial land uses from a  $2.3 \text{ km}^2$  watershed. The summer P budget was dominated by internal loading from sediment (42%), decomposition of *Potamogeton crispus* (20%), and sediment resuspension by motor boat activity (17%). In contrast, external P loadings accounted for only 21% of the P budget (James et al. 2002). The lake was classified as eutrophic to hypereutrophic (Carlson Trophic State Index = 74). Mean summer trophic state indicators were 0.110 mg/L total P, 82 mg/m<sup>3</sup> viable chlorophyll *a* and 1.1 m Secchi transparency. Total alkalinity concentrations were modest at  $\sim 50$  mg/L, and pH averaged  $\sim 9.0$  during the summer due to high algal productivity.

## Methods

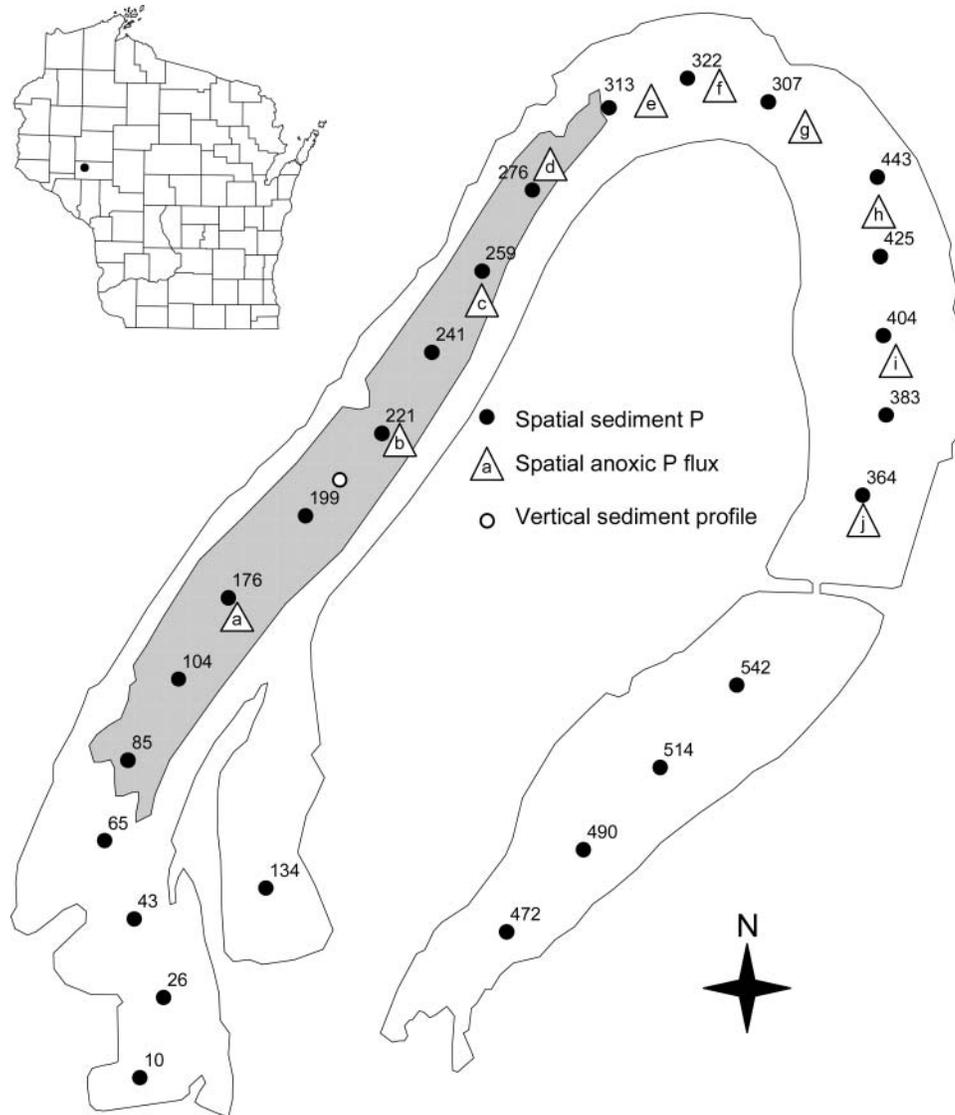
### Sediment sampling

Intact cores were collected at 10 stations in Half Moon Lake in February 2006 for determination of rates of P release under anoxic conditions and redox-P concentrations in the upper 10 cm sediment layer (Fig. 1). In June 2009, sediment cores were collected at 25 stations for determination of spatial variations in redox-P in the upper 4 cm layer. Longer sediment cores collected near station 199 were sectioned at 2–5 cm intervals and analyzed for redox-P and labile organic P. In an unrelated study, sediment cores were collected in 2009 and 2010 using similar methods from the deep basins of nearby Cedar, East Alaska, and Squaw lakes in Wisconsin for comparison with Half Moon Lake redox-P and Al:P ratio trends. A gravity coring device (Aquatic Research Instruments; Hope, ID) equipped with acrylic tubes (6.5 cm dia  $\times$  40 cm ht) was used to collect intact sediment cores. Cores for fractionation were either sectioned in the field or in the laboratory immediately after arrival, and samples were stored on ice and in a refrigerator at 4 C until analysis. Sediment sections for P release determination were sectioned in the laboratory and incubated within 24 h of collection.

