Alum dosage determinations based on the concentration of readily-mobilized phosphorus in the bottom sediments of Squaw Lake, Wisconsin.

Letter Report
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Objectives: The objectives of this work were to determine ranges in the amount of alum required to completely bind phosphorus (P) in the sediment that is associated with internal loading to the lake (i.e., readily-mobilized P). An alum assay method developed by Rydin and Welch (1999) was used to determine alum dosage requirements for the lake.

Background: Diffusion of P from bottom sediments to the water column can represent a substantial nutrient source to algal productivity that may need to be controlled in lakes, particularly if this P reaches the surface waters via turbulent mixing and vertical transport. Under these conditions, it is possible to control sediment P release via an alum (aluminum sulfate) application to the sediment to irreversibly bind P to alum and inhibit diffusive P flux from sediments. The dosage of alum required to inactivate sediment P compounds can be estimated by determining the maximum allowable alum concentration based on the pH and alkalinity of the aquatic system (Kennedy and Cooke 1982). pH is considered in this method because aluminum becomes soluble at a pH value < 6.0 and toxic to the biota. Since alum application lowers the pH of the water temporarily, it is necessary to apply a dosage that will not lower the pH to < 6.0. However, this estimation technique is not suitable for soft water lakes with a low buffering capacity such as Squaw Lake. For these systems, alum must be buffered with sodium aluminate to prevent low pH and Al toxicity.

Alum dosage requirements for softwater lakes can be estimated by considering the rate of internal P loading from the sediment (Kennedy et al., 1987) or the mass of readily-mobilized P in the upper layers of the sediment (Rydin and Welch 1999). Rydin and Welch (1999) developed an assay to determine the amount of alum required to inactivate readily-mobilized P in the sediment. This assay was used to determine alum dose requirements in Squaw Lake.

Findings: The bottom sediments in Squaw lake are very flocculent and loose. Since alum is dense, it is expected to sink into the sediments until it achieves neutral buoyancy. Sinking of the alum layer occurs over several months to a year, depending on the texture of the sediment. It is not known precisely how far an alum layer would sink into the sediments of Squaw Lake. However, an alum layer has been found between the 8 and 12 cm depths in very flocculent sediments of other lakes. A similar sinking pattern is expected to occur in Squaw Lake..

A laboratory study was conducted to determine the rate of internal P loading by bottom sediments in the lake. That rate was 2.7 mg m^{-2} d^{-1} and represents a mass of P of about 340 lbs diffusing into the water over a 5 month period in the summer. This rate of internal P loading falls within the range of rates reported for other eutrophic lakes. The readily-mobilized P in the sediment that can diffuse into the water column is nearly constant in concentration as a function of depth in the sediment (Fig. 1). If the alum layer sinks to the 10-cm depth, the mass of readily-mobilized P compounds in the sediment within that depth range will have to be considered in the determination of alum dosage.

