Aluminum Sulfate-Sodium Aluminate Dosage Requirements for Half Moon Lake, Eau Claire, Wisconsin

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PURPOSE: High phosphorus (P) flux from bottom sediments represents an important source in Half Moon Lake (Eau Claire, Wisconsin) that needs to be controlled in order to drive the system toward P-limitation of algal growth and improve underwater light condition for restoration of native submersed macrophytes. An aluminum (Al) sulfate-sodium aluminate (buffered alum) application represents an effective management technique for binding P in sediment and reducing flux into the water column for algal uptake in soft water lakes. The objectives of this technical document are to estimate the buffered alum dosage required to inactivate ~ 90% of the iron-bound P in the upper 5 cm sediment layer in Half Moon Lake.

BACKGROUND: Bottom sediments usually represent a substantial P source that can subsidize high algal productivity, even when external P loading from the watershed has been reduced. For sediments containing iron (Fe) compounds, P is usually coupled with Fe dynamics and flux to the water column is regulated by oxidation-reduction (i.e., eH) and pH reactions (Mortimer 1971). A thin oxidized microzone exists in the sediment surface layer when the overlying water column is oxygenated. Under these conditions, Fe is in an oxidized state (i.e., Fe^{+3}) in the microzone as Fe(OOH) and adsorbs P, thereby minimizing its diffusion into the overlying water column. However, high pH driven by algal productivity can promote P release from Fe(OOH) via ligand exchange reactions (James et al. 1996). Bacterial reduction of dissolved oxygen and iron from Fe^{+3} to Fe^{+2} in the upper sediment layer results in the development of anoxia, desorption of P, and diffusion out of the sediment. Internal P loading via these recycling pathways can account for a substantial portion of the P economy of aquatic systems and hinder restoration efforts targeted at reducing algal biomass.

Extractable forms of sediment P found to be most active in these eH and pH reactions are the loosely-bound (i.e., adsorbed P and P associated with calcium carbonate; extracted with 1 M ammonium chloride) and Fe-bound (i.e., P associated with Fe(OOH); extracted with 0.11 M bicarbonate-dithionate or BD) fractions (Boström et al. 1982; Nürnberg 1988). Nürnberg (1988) found that the BD-extractable P fraction was a good predictor of rates of total P release from sediment under anoxic conditions, supporting the hypothesis of Mortimer (1971). These P fractions can be immobilized via an alum (aluminum sulfate; $Al_2(SO_4)_3$ xH_2O) application to the sediment to irreversibly bind P to aluminum hydroxides ($Al(OH)_3$) and inhibit P flux from sediments (Cooke et al. 2005). Alum is usually applied to the surface waters over the active sediment area, where it disassociates to form an $Al(OH)_3$ precipitate that then settles to the bottom as a milky white floc and covers the sediment. The hydrolysis of Al leads to the production of hydrogen ions which lowers the pH of the water column. Al toxicity to the biota can occur if the pH falls below 6 and must be considered in dose determination. The dosage of alum can be estimated by determining the maximum allowable concentration based on the pH and alkalinity of the aquatic system (Kennedy and Cooke 1982). The rationale for this dose determination method is to apply a maximum amount of alum to the hypolimnion and yet maintain the pH above 6.0 to prevent Al dissolution. However, this estimation technique is not suitable for soft water lakes with a low buffering capacity. It also does not directly consider control of reactive P stored in the sediment or the rate of sediment P release.

Dosage can also be estimated by considering the mass of BD-extractable P in the upper layers of the sediment. These calculation methods more specifically address the control of sediment P flux and reactive sediment P pools. Unlike the alkalinity-based dosage estimations, calculations based on sediment P require knowledge of the amount of alum required to bind the P fraction extracted with BD. The objectives of this technical document are to estimate the dosage of buffered alum required to inactive ~ 90% of the Fe-bound P in the upper sediment layer of Half Moon Lake, Wisconsin.

STUDY SITE: Half Moon Lake is a relatively small (0.5 km^2 and 8.9 x 10^5 m^3), shallow (mean depth = 1.6 m, maximum depth = 4 m) urban lake located in Eau Claire, Wisconsin (Figure 1). An oxbow of the Chippewa River, the bathymetry resembles that of a river channel. The eastern portion of the lake is isolated by a causeway that restricts water exchange with the rest of the lake. Forty percent of the surface area is less than 2-m deep. External inputs to the lake occur primarily via a storm sewer system that drains residential, commercial, and industrial land uses from a 2.3 km^2 watershed. The P budget has been dominated by internal loading from sediment (42%), decomposition of *P. crispus* and recycling to the water column (20%), and sediment resuspension by motor boat activity (17%). In contrast, external P loading accounts for only 21% of the P budget (James et al. 2002). The lake is classified as eutrophic (Carlson TSI$_{CHLA}$ = 74); mean summer trophic state indicators are 0.110 mg·L^{-1} total P, 82 mg·m^{-3} viable chlorophyll, and 1.1 m Secchi transparency.

The macrophyte community is dominated by *P. crispus*. Turions germinate in late March and the population can occupy greater than 75% of the lake surface area by early June, attaining peak biomass levels greater than 100 g dry mass·m^{-2}. Native submersed and emergent macrophyte species are dominated primarily by *Ceratophyllum* and *Elodea* sp.

