Alum Dosage Determinations Based on Redox-Sensitive Sediment Phosphorus Concentrations

by William F. James and John W. Barko

PURPOSE: The purpose of this demonstration was to examine alum dosage requirements to immobilize loosely bound and iron-bound sediment phosphorus (P) fractions (i.e., redox-sensitive P fractions) in the surface sediments of a eutrophic lake using alum assay procedures developed by Rydin and Welch (1999). This information will be useful in estimating alum dosage for control of internal P flux from sediments of Corps waterways that qualify for treatment.

BACKGROUND: Flux of phosphorus (P) from bottom sediments often represents a substantial nutrient source to algal productivity that needs to be controlled in order to reverse the eutrophication process in lakes and reservoirs. In a wide variety of aquatic systems, P dynamics at the sediment-water interface are regulated by oxidation-reduction interactions between iron compounds and adsorbed P (Mortimer 1971). Extractable fractions of sediment P found to be most active in these redox processes are the loosely bound (i.e., adsorbed P) and iron-bound (i.e., P associated with iron hydroxides) sediment P fractions (Boström et al. 1982; Nürnberg 1988). Therefore, it is desirable to control these redox-sensitive sediment P fractions 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 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 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 in order to more accurately estimate the amount of alum required to control sediment P. Although it is usually not practical to treat reservoirs with alum due to high external P loads and sedimentation rates (James et al. 1991; Cooke et al. 1993), watershed management and long-term reduction of external sediment and P loads may eventually lead to the point where control of internal P loading is feasible in further reversing the eutrophication process in these systems. As part of a lake rehabilitation program to reduce P inputs to a west-central Wisconsin glacial lake (Squaw

Lake), alum dosage requirements to immobilize redox-sensitive sediment P using alum dosage assay techniques described in Rydin and Welch (1999) were examined. Using Al:redox-sensitive P ratios determined in these assay experiments, alum dosages required to immobilize equivalent summer P fluxes from the profundal sediments of this lake were also determined. This method will be applicable in future assessments of alum dosage requirements for lakes and reservoirs.

METHODS: Sediment cores (one core per station) were collected in the north (collection depth = 6.4 m) and south deep basins (collection depth = 8.4 m) of Squaw Lake during winter 2001 for determination of sediment P profiles in the upper 30 cm of the sediment. Sediment samples, collected using a gravity core sampler (core liner = 6.5 cm inner diameter; Wildlife Supply Company, Saginaw, MI), were sectioned in the laboratory at 2-cm intervals between the 0- and 10-cm depths, at 2.5-cm intervals between the 10- and 15-cm depths, and at 5-cm intervals between the 15- and 30-cm depths. Subsamples were dried at 105 °C to a constant weight for determination of moisture content and sediment density (Håkanson 1977). To another mixed sub-sample, sequential extraction of inorganic and organic sediment P fractions were sequentially extracted to determine loosely bound P (0.1 M NH_4Cl-extractable P, loosely bound and $CaCO_3$-adsorbed P), iron-bound P (0.11 M $NaHCO_3$-0.11 M $Na_2S_2O_4$-extractable P), aluminum-bound P (0.1 N NaOH extractable P), calcium-bound P (0.5 N HCl-extractable P), and 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).

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 completely adsorb the loosely bound and iron-bound 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 overnight (~12 hr) 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 the procedures described above.

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 chamber at 18 °C to simulate summer temperature conditions. Anoxic conditions were maintained in each incubation system via continuous gentle bubbling of nitrogen gas through a 60-µm pore size gas diffusing stone placed in the center of the water column of each incubation system. Gas flow was

regulated to each system by gang valves to prevent resuspension of sediment during the incubation period.

Water samples (7 mL) were collected from the sediment incubation systems at daily intervals, filtered through a 0.45-µm filter (Nalge), and analyzed for SRP using colorimetric techniques as described previously. Water removed from the sediment incubation systems was replaced with filtered lake water adjusted to redox and temperature conditions. Rates of P release from profundal sediments (mg m^{-2} d^{-1}) under anoxic conditions were calculated as the change in SRP mass accumulated in the overlying water divided by the surface area of the sediment core incubation system (0.03318 m^2) and the number of days. The effects of dilution by replacement water was factored into the flux calculations.