### Sediment anoxic P flux and P fractionation

Sediment incubation systems for anoxic P flux determination consisted of the upper 10 cm of undisturbed sediment and filtered overlying lakewater (300 mL) contained in acrylic tubes (6.5 cm dia  $\times$  20 cm ht) sealed with rubber stoppers. Tubes were placed in a darkened environmental chamber and incubated at a constant temperature (20 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. Water samples for soluble reactive P (SRP) were collected from the center of each system using an acid-washed syringe and filtered through a  $0.45 \mu\text{m}$  membrane syringe filter. The water volume removed from each system during sampling was replaced by addition of filtered lake water that was previously purged with nitrogen. Soluble reactive P was measured colorimetrically using the ascorbic acid method (APHA 2005). Anoxic P fluxes from the sediment ( $\text{mg/m}^2\text{d}$ ) were calculated as the linear change in mass in the overlying water divided by time (days) and the area ( $\text{m}^2$ ) of the incubation core liner.

Subsamples of homogenized sediment sections were dried at 105 C to constant weight and burned at 500 C for determination of moisture content, sediment density and organic matter content (Håkanson and Jansson 2002). Phosphorus fractionation was conducted according to Hietjjes and



**Figure 1.**—Sediment sampling stations in Half Moon Lake, Wisconsin. The shaded region represents the area below the 3 m contour. Numbers above the solid circles denote station designations.

Lijklema (1980), Psenner and Puckso (1988), and Nürnberg (1988) for the determination of loose-P (1 M  $\text{NH}_4\text{Cl}$  extraction), Fe-P (0.11 M bicarbonate-dithionite extraction [BD]), and Al-P (0.1 N NaOH extraction). A subsample of the NaOH 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 (i.e., undigested) and nonreactive sodium hydroxide-extractable P. All extracts were filtered through a 0.45  $\mu\text{m}$  membrane syringe filter and neutralized before analysis of SRP using standard colorimetric techniques (APHA 2005). The BD extract was gently bubbled with air for 1 h to reoxidize the solution prior to SRP determination. Unless otherwise indicated, sediment

concentrations are expressed as mg/g of dry sediment weight (mg/g DW).

## Alum assays

Sediment collected from 7 stations in Half Moon Lake (Table 1) was used to determine the Al dosage required to bind redox-P using a modification of the Rydin and Welch (1999) method. These samples were chosen to represent a range of redox-P concentrations observed in the lake sediments. Alum ( $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$ ) was combined with 0.1 M sodium bicarbonate to a concentration of 1.4–2.5 g Al/L and adjusted to pH 7.0 with 3 N NaOH to form  $\text{Al}(\text{OH})_3$ . Aliquots of this solution, diluted to a final volume of 10 mL

**Table 1.**—Textural characteristics, organic matter content, and concentrations of redox-sensitive phosphorus (redox-P) for sediment used in alum assays to determine Al:P ratios.

Lake	Station	Moisture Content (%)	Bulk Density (g/cm <sup>3</sup> )	Organic Matter (%)	Redox-P (mg/g DW)
Half Moon	43	64.6	1.259	5.6	0.094
	85	86.3	1.077	14.7	0.339
	176	91.6	1.043	20.6	2.212
	199	91.6	1.041	23.0	0.341
	241	90.4	1.049	20.2	1.511
	404	91.1	1.042	25.2	0.152
	490	94.3	1.023	34.2	1.115
Cedar <sup>a</sup>		94.1	1.037	33.2	0.254
East Alaska <sup>b</sup>		92.9	1.034	24.3	0.302
Squaw <sup>c</sup>		89.9	1.066	22.7	0.548

<sup>a</sup> Average of 4 stations; <sup>b</sup> Average of 3 stations; <sup>c</sup> Average of 5 stations.

with distilled water, were added to centrifuge tubes containing fresh sediment equivalent to 25 mg dry mass to obtain Al concentrations ranging from zero (i.e., control) to >300 mg Al/g DW sediment. The assay tubes were shaken for a minimum of 2 h at 20 C in a dark environmental chamber, centrifuged at 500 G to concentrate the sediment and decanted for redox-P determination. The same assay procedures were performed on sediment collected from Cedar, East Alaska and Squaw lakes (Table 1). Measurements performed on a subset of decanted samples indicated that pH ranged between 7 and 8 after exposure to Al(OH)<sub>3</sub>.

The Al:P ratio (mass basis) was estimated as the concentration (mg/g DW) of Al required to remove 90% of the redox-P (mg/g DW). This calculation differed from Rydin and Welch (1999) in that they used the concentration of Al-P formed while I used the redox-P lost to the Al(OH)<sub>3</sub> floc. Earlier studies on Al-treated Half Moon Lake sediment found that a precipitate interference developed in the NaOH extraction during SRP analysis as a result of lowering the pH after addition of the acidic ascorbic acid-molybdate combined reagent (W.F. James, Engineer Research and Development Center, Feb 2004, unpubl.). The precipitate only occurred for sediments with added Al, rendering absorbance determination at 880 nm on a spectrophotometer untenable. Because sediment organic matter content was high (~25%), this reaction was believed to be the outcome of coprecipitation between organic acids and Al at low pH (Cheng et al. 2004). Nonetheless, others have shown that the mass of redox-P removed is equivalent to the mass of Al-P formed (Rydin and Welch 1999, James 2005, Pilgrim et al. 2007). Redox-P bound by Al(OH)<sub>3</sub> was calculated as the difference between the initial and final redox-P concentration. While I chose 90% redox-P inactivation to reduce internal P loading

to near zero, percentage redox-P inactivation can be based on the internal P loading reduction that is required to meet water quality improvement goals as suggested by Pilgrim et al. (2007). Thus, redox-P inactivation may be much lower than 90% depending on the desired water quality response.