METHODS:

Sediment P fractionation. Sediment cores were collected at 29 stations in Half Moon Lake in July, 2009, for determination of BD-extractable P concentrations in the upper 5-cm layer (Figure 1). Subsamples were dried at 105 °C to a constant weight and burned at 500 °C for determination of moisture content, sediment density, and organic matter content (Håkanson 1977). To determine BD-extractable P, 12.5 milliliters of a solution of 0.11 M NaHCO$_3$ - 0.11 M Na$_2$S$_2$O$_4$ (sodium bicarbonate-sodium dithionate; BD) was added to 25 mg dry mass equivalent of fresh sediment contained in 50 mL centrifugation tubes. The tubes were gently shaken, incubated in a 40 °C water bath for 30 minutes, and centrifuged for 45 min at 500 g to clarify the mixture (Nürnberg 1988). The extract was filtered through a 0.45 μm membrane syringe filter and gently bubbled with air for 1 hour to reoxidize the solution. Filtrate was analyzed for soluble reactive P (SRP) using standard colorimetric techniques (APHA 2005).

Alum dosage assays. Sediment from six of the sampling stations were used for determination of the dosage of alum (as Al) required to immobilize BD-extractable P using a modification of the Rydin and Welch (1999) assay method. These samples were chosen to represent the range of BD-extractable P concentration observed in the lake

sediments. Alum (as aluminum sulfate; $Al_2(SO_4)_3 \cdot 18 H_2O$) was diluted with 0.1 M sodium bicarbonate ($NaHCO_3$) to a concentration of 1.4 to 2.5 g Al L^{-1} (at pH 7.0). 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 mass of fresh sediment to obtain Al concentrations ranging from 0 (i.e., control) to > 300 mg Al g^{-1} sediment. The assay tubes were shaken over night (~ 12 hours) at 20 ^{o}C in a darkened environmental chamber and centrifuged at 500 g to concentrate the sediment. The treated sediments were then extracted with BD using procedures described above.

Al:P ratios were estimated as concentration of alum (as Al) required to bind 90% of the BD-extractable P. This calculation differed from Rydin and Welch (1999) in that they used the concentration of aluminum-bound P (as extracted in 0.1 N sodium hydroxide) formed versus BD-extractable P lost to the alum floc. Earlier studies on Half Moon Lake sediment found that an interference in the form of a precipitate developed during the NaOH extraction which rendered determination of Al-bound P formed on the alum floc untenable. This precipitate was believed to be the outcome of reaction between soluble organic acids and alum during the NaOH extraction procedure.

Buffered alum dosage estimation. Al dosage was estimated as the concentration (g·m^{-2}) required to bind BD-extractable P in the upper 5-cm sediment layer. This sediment depth was chosen based on observations of the position of the alum floc in sediments subjected to an alum application in field enclosures deployed in Half Moon Lake. The alum floc was located within the upper 4-cm layer one year after application (James, unpubl. data). The dry mass concentration of BD-extractable P (mg·g^{-1}) was converted to an areal concentration (g·m^{-2}) as,

$$BD\text{-}P \ (g·m^{-2}) = BD\text{-}P \ (mg·g^{-1}) \cdot \rho \ (g·cm^{-3}) \cdot \theta \cdot h \ (m) \cdot 1000000 \ (cm^3·m^{-3}) \cdot 0.001 \ (g·mg^{-1}) \qquad 1)$$

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

$$Al \ (g·m^{-2}) = BD\text{-}P \ (g·m^{-2}) \cdot Al{:}P_{90\%} \qquad\qquad 2)$$

where, $Al{:}P_{90\%}$ was the binding ratio required to adsorb 90% of the BD-extractable P in the sediment. Al dosage requirements at the 29 sampling stations were plotted spatially using ArcGIS 9.1 (Environmental Systems Research Institute, Inc). Treatment areas were delineated based on spatial variations in Al dosage. Average dosage for each area was entered into a spreadsheet to calculate the gallons of aluminum sulfate and sodium aluminate required for each area. Buffered alum costs to treat the lake were estimated as the total gallons of each solution required by $1.50 gal^{-1} for aluminum sulfate and $4.65 gal^{-1} for sodium aluminate. A setup cost of ~ $7,000 was added to the buffered alum cost to account for labor and other costs associated with application.

RESULTS AND DISCUSSION:

An example of changes in BD-extractable P versus increasing alum concentration is shown in Figure 2. BD-extractable P declined in an exponential pattern as a function of increasing alum concentration due to irreversible transfer of P from Fe compounds to Al (Figure 2a). Over 60% of an initial BD-extractable P concentration of 0.149 mg·g^{-1} was bound with a modest Al concentration addition of 2.8 mg·g^{-1} (Figure 2b). However, P binding diminished exponentially at higher Al concentrations. This pattern was probably due to increased competition for binding sites on the alum floc by other constituents as Al concentration increased. The concentration of Al required to bind 90% of the BD-extractable P was ~ 22.8 mg·g^{-1} for this particular example (Figure 2), resulting in an Al:P$_{90\%}$ of 170 (i.e., 22.8 mg Al·g^{-1} required to bind 0.134 mg P·g^{-1}). This ratio was considerably higher than the 1:1 ratio that has been typically used for alum dosage estimation.

In contrast, sediment with a much higher BD-extractable P concentration of 2.0 mg·g^{-1} required only a slightly greater concentration of Al to achieve 90% inactivation (Figure 3). In this example, 40.1 mg Al·g^{-1} were needed to bind 90% of the BD-extractable P, resulting in an Al:P$_{90\%}$ of only 22. For all sediments assayed, the Al:P$_{90\%}$ ratio varied in a negative exponential pattern as a function of increasing initial BD-extractable P concentration (Figure 4). Thus, the Al:P$_{90\%}$ ratio exceeded 150 for initial BD-extractable P concentrations less than 0.15 mg·g^{-1}, and ~ 20 for concentrations greater than ~ 2.0 mg·g^{-1}. Competition for binding sites by other constituents may be responsible for this pattern. At lower initial BD-extractable P concentrations, a higher Al:P$_{90\%}$ ratio is required because other constituents are competing with BD-extractable P for binding sites. At higher concentrations of BD-extractable P, a lower stoichiometric ratio is needed because there is more P relative to other constituents to compete for binding sites on the alum floc.