RESULTS AND DISCUSSION: An example of variations in the concentration of loosely bound and iron-bound sediment P (i.e., redox-sensitive sediment P) as a function of alum concentration is shown in Figure 1 for the north basin of Squaw Lake. Redox-sensitive sediment P declined exponentially as a function of increasing alum concentration (Figure 1). All of the loosely bound P was adsorbed at alum concentrations less than 10 mg g^{-1}. Remaining iron-bound P concentrations
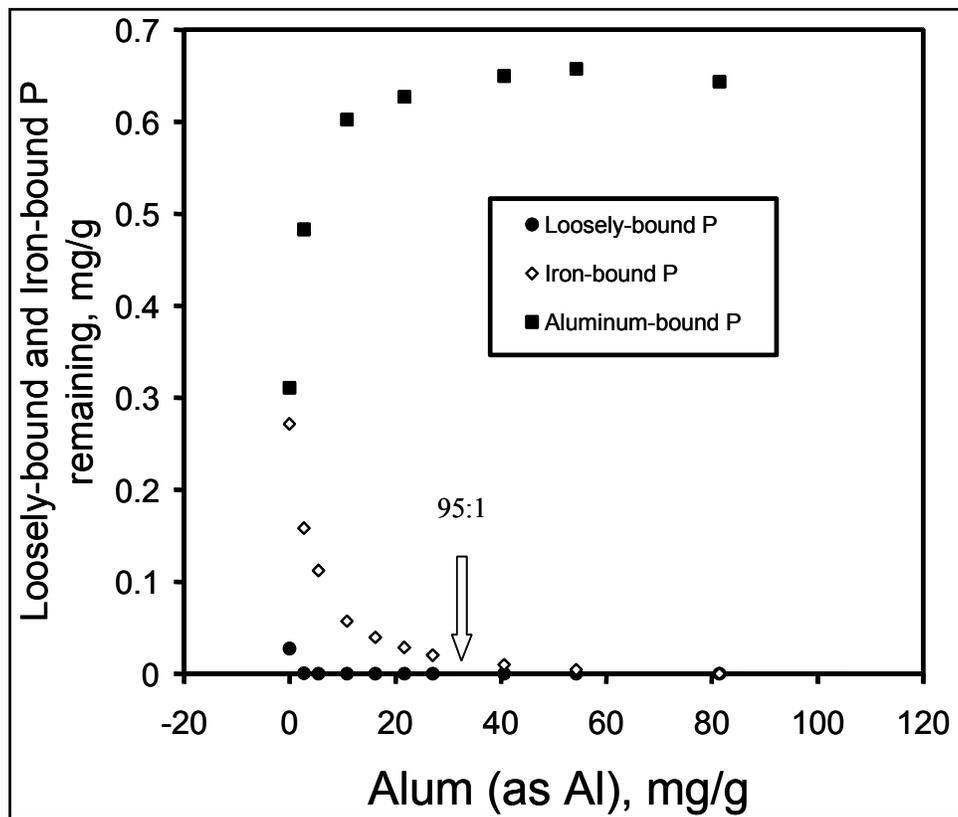

Figure 1. Variations in loosely bound, iron-bound, and aluminum-bound sediment phosphorus (P) as a function of alum (as Al) concentration. Arrow indicates Al:redox-sensitive P ratio required to immobilize the loosely bound and iron-bound sediment P fractions

approached zero as the alum concentration exceeded 30 mg g^{-1}, indicating an Al:redox-sensitive P ratio of ~95:1 by weight. The aluminum-bound P fraction increased exponentially as a function of increasing alum concentration, accounting for depletion of loosely bound and iron-bound P. This pattern indicated inactivation of loosely bound and iron-bound P by the alum via adsorption. Similarly, Rydin and Welch (1999) found that Al:redox-sensitive P ratios of approximately 100:1 were required to sequester redox-sensitive sediment P in four different Wisconsin lake sediments.