## Results

### *Variations in sediment characteristics and fluxes*

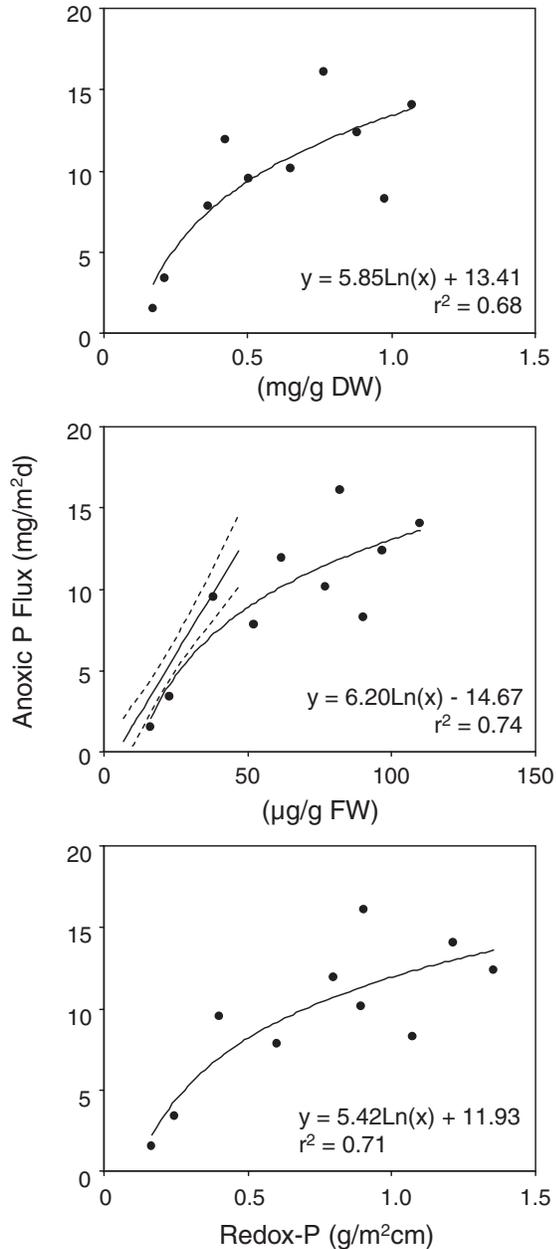
Anoxic P fluxes ranged between 1.5–16.1 mg/m<sup>2</sup>d and increased in a nonlinear pattern as a function of increasing redox-P concentrations (Fig. 2). Flux increases were rapid and linear for redox-P concentrations <0.5 mg/g DW ( $r^2 = 0.97$ ; Fig. 2a), and they increased to a lesser extent as redox-P exceeded that threshold. Relationships between anoxic P flux and redox-P fell near ranges reported by Nürnberg (1988) for redox-P concentrations <50  $\mu\text{g/g}$  of sediment fresh weight (mg/g FW; Fig. 2b). However, patterns were nonlinear for higher redox-P concentrations. Nonlinear relationships were also observed between volume-based redox-P concentration (g/m<sup>2</sup>cm) and anoxic P fluxes (Fig. 2c). Overall, anoxic P fluxes were greatest in the western and northern regions of the lake.

The dominant form of mobile P (i.e., loose-P+Fe-P+labile organic P; range = 50–93%) in the upper 16 cm sediment layer was Fe-P (Fig. 3). Concentrations exceeded 1.5 mg/g in the upper 4 cm and declined to <0.5 mg/g below the 5 cm depth. Labile organic P represented the next dominant mobile P form (range = 5–41%), and concentrations were relatively constant over most of the vertical sediment column, ranging between 0.066 and 0.282 mg/g. In contrast, loose-P concentrations were very low throughout the sediment vertical profile and represented <3% of the mobile P.

There were also pronounced horizontal variations in redox-P in the upper 4 cm sediment layer (Fig. 4). Concentrations were greatest in the western arm and declined to lower values in the eastern and southern portions of the lake. In particular, redox-P exceeded 2.0 mg/g in the slightly deeper western arm and was an order of magnitude lower in other regions of the lake. In the southwestern region of the main oxbow channel and in the nearby small embayment, redox-P concentrations were <0.10 mg/g.