Because sediment P concentrations can vary spatially as a result of bathymetry and delta formation, variations in Al:P stoichiometry need to be considered for accurate alum dose calculation on a lakewide scale. For instance, an Al:P ratio of 10:1 would inactivate ~ 60% of the BD-extractable P for sediments depicted in Figure 3 (Table 1). However, the same ratio would result in an under dosage by 77% for sediments with a BD-extractable P concentration of 0.149 mg·g^{-1} (Figure 2). Although Al:P ratio of 100:1 would be effective in binding BD-extractable P at both stations, it would result in substantial overdosing and be cost ineffective for sediments with the higher BD-extractable P concentration (Table 1).

For Half Moon Lake, there were distinct spatial variations in BD-extractable P concentrations (Figure 5). Concentrations were greatest in the slightly deeper western arm and declined to lower values in the northern, eastern, and southern portions of the lake. In particular, concentrations in excess of 1.5 mg·g^{-1} were very high relative to those reported for lakes in North America (Nürnberg 1988), and coincided with very high rates of P release from anoxic sediment on the order of 10 to 15 mg·m^{-2}·d^{-1} (W.F. James unpublished data).

Regression equations developed for $Al:P_{90\%}$ versus BD-extractable P (Figure 4) were used to estimate spatial variations in the $Al:P_{90\%}$ (Figure 6). The ratio approached 20 in the western arm of the lake and 100 or greater in other regions (the maximum $Al:P_{90\%}$ was set to 150 for calculation purposes). To estimate the alum dosage for various regions of the lake, I used equations 1 and 2 and chose an h of 4 cm (i.e., binding of BD-extractable P in the upper 5-cm layer). As shown in Figure 7, a higher alum dosage would be needed for the western arm versus other areas of the lake.

Two dosage treatment zones were delineated based on the spatial variations in alum dosage concentration shown in Figure 8. The first treatment zone required an Al dosage of 150 $g \cdot m^{-2}$. The western arm of the lake encompassed most of this zone. The second treatment zone encompassed most of the eastern arm and southern embayment of the lake and required an average Al dosage of 75 $g \cdot m^{-2}$. The estimated lakewide areal alum dosage was $\sim$ 115 $g \cdot m^{-2}$ and the volumetric dosage was $\sim$40 $g \cdot m^{-3}$. The volumetric dosage estimated for Half Moon Lake fell in the high range relative to alum dosages reported for other systems (Table 2; see Cooke et al. 2005). However, this observation was not surprising given the high concentrations of BD-extractable P observed in the sediments of Half Moon Lake. In general, higher volumetric dosages coincided with greater longevity of effective sediment P control, which is an important goal in alum dosage strategy (Table 2).

The calculation of gallons of aluminum sulfate and sodium aluminate required to treat each zone in the lake are shown in Table 3. For zone 1, the Al concentration ($g \cdot m^{-2}$) was multiplied by the treatment area to calculate Al mass (kg). This mass was converted to total lbs using the conversion factor 2.2046 $lb \cdot kg^{-1}$. Pounds of Al mass were converted to gallons of aluminum sulfate and sodium aluminate using the calculations and conversion factors shown in Table 3. One part of sodium aluminuate is required per two parts aluminum sulfate in order to buffer the pH during application to $\sim$ 7. The cost estimate is shown in Table 4. Total cost, including setup and labor was estimated at $388,106.

One unknown in the approach to estimating alum dosage presented here is the effect of aging on Al:P stoichiometry. The current assay approach to estimating Al:P ratios addressed immediate control of BD-extractable P. However, Rydin et al. (2000) reported that Al:P stoichiometry approached $\sim$ 11 in lake sediments that had been treated with alum 6 to 21 years previously. Reitzel et al. (2003) suggested that a molar ratio of 4:1 was sufficient to immobilize sediment P in Lake Sonderby, Denmark. Dugopolski et al. (2008) found that alum binding efficiency was low shortly after alum application, implying that full binding saturation at an Al:P ratio of $\sim$11 may take on the order of months or years. If so, use of higher ratios based on assay results could lead to over dosage in the long term and cost overruns. In contrast, inefficient binding could result in poor control of internal P loading for many years until binding saturation is finally achieved, suggesting that higher ratios may be needed to counteract short-term inefficiencies in binding P by the alum floc. For Half Moon Lake, attainment of a long-term Al:P binding ratio of $\sim$ 11 at the suggested dosage of 115 $g \cdot m^{-2}$ would be equivalent to treating the upper $\sim$20 cm sediment layer, assuming that the BD-extractable P

concentration was relatively constant with sediment depth. If this projected binding ratio was indeed reached in Half Moon Lake, the alum treatment would still be considered a success rather than a cost overrun because BD-extractable P concentrations are high in the deeper sediment layers as well (W.F. James unpublished data)and should be inactivated to insure effective, long-term control of diffusive P flux from sediment. Field case studies on lake sediments treated with high doses of alum are needed in order to verify laboratory assay findings and to more accurately evaluate optimal (and cost effective) Al:P binding ratios for use in sediment P-based dosage calculations.

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Rydin, E., and Welch, E.B. 1999. Dosing alum to Wisconsin lake sediments based on in vitro formation of aluminum bound phosphate. *Lake Reser. Manage.* 15:324-331.