The profundal sediments in the two basins of Squaw Lake exhibited a moisture content greater than 95 percent and a bulk density less than 0.05 g mL^{-1} over the upper 12.5-cm depth (Figure 2). Moisture content declined, while bulk density increased, at sediment depths greater than 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} (±0.104S.E.; Figure 3). Aluminum-bound P and iron-bound P accounted for 48 percent and 35 percent of the inorganic sediment P, respectively. Loosely bound P and calcium-bound P each accounted for 9 percent 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.
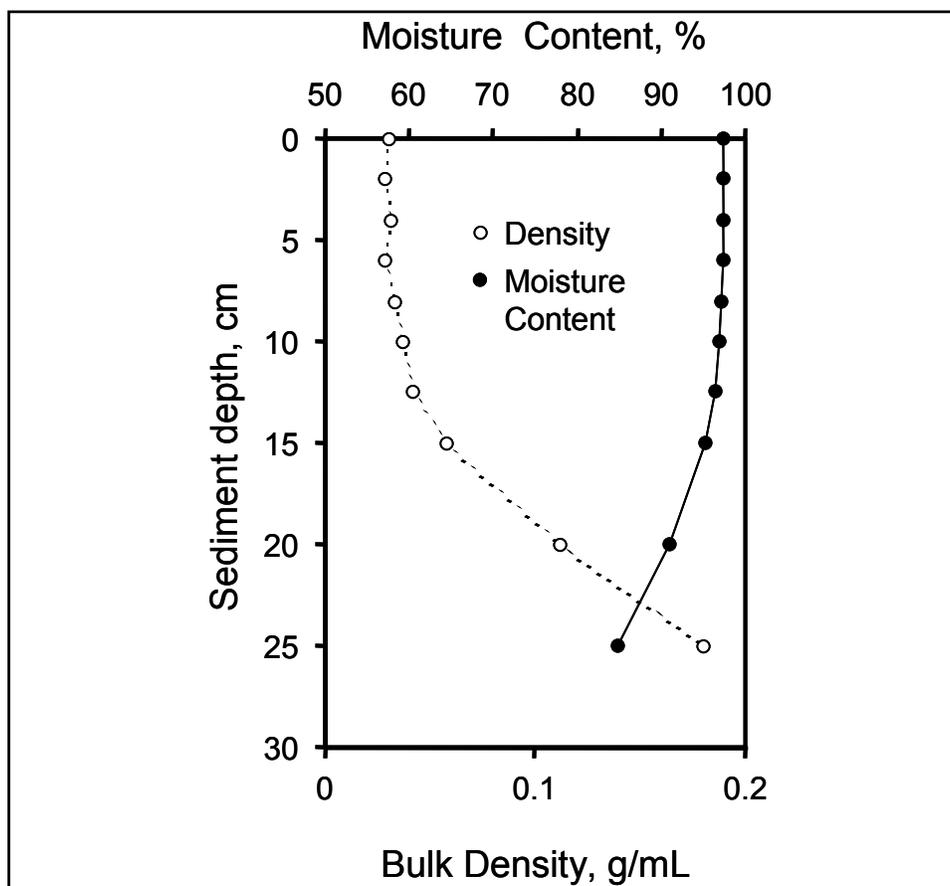