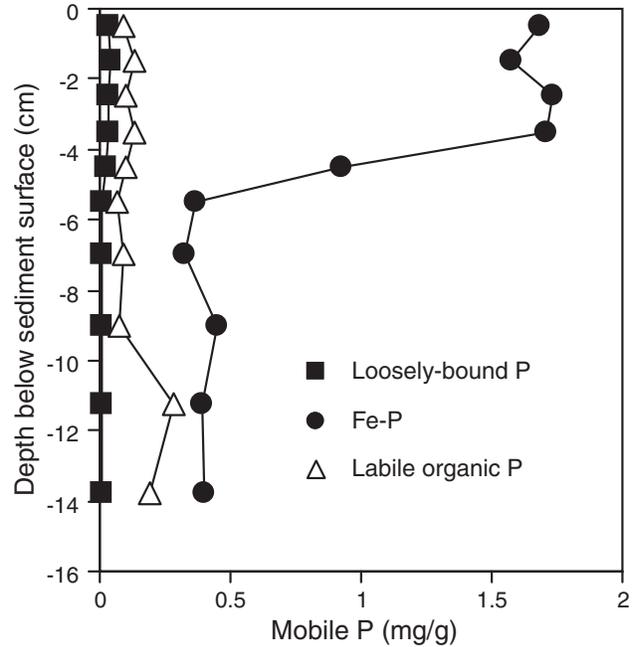
### *Aluminum:phosphorus ratios*

Redox-P declined in an exponential pattern as a function of increasing Al concentration (Fig. 5a). For instance, more than 60% of an initial redox-P concentration of 0.149 mg/g was removed with a modest Al concentration addition of 2.8 mg/g for sediment collected at station 404 (Fig. 5b).

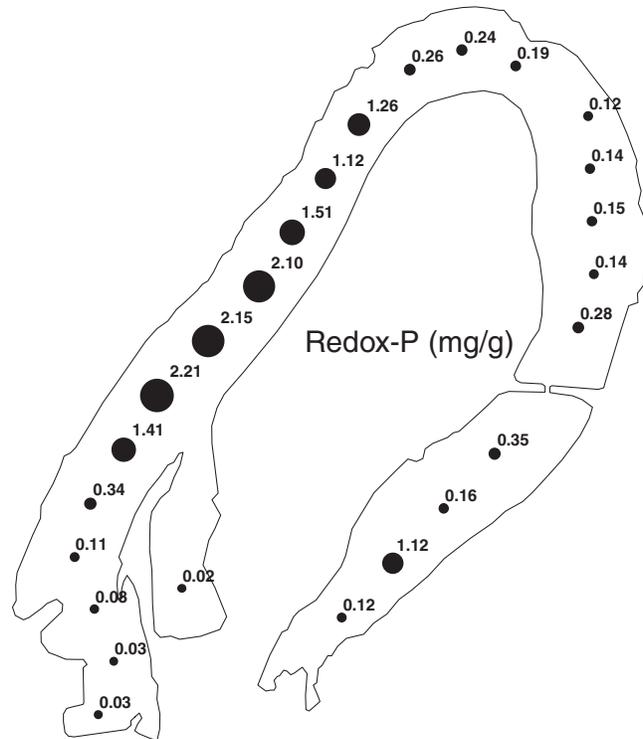


**Figure 2.**—Relationships between redox-sensitive phosphorus (redox-P) concentration and anoxic phosphorus (P) flux for sediments in Half Moon Lake. The solid regression and dashed 95% confidence limit lines shown in the middle panel are from Nürnberg (1988). The maximum redox-P concentration in that regression equation was  $\sim 45 \mu\text{g P/g}$  fresh weight (FW) sediment (Nürnberg 1988). Anoxic P fluxes were greatest in the western and northern regions of the lake.

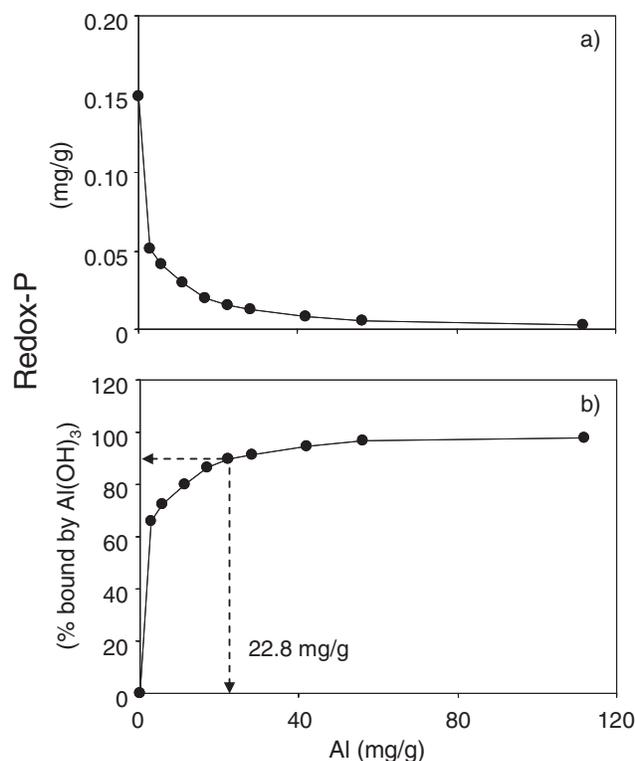
Iron-bound P removal by  $\text{Al}(\text{OH})_3$  diminished exponentially at higher Al concentrations. The Al concentration required to remove 90% of the redox-P was 22.8 mg/g (Fig. 5b), resulting in an Al:P<sub>90%</sub> ratio of 170:1 (i.e., 22.8 mg Al/g required to remove 0.134 mg redox-P/g). In contrast, sediment with an order of magnitude higher redox-P concentration of



**Figure 3.**—Vertical variations in loosely-bound, iron-bound (Fe-P) and labile organic phosphorus (P) concentrations in Half Moon Lake sediment.