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Table 1. The aluminum:phosphorus ratio (Al:P), areal concentration of Al, and percentage of bicarbonate-dithionate-extractable P (BD-P) bound by alum for sediments with a relatively low (left column) versus high (right column) BD-P concentration.

BD-P = 0.149 mg g^{-1}			BD-P = 2.00 mg g^{-1}		
Al:P	Al (g m^{-2})	BD-P bound (%)	Al:P	Al (g m^{-2})	BD-P bound (%)
170 (measured)	95.5	90	22 (measured)	177	90
1	0.6	2	1	8	5
10	5.6	23	10	80.5	60
100	56.2	83	100	805	100

Table 2. A comparison of alum dosage rates for different lakes in North America and the observed longevity of treatment success based on Welch and Cooke (1999). Longevity was defined as the number of years since treatment that total phosphorus has been reduced in the surface waters by the percentages listed in parentheses. Estimated alum dosage for Half Moon Lake is 40 g·m^{-3}.

Lake	Alum Dose (g Al m^{-3})	Observed Longevity (years)
Unstratified		
Long Kitsap Co.	5.5	11 (30%)
Pickerel	7.3	<1
Long Thurston Co. North	7.7	>8 (56%)
Pattison North	7.7	7 (29%)
Wapato	7.8	<1
Erie	10.9	>8 (75%)
Campbell	10.9	>8 (46%)
Stratified		
Eau Galle	4.5	<2
Morey	11.7	8 (60%)
Cochnewagon	18	6 (0%)
Dollar	20.9	18 (68%)
Annabessacook	25	13 (41%)
West Twin	26	18 (66%)
Irondoquoit Bay	28.7	5 (24%)
Kezar	30	9 (37%)

Table 3. Estimation of gallons of aluminum sulfate and sodium aluminate for dosage zones 1 and 2 (see Figure 8 for the location of these areas).

Dosage zone	Variable	Value	Calculation
1	Al concentration, g m^{-2}	150	
	Area, m^{-2}	233111	
	Al mass, kg	34967	(Al, g m^{-2} x area, m^2)/1000
	Al mass, lbs	77087	Al, kg x 2.2046 lb kg^{-1}
	Aluminum sulfate, gal	68608	Al, lb x 0.89
	Sodium Aluminate, gal	34304	Aluminum sulfate, gal / 2
2	Al concentration, g m^{-2}	75	
	Area, m^{-2}	210846	
	Al mass, kg	15813	(Al, g m^{-2} x area, m^2)/1000
	Al mass, lbs	34862	Al, kg x 2.2046 lb kg^{-1}
	Aluminum sulfate, gal	99635	Al, lb x 0.89
	Sodium Aluminate, gal	49818	Aluminum sulfate, gal / 2

Table 4. Estimated costs to treat Half Moon Lake.

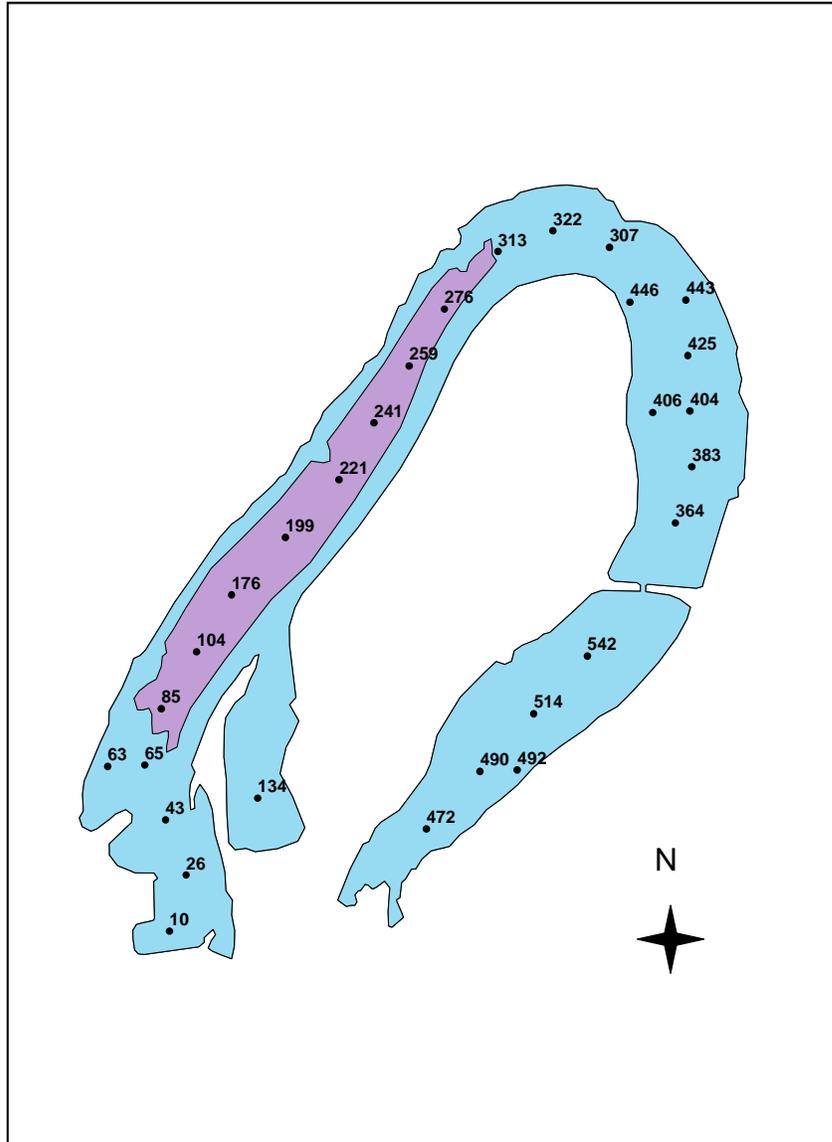| Cost analysis		
90% inactivation of BD-extractable P in the upper 4-cm sediment layer		
Aluminum sulfate @ $1.50/gal	99,635 gal	$149,453
Sodium aluminate @ $4.65/gal	49,818 gal	$231,654
Transport of alum to site and labor for application		$7,000
Total		$388,106