Figure 2. Variations in mean sediment moisture content and bulk density as a function of sediment depth for the north and south deep basins of Squaw Lake
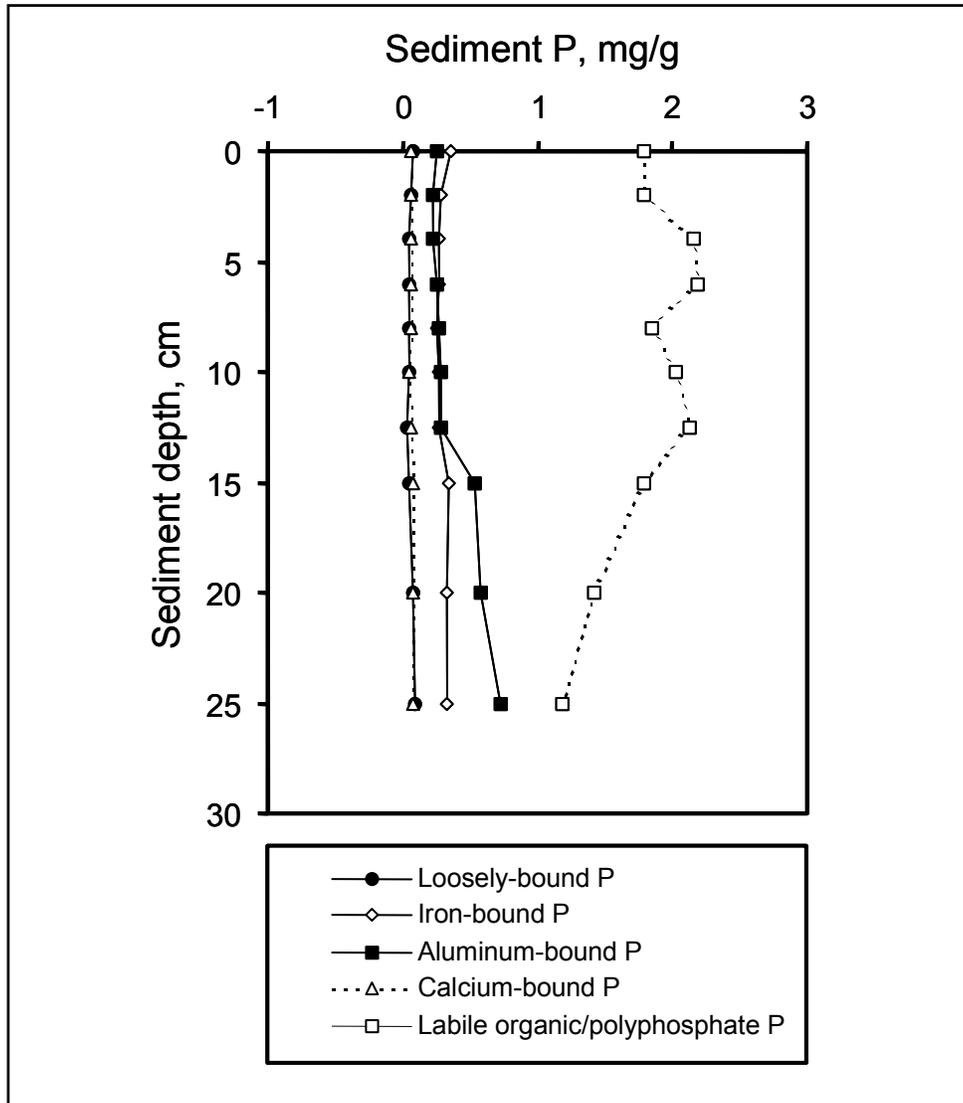
Figure 3. Variations in mean sediment phosphorus (P) fractions as a function of sediment depth for the north and south deep basins of Squaw Lake