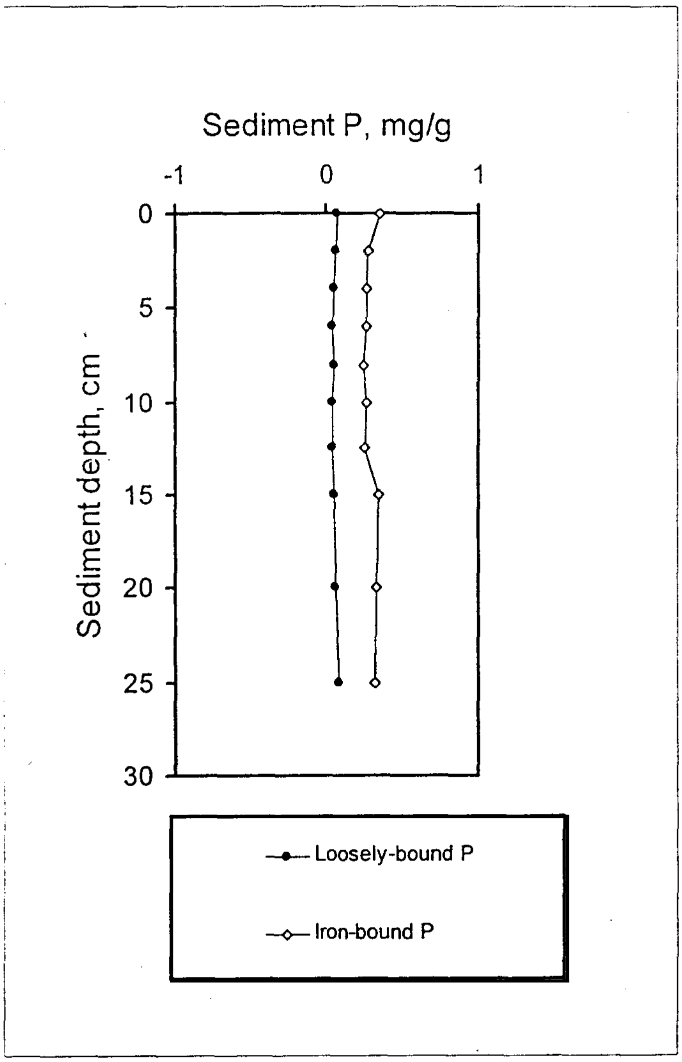

Figure 1. Concentrations of readily-mobilized P (i.e., loosely-bound and iron-bound P) in the bottom sediments of Squaw Lake.

We found from the Rydin and Welch (1999) assay results that it took about 100 parts of aluminum to bind 1 part of readily-mobilized P in the sediment. Based on this finding, we calculated the amount of alum that would be required to treat the lake sediments at a depth of 5 feet below the water surface to immobilize this sediment P (i.e., those compounds shown in Fig. 1). We provide a range of treatments and associated estimated costs in Table 1. The treatment estimates are based on the extent of the sediment layer to be treated. For instance, treatment of the upper 10 cm of the sediment layer in the lake with buffered alum would require 126849 gallons and cost ~ $234,000. Costs include an estimate of equipment mobilization to the lake. We also includes a estimate cost for treating the sediments based on the amount of internal P loading anticipated to occur during the summer period.

Table 1. The sediment layer in column 1 represents the thickness of sediment in the lake bottom. Column 2 shows the approximate gallons of buffered alum (i.e., aluminum sulfate and aluminate) required to bind all of the readily-mobilized P in the sediment layer. Column 3 shows the approximate cost to dose the lake. The cost includes equipment mobilization costs.

Sediment layer (cm)	Buffered Alum ($g\ m^{-2}$)	Buffered alum (gallons)	Cost of buffered alum ($1000)
Upper 2 cm	26.8	29473	54
Upper 4 cm	50.2	55196	102
Upper 6 cm	70.7	77688	143
Upper 8 cm	91.8	100906	186
Upper 10 cm	115.4	126849	234
Upper 12.5 cm	144.0	158267	291
1 year internal P load	41.0	35391	65

One unknown is how far the alum layer will sink into the sediment. But, 8-12 cm seems to be a reasonable estimate. Another unknown is how much of the bottom sediment layer contributes to diffusive P loading in the summer in Squaw Lake.

Previous alum dosage determinations for other lakes have used a theoretical ratio of 1 part aluminum to bind 1 part of phosphorus. Our assay suggests that this ratio is higher by 100 fold. The higher ratio requirement we found may reflect competition for binding sites on the alum floc by other compounds in addition to P. Rydin and Welch (1999) reported finding the Al:P ratio of 100:1 in their work, which is what we found for Squaw Lake. Use of a higher ratio in the alum dosage determination (as done for Squaw Lake) translates into greater gallon requirements and greater cost than use of a 1:1 ratio.

Recommendations: Treating the upper 8-10 cm sediment layer would provide control of readily-mobilized sediment P within the anticipated sinking depth range of the alum floc and represents the equivalent P mass equivalent of ~ 3 to 3.5 years of the estimated summer internal P. The high ratio used in computing the alum dosage insures that all readily-mobilized P within the upper 8-10 cm of the bottom sediment layer will be immobilized. Cost and affordability need to be factored into the final determination. Since we do not know the sinking depth of the alum, another treatment option is to apply alum to control the readily-mobilized P in the upper 4-5 cm sediment layer (i.e., one half the dosage of the previous scenario) and monitor the sinking depth of the alum layer in the sediment over several years. If the final sinking depth is greater than 5 cm, another alum application could be conducted to treat the additional readily-mobilized P that was not accounted for in the first application. Costs would have to be adjusted to account for a second equipment mobilization.

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ALUM:REDOX-SENSITIVE PHOSPHORUS RATIO CONSIDERATIONS IN THE ESTIMATION OF ALUM DOSAGE FOR CONTROL OF SEDIMENT PHOSPHORUS

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diffusive P flux from sediments. The dosage of alum required to inactivate redox-sensitive sediment P compounds can be estimated by determining the maximum allowable alum concentration based on the pH and alkalinity of the aquatic system (Kennedy and Cooke 1982). However, this estimation technique is not suitable for soft water lakes with a low buffering capacity.