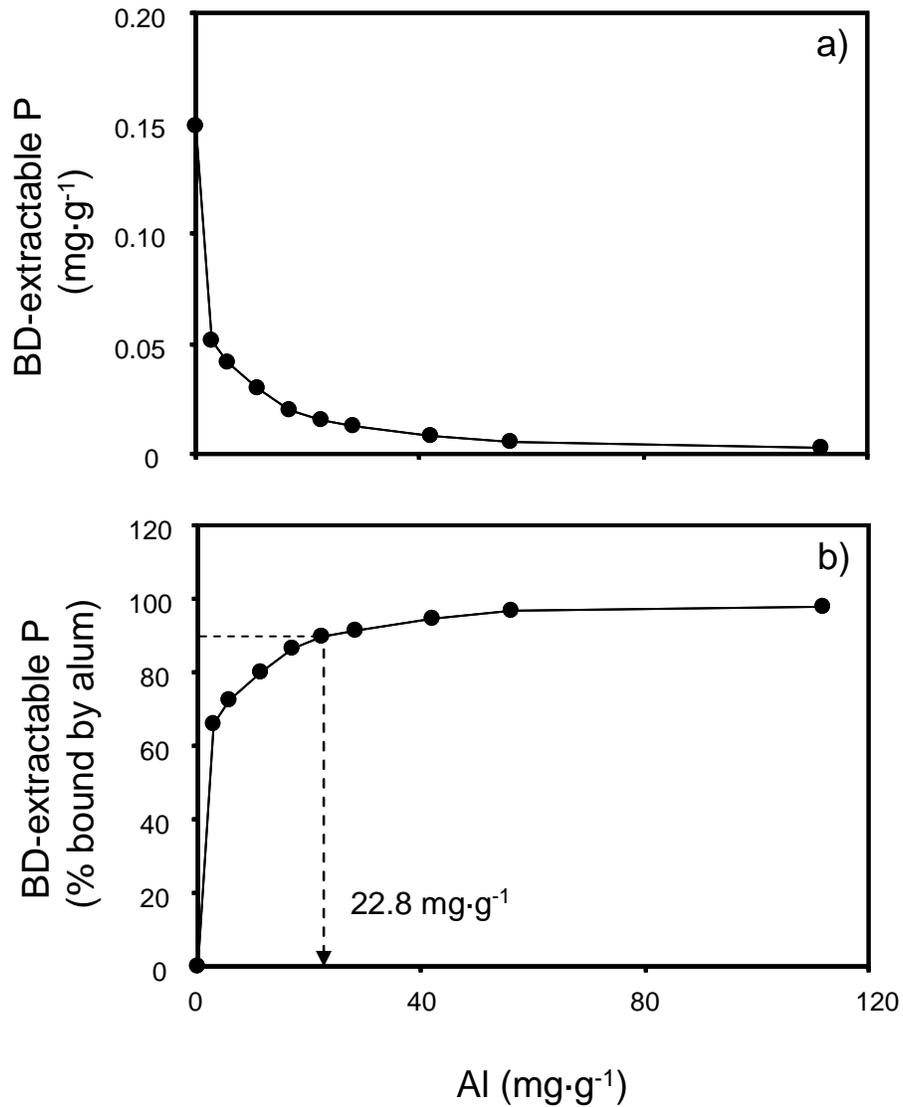Figure 1. Sediment sampling stations on Half Moon Lake, Wisconsin. Lavender area represents the 3-m contour.
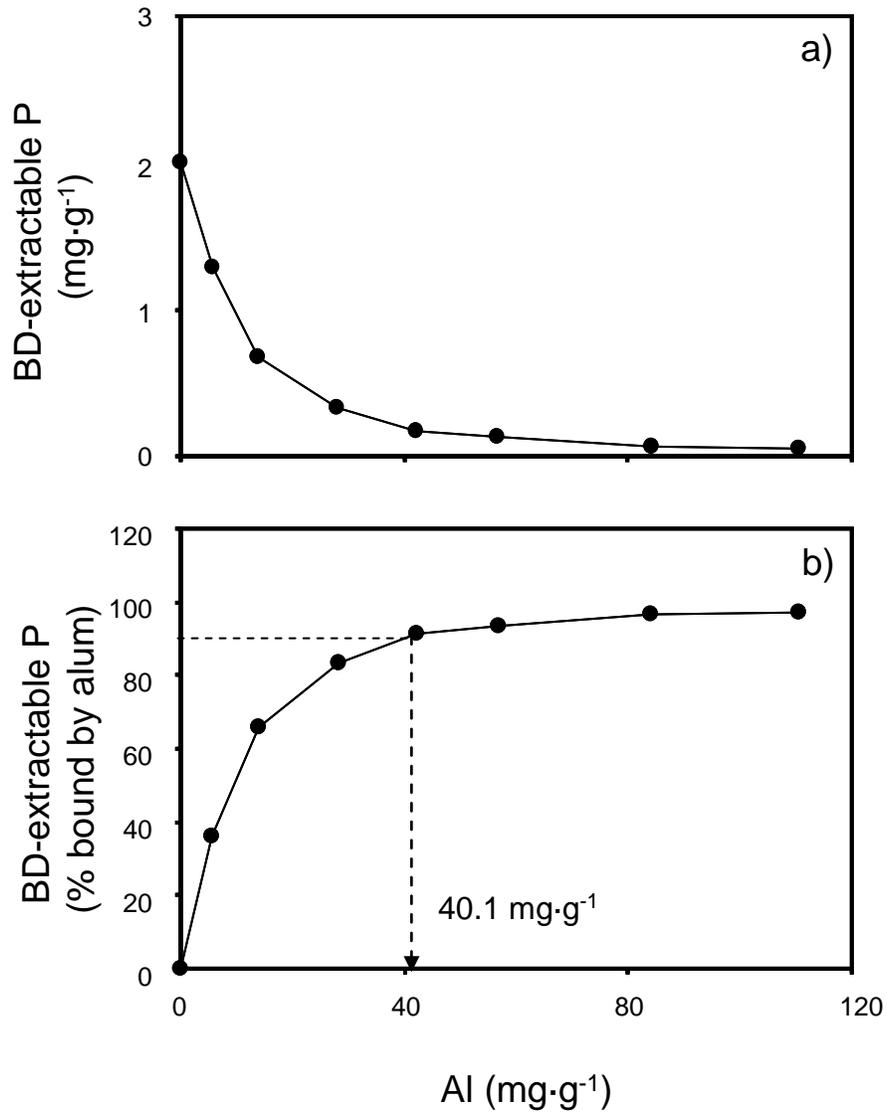
Figure 2. Relationships between aluminum (Al) concentration and the concentration of BD-extractable phosphorus (P) remaining in sediment (a) and the percentage of BD-extractable P bound by alum versus the Al concentration for sediment collected at station 404 (see Figure 1). Dotted lines designate the concentration of Al required to bind 90% of the BD-extractable P. BD-extractable P is expressed as mg·g dry sediment mass[-1].