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 were determined in order to estimate concentrations of alum (as Al) required to immobilize various levels of sediment P (Figure 4a). 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 the 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
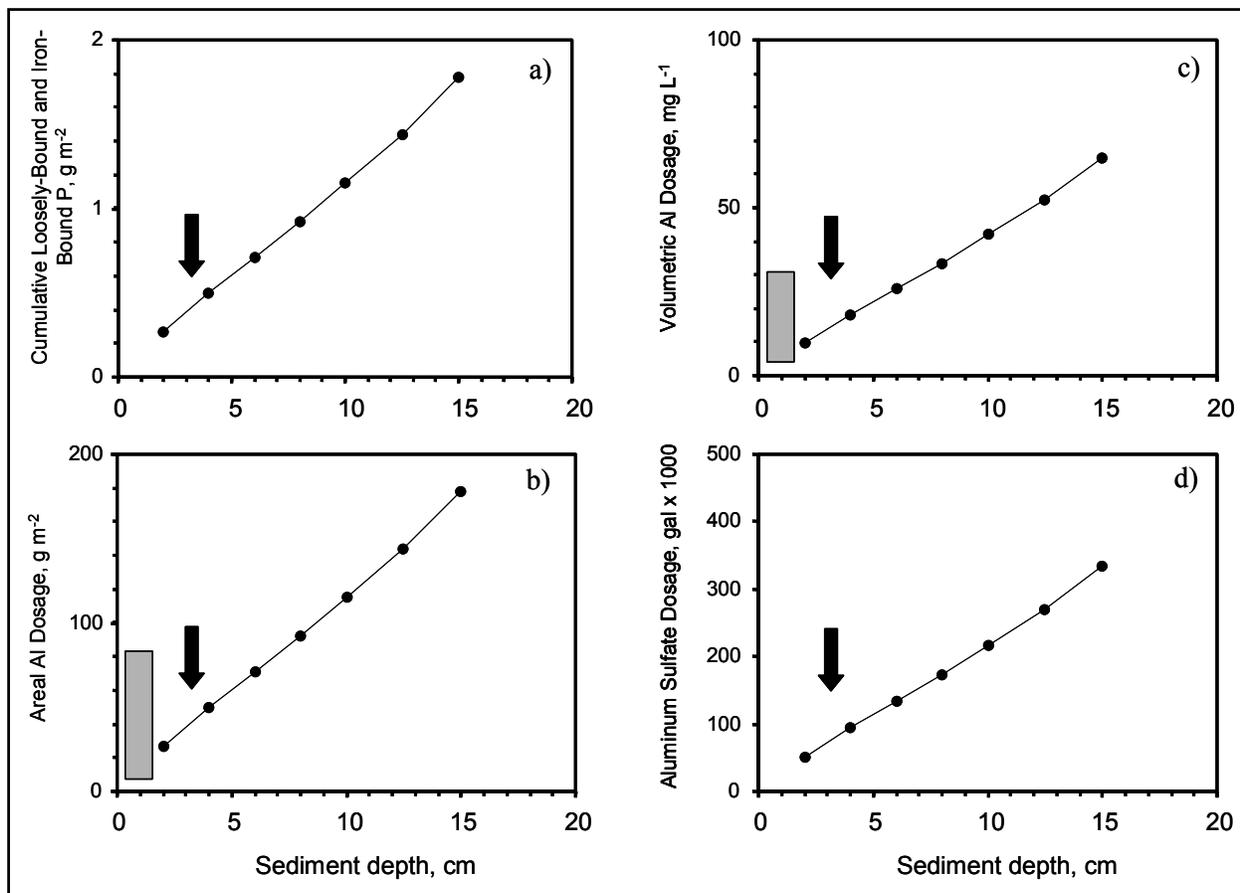
Figure 4. Variations in a) the cumulative concentration of loosely bound and iron-bound (i.e., redox-sensitive) sediment P, b) alum (as Al) dosage requirement to bind redox-sensitive sediment P, c) equivalent volumetric Al dosage, and d) equivalent aluminum sulfate dosage required as a function of sediment depth. Arrow represents the equivalent redox-sensitive sediment P and alum dosage requirement for controlling internal P loading over one summer period, based on laboratory sediment incubations. Grey bars represent ranges in areal and volumetric Al dosages for other treated lakes (Welch and Cooke 1999; Rydin et al. 2000)

the hypolimnetic sediments (Figures 4b-4d). 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 (greater than 90 percent) profundal sediments of Mirror and Shadow Lakes, Wisconsin, an alum layer was found between 8 and 12 cm below the sediment surface ten years after an alum treatment (Garrison and Ihm 1991).

Mean rates of P release from anoxic profundal sediments of Squaw Lake, measured in the laboratory, were 2.7 mg m^{-2} d^{-1} (±0.5 S.E.; n = 6; data pooled for both stations). Based on reports that Squaw Lake exhibits anoxic conditions at depths greater than 2 m during the summer,[1] the mass of P accumulating in the hypolimnion via sediment internal loading from May through September (152 days) was estimated at 153 kg, or 0.41 g P m^{-2}. The latter P concentration was equivalent to the

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[1] Personal communication, R. Swanson, Professor, Plant and Earth Science Department, University of Wisconsin-River Falls, River Falls, Wisconsin.

concentration of redox-sensitive sediment P in the upper 3.2 cm of profundal sediment of the lake. Thus, control of summer internal P loading in Squaw Lake over one summer would require a dosage of 41 g Al m^{-2} (100×0.41 g P m^{-2}).