Dosage can also be estimated by considering the rate of internal P loading from the sediment (Kennedy et al., 1987) or the mass of redox-sensitive P in the upper layers of the sediment (Rydin and Welch 1999). An assumption often used in these latter calculations is that P binds to alum at or near a 1:1 ratio. However, Rydin and Welch (1999) have recently demonstrated that the alum (as Al):redox-sensitive P binding ratio is more on the order of 100:1. The higher ratio requirement may reflect competition for binding sites by other compounds in addition to P. This recent finding is of critical importance because alum dosages based on internal P loadings or redox-sensitive sediment P may be severely underestimated if the ratio used to calculate the amount of alum required to inactivate P is 1:1. Since alum treatments in lakes are expensive, it is important to estimate an adequate dosage for reduction of internal P loading in a cost-effective manner, as under-dosing alum could lead to short-lived P control and unrealized expectations (Rydin and Welch 1999).

More information is needed regarding stoichiometric relationships between alum and redox-sensitive P in sediments order to more accurately estimate the amount of alum required to control sediment P in lakes. As part of a lake rehabilitation program to reduce P inputs to a west-central Wisconsin glacial lake (Squaw Lake), we examined alum dosage requirements to immobilize redox-sensitive sediment P using alum dosage assay techniques described in Rydin and Welch (1999). Using Al:redox-sensitive P ratios determined in these assay experiments, we also determined alum dosages required to immobilize summer P fluxes from the profundal sediments of this lake.

labile organic/polyphosphate P (Psenner and Puckso 1988; Nürnberg 1988). All extractions were filtered through a 0.45 μm membrane filter (Nalge) prior to analysis for soluble reactive P (SRP) using standard colorimetric techniques (APHA 1992). Labile organic/polyphosphate P was determined colorimetrically after persulfate digestion of a portion of the filtered 0.1 N NaOH extraction (Psenner and Puckso 1988).

Alum Dosage Assays. The upper 5 cm from two additional sediment cores, collected in the north and south basins, were carefully homogenized for determination of the quantity of alum (as Al) required to bind the loosely-bound and iron-bound P fractions in the sediments using the Rydin and Welch (1999) assay method. Alum (aluminum sulfate; $Al_2(SO_4)_3 \bullet 18\ H_2O$; 4.2 % Al; Allied Chemical) was diluted with 0.1 M sodium bicarbonate ($NaHCO_3$) to a concentration of 0.7 g Al L^{-1}. Aliquots of this solution (diluted to a final volume of 10 mL with distilled water) were added to centrifuge tubes containing the equivalent of 0.3 g dry mass of fresh sediment to obtain alum concentrations ranging from 0 (i.e., control) to 80 mg Al g^{-1} sediment. The assay tubes were shaken over night (~ 12 hours) at 20 °C in a darkened environmental chamber, then centrifuged at 500 g to concentrate the sediment and remove the alum solution. The sediments were then fractionated for loosely-bound, iron-bound, and aluminum-bound P using procedures described above.

Rates of P release from profundal sediments under anoxic conditions. Replicate sediment cores were collected from the same stations located in the north and south basins of Squaw Lake (three sediment cores from each station) for the determination of rates of P release under anoxic conditions using methods described in James et al. (1995). The upper 10 cm of sediment were carefully extruded intact into an incubation chamber (25 cm height). Filtered (Gelman A/E glass fiber) lake water (0.3 L), collected from Squaw Lake, was slowly siphoned back into the sediment incubation systems to serve as overlying water. The sediment incubation systems were sealed with rubber stoppers and placed in a darkened, temperature-controlled environmental

The profundal sediments in the two basins of Squaw Lake exhibited a moisture content > 95% and a bulk density < 0.05 g mL^{-1} over the upper 12.5 cm depth (Fig. 2). Moisture content declined, while bulk density increased, at sediment depths > 12.5 cm; however, they were still very flocculent. Over all depths and stations, mean inorganic P (i.e., loosely-bound P, Fe-P, Al-P, and Ca-P) was 0.704 mg g^{-1} (± 0.044 S.E.) while mean labile organic/polyphosphate P was much higher at 2.030 mg g^{-1} (± 0.104 S.E.; Fig. 3). Aluminum-bound P and iron-bound P accounted for 48% and 35% of the inorganic sediment P, respectively. Loosely-bound P and calcium-bound P each accounted for 9% of the inorganic P fraction. While most inorganic P fractions exhibited only small fluctuations as a function of depth, labile organic/polyphosphate P concentrations were greatest in the upper 15 cm and declined with increasing depth.