**Figure 4.**—Horizontal variations in the redox-sensitive phosphorus (redox-P) concentration in the upper 4 cm sediment layer of Half Moon Lake. Dot size varies in proportion to concentration.



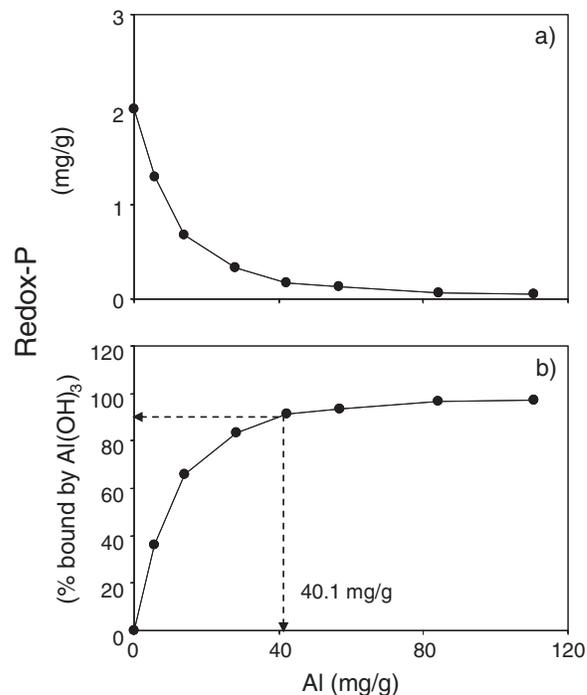
**Figure 5.**—Relationships between (a) aluminum (Al) concentration and the concentration of redox-sensitive phosphorus (redox-P) remaining in sediment and (b) the percentage of redox-P removed by aluminum hydroxide precipitates ( $\text{Al}(\text{OH})_3$ ) versus the Al concentration for sediment collected at station 404 (see Fig. 1). Dotted lines designate the concentration of Al required to remove 90% of the redox-P.

2.0 mg/g (i.e., station 241) required only a 2-fold greater Al concentration of 40.1 mg/g to achieve 90% removal, resulting in an Al:P<sub>90%</sub> ratio of only 22:1 (Fig. 6).

For all Half Moon Lake sediments assayed, the Al concentration required to remove 90% of the redox-P increased linearly with increasing initial redox-P concentration (Fig. 7a). The Al:P<sub>90%</sub> ratio varied in a negative exponential pattern with increasing redox-P concentration (Fig. 7b). Sediments assayed from deep basins of Cedar, East Alaska and Squaw lakes generally exhibited a trend similar to that of Half Moon Lake (Fig. 8); however, the Al:P ratio was higher for Squaw Lake sediment and lower for Cedar and East Alaska lake sediments relative to redox-P concentration when compared with Half Moon Lake. Overall, the Al:P<sub>90%</sub> ratio exceeded 150:1 when the redox-P concentration was <0.20 mg/g, and it approached 20:1 for concentrations exceeding 2.0 mg/g.

### Lake-wide Al dosage considerations

The regression equation developed for Al:P<sub>90%</sub> ratio versus redox-P concentration (Fig. 7b) was used to estimate hor-

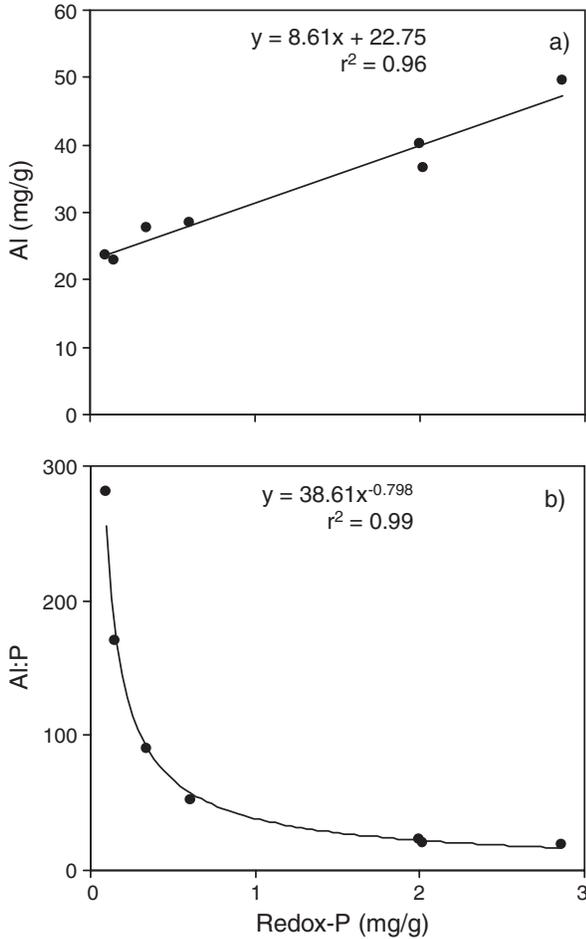


**Figure 6.**—Same as Fig. 5 except for station 241 with a 10-fold greater redox-sensitive phosphorus (redox-P) concentration.