An important finding of this study is that use of an Al:redox-sensitive P stoichiometric ratio much greater than 1:1 is necessary in order to more accurately estimate the amount of alum required to immobilize redox-sensitive sediment P in lakes. Al:redox-sensitive P ratio results of 100:1 from this study support the earlier findings of high Al:redox-sensitive P ratio requirements for Wisconsin Lake sediments found by Rydin and Welch (1999). However, Rydin et al. (2000) found in several treated Washington Lakes that this ratio approached 11:1, based on sediment core analysis of aluminum-bound P versus alum dosage, suggesting that the ratio requirement may vary.

In other lake alum treatments, dosage calculations based on internal P loading have used much lower Al:P ratios (i.e., 1:1 for Eau Galle Reservoir; 11.3 g Al m^{-2} or 4.5 mg Al L^{-1}; Kennedy et al.1987; 5:1 for Lake Delavan; 12 g Al m^{-2} or 2.3 mg Al L^{-1}; Rydin and Welch 1999) to estimate alum concentrations, which may explain why sediment P control was short-lived (i.e., 1-2 years) in these systems. In contrast, estimates of alum dosage based on redox-sensitive sediment P concentrations or internal P loading rates and a 100:1 ratio are much higher (see Rydin and Welch (1999); James et al. (2000)) and seem to be more in line with maximum allowable dosage estimates determined as a function of alkalinity and pH for hard water lakes (Kennedy and Cooke 1982; Rydin and Welch 1999). For instance, the authors suggest that much higher dosages of 41 g Al m^{-2} (15 mg Al L^{-1}), for control of summer internal P loading from sediments, or 115 g Al 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. 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 buffered with sodium aluminate in order to prevent low pH and the appearance of toxic levels of Al.

One of the current unknowns in estimating alum dosage based on the mass of redox-sensitive sediment P is the optimal depth of sediment to control for P inactivation. Considerations include inactivation of redox-sensitive P over the sinking depth range of the alum floc and provision for some additional control of P migrating upward from below this depth. Welch and Cooke (1999) found evidence of excess aluminum in the sediment above background levels over a 20-cm depth in West Twin Lake, OH, 16 years after treatment, suggesting substantial sinking and mixing of the floc over time. Rydin et al. (2000) reported finding the presence of aluminum peaks above background levels, and excess aluminum-bound sediment P, at sediment depths ranging between 3 and 8 cm, for Washington Lakes that were treated between 7 and 21 years before core analysis. Rydin and Welch (1999) suggested a minimum treatment depth of the upper 4-cm sediment layer. For Squaw Lake, which has very low-density sediments, alum could conceivably sink though the upper 10-cm layer, as was observed for other similar low-density sediments (Garrison and Ihm 1991). Thus, treatment to immobilize redox-sensitive P in the upper 10 cm using a 100:1 ratio (Al:redox-sensitive sediment P) should be considered for maximum P control effectiveness in this lake.

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 similar high labile organic/polyphosphate P concentrations have recently been found in the sediments of two other northern Wisconsin glacial lakes (Wapogassett and Bear Trap Lakes; unpublished data). It is not currently known what impact this sediment P fraction has on internal P loading. Rydin and Welch (1998, 1999) found that alum additions did not directly impact this sediment P fraction. However, bacterial mineralization of this fraction could be an important source of internal P loading after an alum treatment (Gächter et al. 1988, Jensen and Andersen 1992, Gächter and Meyer 1993). If dosage is high enough (i.e., use of a 100:1 ratio by weight), the alum layer may be effective in adsorbing mineralized 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 and reservoirs in order to further improve calculations of alum dosage.

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