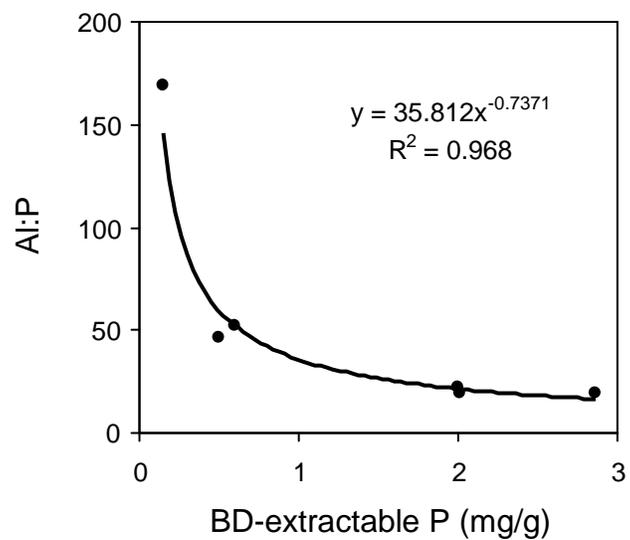
Figure 3. Relationships between aluminum (Al) concentration and the concentration of BD-extractable phosphorus (P) remaining in sediment (a) and the percentage of BD-extractable P bound by alum versus the Al concentration for sediment collected at station 241 (see Figure 1). Dotted lines designate the concentration of Al required to bind 90% of the BD-extractable P. BD-extractable P is expressed as mg·g dry sediment mass[-1].