izontal variation in the Al:P<sub>90%</sub> ratio for Half Moon Lake (Fig. 9). The ratio approached 20:1 in the western arm of the lake and exceeded 150:1 in other regions. The maximum Al:P<sub>90%</sub> ratio was set to 150:1 for Al dosage calculation purposes. To treat the upper 4 cm sediment layer, a much higher Al dosage was needed for the western and northern arm versus other areas of the lake (Fig. 10). The unusually high Al concentration of 316 g/m<sup>2</sup> at station 313 reflected a higher sediment bulk density and thus higher area-based redox-P concentration. The overall average Al dosage estimate was ~140 g/m<sup>2</sup>. With funding constraints, uniform concentration areas of 75 and 150 g Al/m<sup>2</sup> were established for the eastern and western arm, respectively, resulting in an area-based dosage of 115 g/m<sup>2</sup> (treatment area =  $4.4 \times 10^5$  m<sup>2</sup>; Fig. 10) and the volumetric dosage of 40 g/m<sup>3</sup> ( $115$  g/m<sup>2</sup> ·  $4.4 \times 10^5$  m<sup>2</sup> /  $12.9 \times 10^5$  m<sup>3</sup>) for the entire lake.

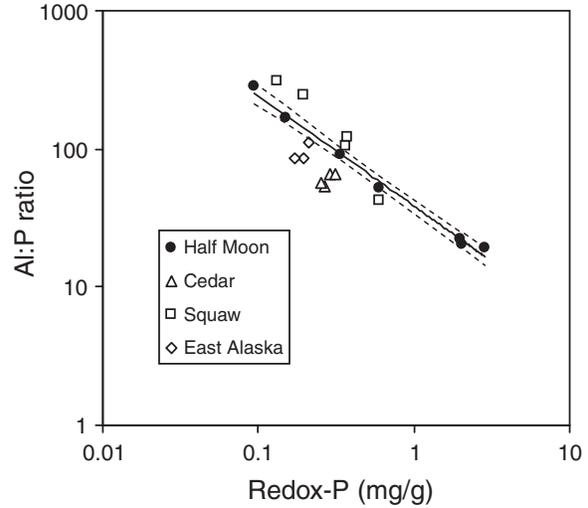
## Discussion

Pilgrim et al. (2007) used linear relationships between redox-P and anoxic P flux as a basis for predicting reduction in the rate of internal P loading after alum treatment. Similarly, anoxic P flux increased as a function of increasing redox-P concentration for Half Moon Lake. Although non-linear, this pattern suggested that inactivating redox-P would result in substantial reduction in internal P loading and thus

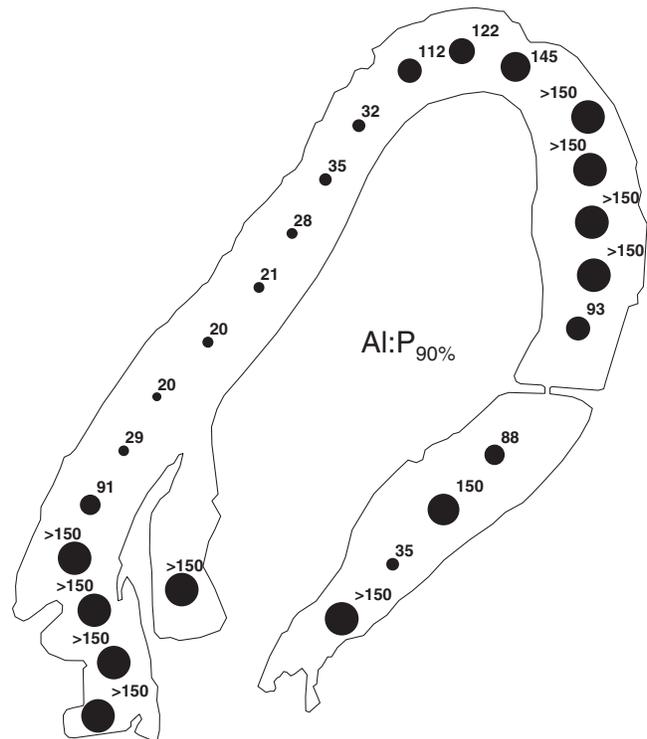


**Figure 7.**—Relationships between (a) the aluminum (Al) concentration and (b) the aluminum:phosphorus ratio (Al:P<sub>90%</sub>) needed to remove 90% of the redox-sensitive phosphorus P (redox-P) versus the initial redox-P concentration in the sediment for Half Moon Lake.