We determined the cumulative areal concentration (g P m^{-2}) of redox-sensitive sediment P for the profundal sediments of Squaw Lake between the sediment surface and a 30-cm sediment depth in order to estimate concentrations of alum (as Al) required to immobilize various levels of sediment P (Fig. 3a). Areal concentrations of redox-sensitive sediment P increased from 0.27 g P m^{-2} in the upper 2 cm to 1.15 g P m^{-2} at a sediment depth of 10 cm. The areal redox-sensitive sediment P concentration over the entire 30 cm depth was 8.75 g P m^{-2}.

Alum dosage concentrations required to control redox-sensitive sediment P in Squaw Lake were calculated based on the use of an Al:redox-sensitive P ratio of approximately 100:1, determined from the laboratory assay experiment for these sediments. For instance, immobilization of redox-sensitive sediment P in upper 10 cm of the profundal sediment of Squaw Lake would require an areal alum concentration of 115 g Al m^{-2} or a total mass of 34 metric tons of alum (as Al) applied to the hypolimnetic sediments (Fig. 3b-d). Given the very high moisture content and low bulk density of the sediments in the upper 10 cm, it is likely that alum could sink to near the 10-cm sediment depth in this lake. In the high moisture content (> 90%) profundal sediments of Mirror and Shadow Lakes, Wisconsin, an alum layer was found

m^{-2} (42 mg Al L^{-1}), for immobilization of redox-sensitive sediment P in the upper 10 cm of the sediment, are required for effective sediment P control in Squaw Lake. Welch and Cooke (1999) found that higher alum dosages were positively related to P control longevity and negatively related to P release rates from sediments, indicating that higher dosages were more effective in P control. Our volumetric dosage estimates for Squaw Lake, falling within the upper end of their dosage versus longevity relationships, would suggest potential for long-term effectiveness in this lake. Since the lake is poorly buffered (alkalinity ~25 mg $CaCO_3$ L^{-1}; unpublished data), alum would have to be strongly buffered with sodium aluminate in order to prevent low pH and the appearance of toxic levels of Al.

Another consideration in the management of sediment P in this lake is the potential role that labile organic/polyphosphate sediment P concentrations may play in the P economy of the lake after an alum treatment. Concentrations of this sediment P fraction are unusually high in this lake and we have recently found similar high labile organic/polyphosphate P concentrations in the sediments of two other northern Wisconsin glacial lakes (Wapogassett and Bear Trap Lakes; unpublished data). We currently do not know what impact this sediment P fraction has on internal P loading in the lake. Rydin and Welch (1999) found that alum additions did not directly impact this sediment P fraction for profundal sediments in Lake Delavan. However, bacterial conversion of this fraction to soluble P via mineralization (Jensen and Andersen 1992) or hydrolysis of bacterial polyphosphates to SRP under anaerobic conditions (Gächter et al. 1988; Gächter and Meyer 1993; Hupfer and Gächter 1995) may be an important source of internal P loading after an alum treatment. If dosage is high enough (i.e., use of a 100:1 ratio by weight), the alum layer may be effective in adsorbing hydrolyzed P from this fraction in the short-term. But as the alum layer sinks below the surface and becomes buried by new sediment, its effectiveness in controlling this potential source of P will probably diminish. More information is needed regarding the importance of this sediment P fraction to the internal P load of lakes in order to further improve calculations of alum dosage.