Figure 4. Relationships between the alum (as aluminum; Al) to phosphorus (P) binding ratio (Al:P ratio) and the initial BD-extractable P concentration in sediment. BD-extractable P is expressed as mg·g dry sediment mass^{-1}.
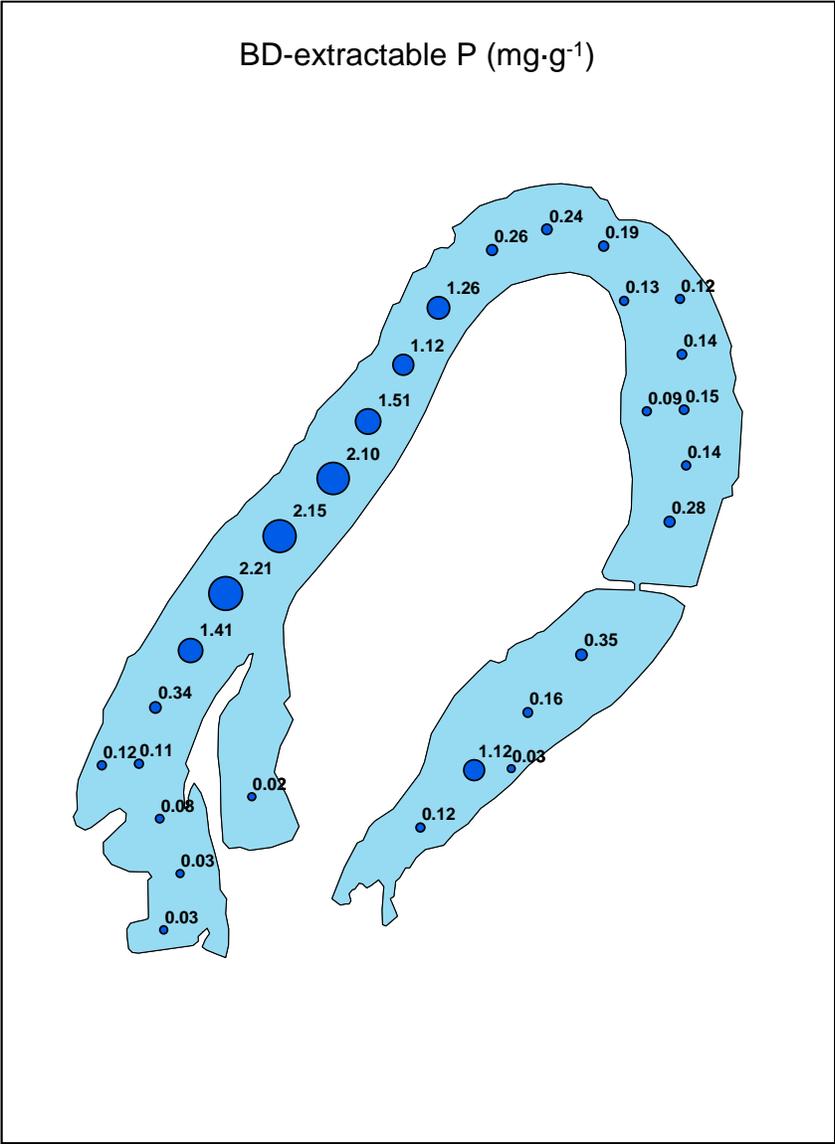
Figure 5. Spatial variations in the BD-extractable phosphorus (P) concentration in the upper 4-cm sediment layer. BD-extractable P is expressed as mg·g dry sediment mass[-1].
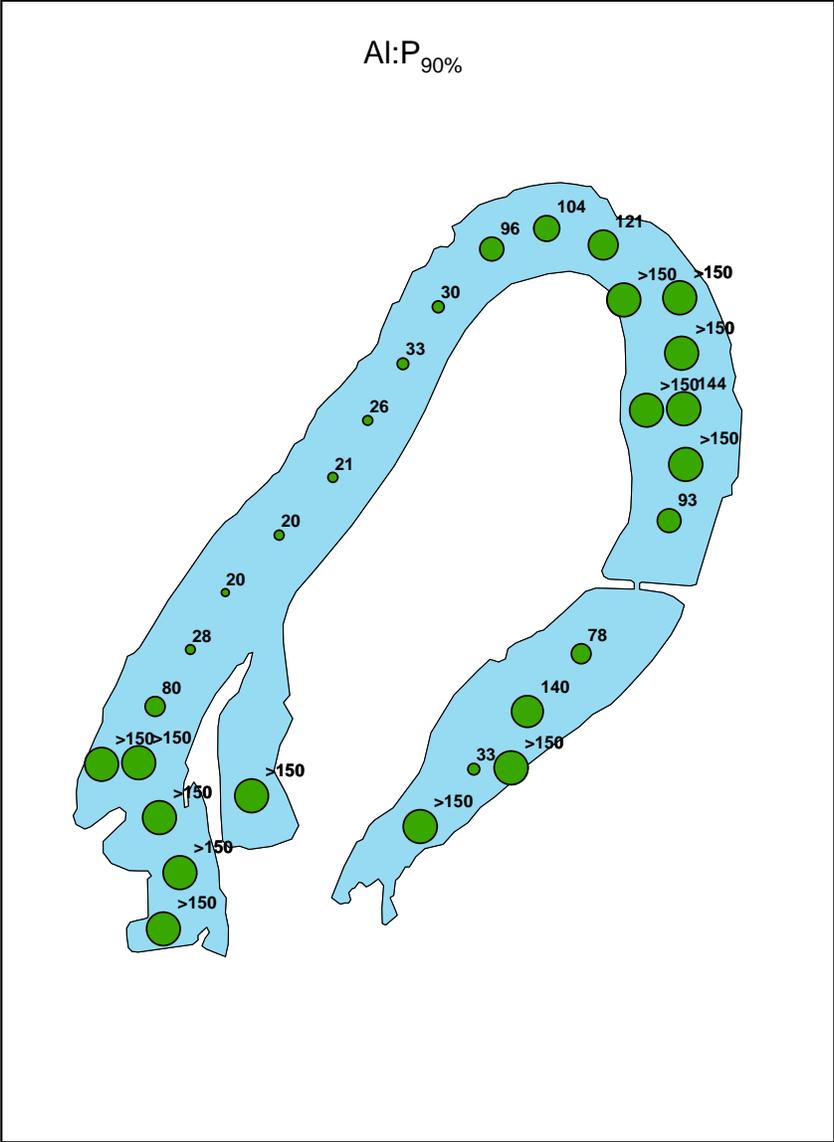