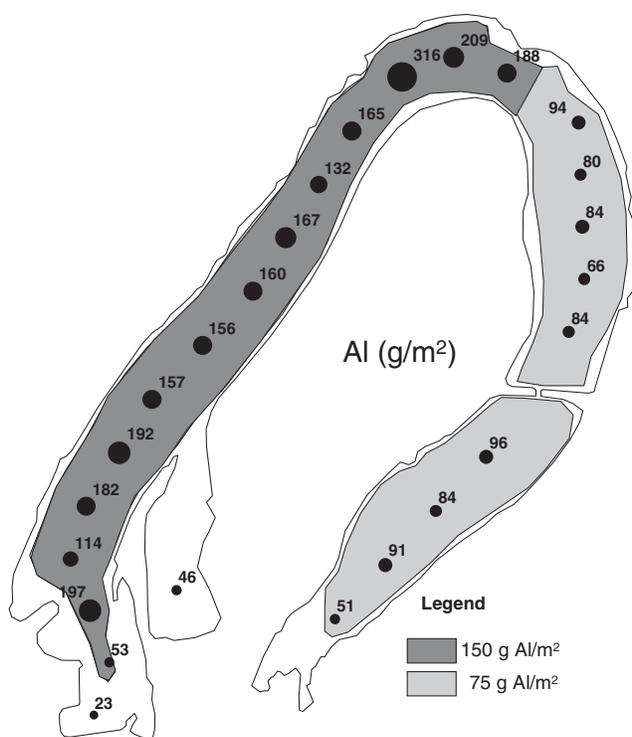
provided justification for treating the lake with alum. In addition, anoxic P flux was high, particularly in the western region of the lake, and comparable to fluxes measured for other eutrophic lakes in the upper Midwest United States (Pilgrim et al. 2007). Vertical sediment P profiles collected in the western arm also indicated that concentrations were elevated primarily in the upper 4 cm layer and should be targeted for inactivation. In contrast, labile organic P concentrations were low relative to redox-P and accounted for only ~6% of the mobile P pool in this sediment layer. Although labile organic P can represent an important source of internal P loading (Hupfer et al. 2004, Reitzel et al. 2007, Ahlgren et al. 2011), it did not seem as significant relative to the high redox-P concentrations in regulating internal P loading in Half Moon Lake.



**Figure 8.**—Relationships between the aluminum:phosphorus binding ratio (Al:P<sub>90%</sub>) needed to remove 90% of the redox-sensitive phosphorus P (redox-P) versus the initial redox-P concentration for various lakes in west central Wisconsin (USA). Dotted lines represent 95% confidence limits for Half Moon Lake regression relationships.



**Figure 9.**—Horizontal variations in the aluminum:phosphorus binding ratio (Al:P<sub>90%</sub>) required to remove 90% of the redox-sensitive phosphorus concentration in the upper 4 cm sediment layer of Half Moon Lake. The Al:P<sub>90%</sub> was estimated using the regression equation shown in Fig. 7b. Dot size varies in proportion to the ratio.



**Figure 10.**—Spatial variations in the aluminum (Al) dosage concentration required to remove 90% of the redox-sensitive phosphorus in the upper 4 cm sediment layer of Half Moon Lake. Shaded areas represent future Al treatment zones. Dot size varies in proportion to Al concentration.

An important finding in this study was the occurrence of a negative nonlinear relationship between the redox-P concentration and the Al:P ratio for sediment collected in Half Moon Lake. The pattern could be attributed primarily to the wide variation in redox-P concentration because, with the exception of station 43, assayed sediments exhibited very similar textural and organic matter characteristics. This pattern suggested competition for binding sites on the  $\text{Al}(\text{OH})_3$  floc by redox-P in relation to other constituents. Others have demonstrated competition between  $\text{PO}_4^{-3}$  and HA for binding sites on  $\text{Al}(\text{OH})_3$ . Because Half Moon Lake sediment organic matter content was relatively high, HA may have impacted redox-P binding efficiency. For instance, Guan et al. (2006) showed that removal of added  $\text{PO}_4^{-3}$  by  $\text{Al}(\text{OH})_3$  decreased in the presence of HA at neutral pH, attributing this pattern to competition for binding sites due to surface coverage by sorbed HA on the floc. De Vicente et al. (2008b) found that HA and silicate decreased  $\text{PO}_4^{-3}$  removal efficiency by  $\text{Al}(\text{OH})_3$ . Their results also indicated that  $\text{PO}_4^{-3}$  removal efficiency was improved at higher  $\text{PO}_4^{-3}$  concentrations. Similarly, the Al:P ratio declined as a function of higher concentrations of redox-P as found in the present study, suggesting successful competition for binding sites

with increasing  $\text{PO}_4^{-3}$ . However, de Vicente et al. (2008b) cautioned that some of the  $\text{PO}_4^{-3}$  removal observed in their study may have been due to formation  $\text{Al-PO}_4^{-3}\text{-HA}$  complexes versus sorption onto  $\text{Al}(\text{OH})_3$ , although this reaction predominately occurs under conditions of low pH (<4; Cheng et al. 2004). More experimental research is needed to better understand mechanisms affecting redox-P binding efficiency for natural sediments. Nevertheless, the present findings suggest that the initial redox-P concentration is an important factor contributing to variations in the Al:P ratio.

Sediment from nearby Wisconsin lakes collectively exhibited similar nonlinear trends between the Al:P ratio and redox-P that fell within ranges observed for Half Moon Lake, lending further support to the hypothesis that competition for binding sites on the  $\text{Al}(\text{OH})_3$  floc increased with increasing redox-P concentration. In particular, sediment collected from 5 locations in Squaw Lake exhibited a wide range in redox-P concentration, similar to that of Half Moon Lake, and the Al:P ratio varied between 42 and 310. However, nearly all points fell outside the 95% confidence limits developed for Half Moon Lake, indicating that individual lake sediments should be examined to accurately estimate relationships between redox-P and Al:P ratios. Other factors such as HA and silicate concentration (Guan et al. 2006, de Vicente et al. 2008b), pH (Cheng et al. 2004), and changes in the crystalline structure of  $\text{Al}(\text{OH})_3$  over time (Lijklema 1980, Berkowitz et al. 2006, de Vicente et al. 2008a) can affect the Al:P binding ratio and subsequent Al dosage.