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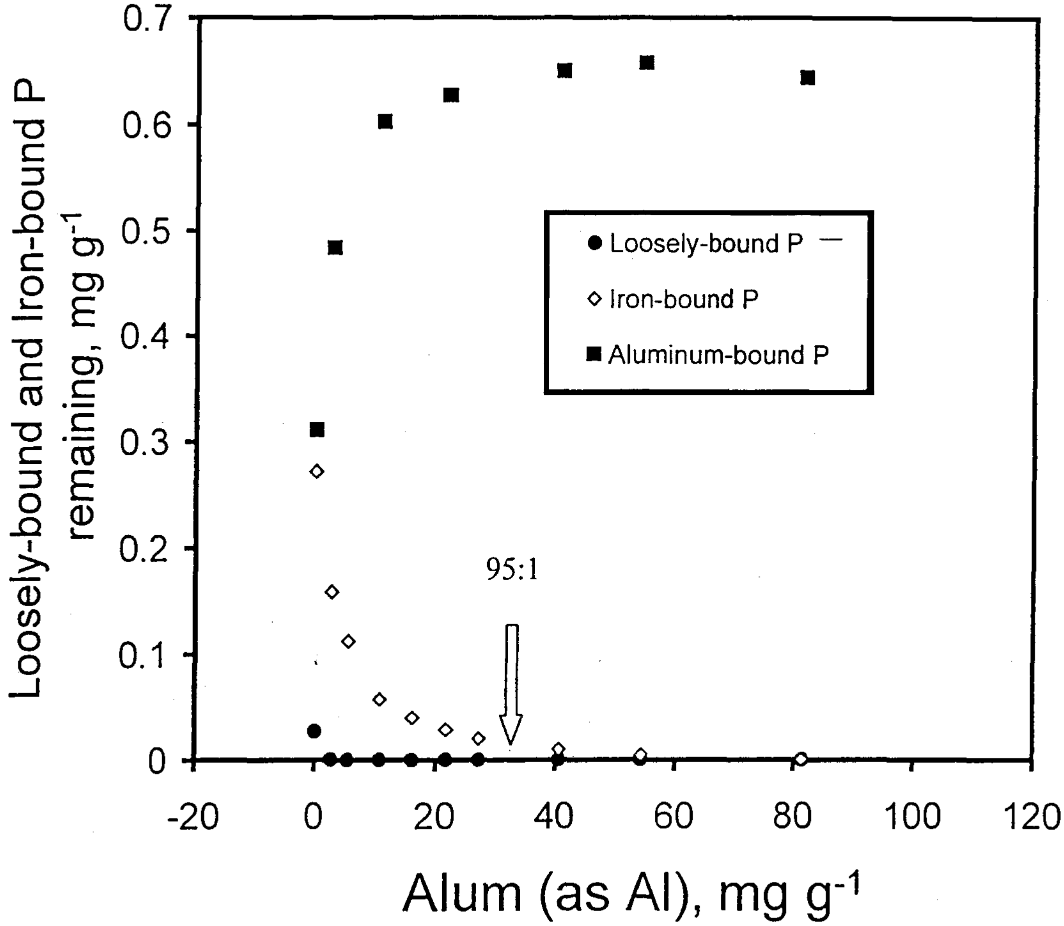

Figure 1. Variations in loosely-bound, iron-bound, and aluminum-bound sediment phosphorus (P) as a function of alum (as Al) concentration. Arrow indicates Al: redox-sensitive P ratio required to immobilize the loosely-bound and iron-bound sediment P fractions.

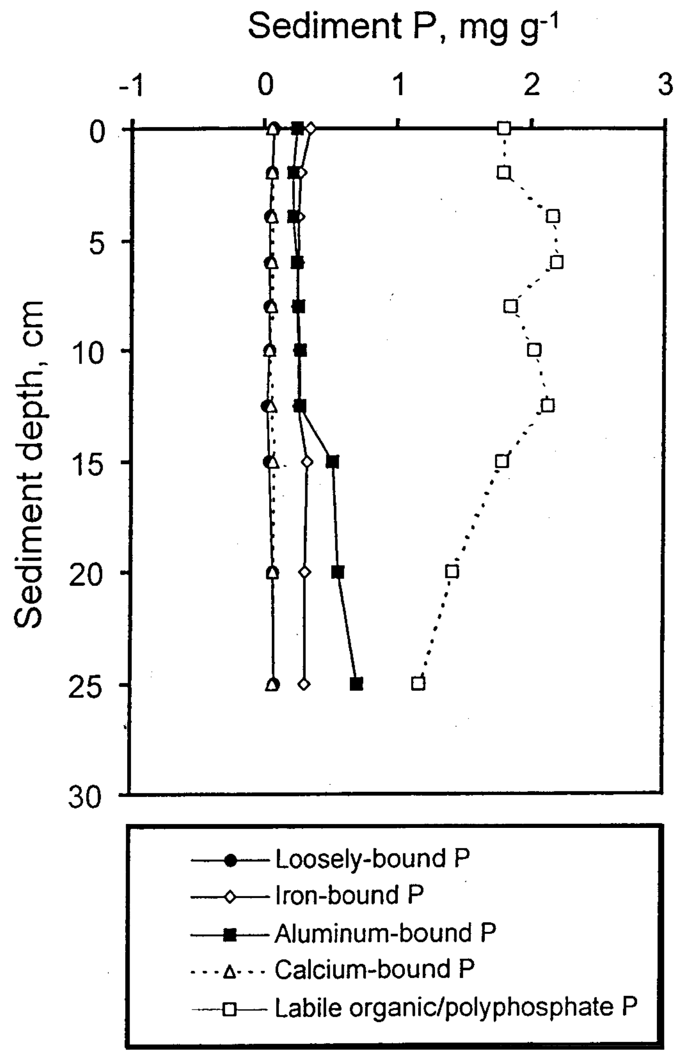

Figure 3. Variations in mean sediment phosphorus(P) fractions as a function of sediment depth for the north and south deep basins of Squaw Lake.