Figure 6. Spatial variations in the alum (as aluminum; Al) to phosphorus (P) binding ratio required to inactivate 90% of the BD-extractable phosphorus (P) concentration ($Al:P_{90\%}$) in the upper 4-cm sediment layer.
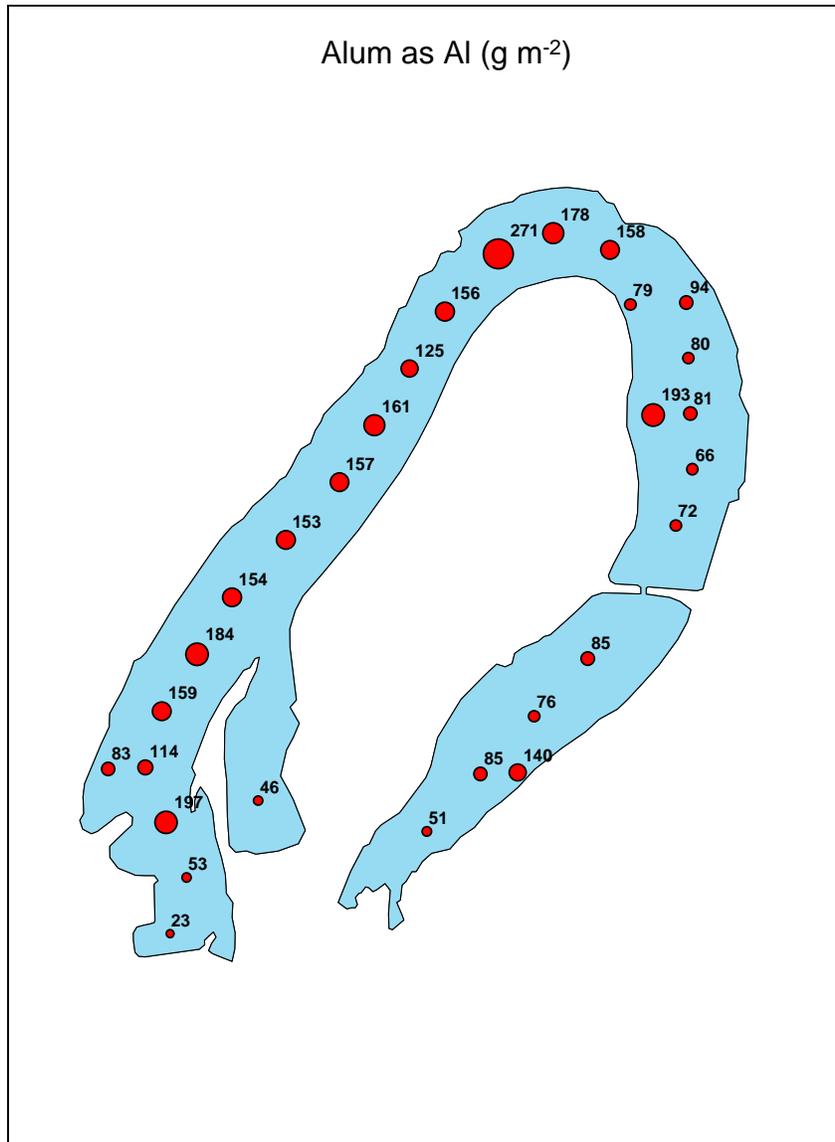
Figure 7. Spatial variations in the alum (as aluminum; Al) dosage concentration required to inactivate 90% of the BD-extractable phosphorus (P) concentration ($Al:P_{90\%}$) in the upper 4-cm sediment layer.
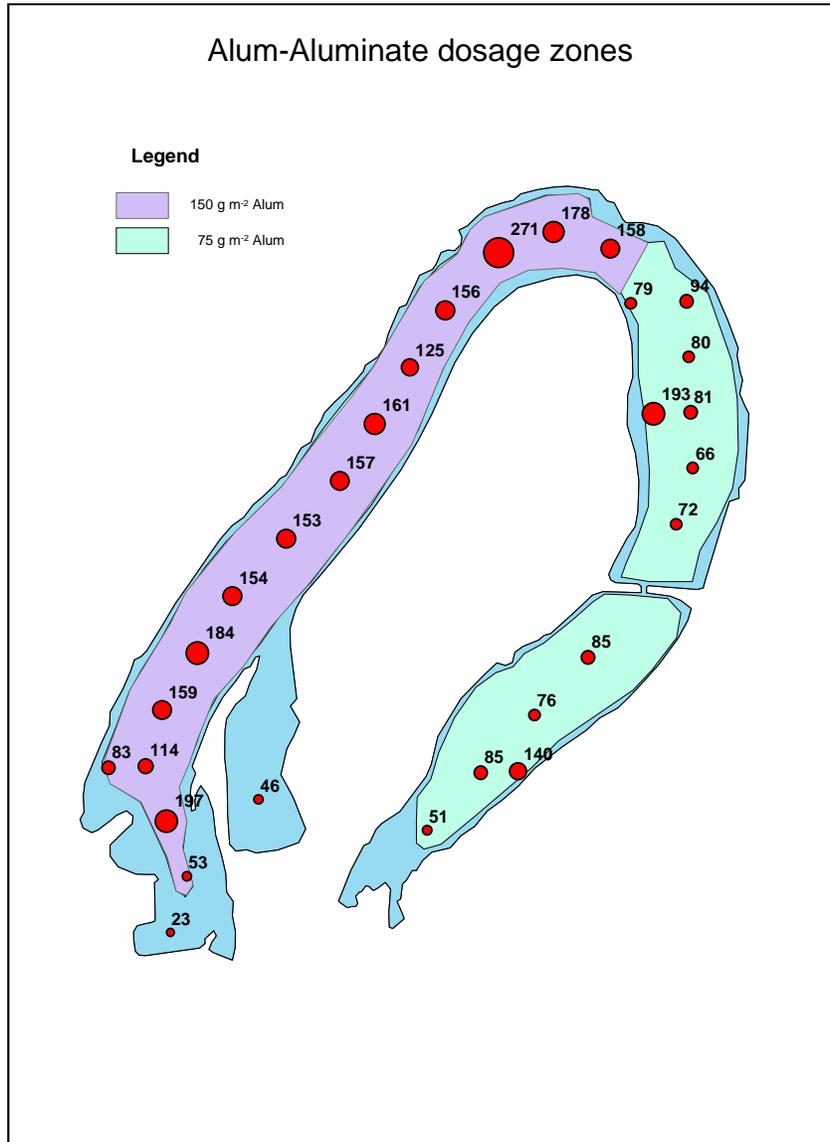
Figure 8. Areas of treatment and dosage concentrations in Half Moon Lake.