For Half Moon Lake, I considered inactivating the more rapidly mobilized redox-P pool in the upper 4 cm sediment layer and calculated Al dosage based on horizontal variations in redox-P. Short-term laboratory assays to estimate removal of redox-P did not address control of the less important, gradually released labile organic P and P diffusing upward from deeper sediment layers or downward from fresh sediment layers deposited on top of the  $\text{Al}(\text{OH})_3$  floc. Mineralization of organic P and vertical  $\text{PO}_4^{-3}$  diffusion in anoxic sediment represent slower fluxes that must be estimated independently for incorporation into an overall Al dosage.

Lewandowski et al. (2003) provided experimental evidence for diffusive P flux from deeper layers and freshly deposited sediment to the  $\text{Al}(\text{OH})_3$  layer. They indicated that P diffusing from these layers could sorb onto unoccupied sites on iron oxyhydroxides that were previously stripped of  $\text{PO}_4^{-3}$  if  $\text{Al}(\text{OH})_3$  binding sites were already filled due to underdosing with respect to these other sources. However, it is currently difficult to precisely determine the size of the mobile P pool active in diffusion to the  $\text{Al}(\text{OH})_3$  layer over time and is beyond the scope of the present study to suggest methods or protocols for estimating Al dosage to account for these sources.

In those cases where labile organic P concentrations are high, Reitzel et al. (2003, 2005) and de Vicente et al. (2008a) discussed methodology and approaches for incorporating this source into Al dosage calculations. Assuming that the entire labile organic P pool will be converted to  $\text{PO}_4^{-3}$  in time, its concentration could be added to the redox-P concentration to calculate Al dosage (Reitzel et al. 2003). In the case of Half Moon Lake, the mobile P concentration could be substituted for redox-P in the regression equation developed (Fig. 7a) to estimate dosage. Because the labile organic P was low relative to redox-P in the upper sediment layer of Half Moon Lake, the overall dosage would not increase by much.

Uncertainty remains, however, regarding whether simply increasing Al dosage to account for these future P sources will result in the desired longer-term control. For instance, de Vicente et al. (2008a) showed that aging of the  $\text{Al}(\text{OH})_3$  floc without previously sorbed  $\text{PO}_4^{-3}$  could result in substantially reduced future binding efficiency (up to 75% reduction in adsorption capacity over 90 d) due to changes in crystalline structure of the floc (Berkowitz et al. 2005). They suggested that smaller doses spread out over several years, versus one large dose, might maintain higher binding efficiencies for these future P sources. In addition, longer-term changes (i.e., years) in Al binding efficiency and capacity and processes that result in lowering of the Al:P ratio (Rydin et al. 2000) remain poorly understood (Berkowitz et al. 2006). More research is needed to clarify both dosage estimation and application strategies for longer-term control of labile organic P and P diffusion from adjacent sediment layers.

The area-based dosage I considered for Half Moon Lake was high relative to dosages reported in Rydin and Welch (1999), but not unprecedented: Lake Süsser See (Germany) received incremental applications between 1977 and 1992 that totaled  $100 \text{ g Al/m}^2$  (Lewandowski et al. 2003); Lake Tiefwareensee (Germany) received a dosage of  $137 \text{ g Al/m}^2$  (Wauer et al. 2009); and Green Lake, Washington, was treated at a dosage of  $94 \text{ g Al/m}^2$  (Dugopolski et al. 2008). The targeted Al:P ratio generally ranged between 2:1 and  $>10:1$ , and all treatments were successful in reducing P in the water column and sediment. In contrast, lower area-based doses in which the Al:P ratio was low relative to the mass of redox-P resulted in limited longevity of sediment P control (i.e., 1–2 y; Rydin and Welch 1999). Case studies include Lake Delavan, Wisconsin, which received an average area-based dosage of  $\sim 20 \text{ g Al/m}^2$  derived from a theoretical 1:1 Al:P ratio (Robertson et al. 2000) versus an estimated  $\sim 150 \text{ g Al/m}^2$  dosage and a 100:1 Al:P ratio based on the formation of Al-P in sediments exposed to  $\text{Al}(\text{OH})_3$  in the laboratory (Rydin and Welch 1999). Eau Galle Reservoir, Wisconsin, experienced short-lived sediment P control (James et al. 1991) due to Al under dosage ( $11.3 \text{ g Al/m}^2$ ), which was based on a 1:1 Al:P ratio,

and unusually high external sediment and P loading during the treatment year that immediately buried the  $\text{Al}(\text{OH})_3$  floc.

The volumetric dosage estimated for Half Moon Lake also fell in the high range relative to Al dosages reported for other systems (Cooke et al. 2005), which was not surprising given the high redox-P concentrations in Half Moon Lake sediment. In particular, redox-P concentrations in excess of  $1.5 \text{ mg/g}$  were high relative to those reported for lakes in North America (Nürnberg 1988). In general, higher volumetric dosages have coincided with greater longevity of effective sediment P control, which is an important goal in Al dosage strategy (Cooke et al. 2005). The area-based dosage estimated for Half Moon Lake was targeted toward immediate binding of high redox P concentrations in the upper sediment layer and saturation of the  $\text{Al}(\text{OH})_3$  floc with this  $\text{PO}_4^{-3}$ . However, future applications may be needed to address P sources diffusing from adjacent sediment layers and mineralization and hydrolysis of labile organic P if the P-impooverished particles settling onto the floc cannot offset these fluxes.

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