

Optimization of aluminum treatment efficiency to control internal phosphorus loading in eutrophic lakes

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ABSTRACT

Historical accumulation of phosphorus (P) in lake sediment often contributes to and sustains eutrophic conditions in lakes, even when external sources of P are reduced. The most cost-effective and commonly used method to restore the balance between P and P-binding metals in the sediment is aluminum (Al) treatment. The binding efficiency of Al, however, has varied greatly among treatments conducted over the past five decades, resulting in substantial differences in the amount of P bound per unit Al. We analyzed sediment from seven previously Al treated Swedish lakes to investigate factors controlling binding efficiency. In contrast to earlier work, lake morphology was negatively correlated to binding efficiency, meaning that binding efficiency was higher in lakes with steeply sloping bathymetry than in lakes with more gradually sloping bottoms. This was likely due to Al generally being added directly into the sediment, and not to the water column. Higher binding efficiencies were detected when Al was applied directly into the sediment, whereas the lowest binding efficiency was detected where Al was instead added to the water column. Al dose, mobile sediment P and lake morphology together explained 87% of the variation in binding efficiency among lakes where Al was added directly into the sediment. This led to the development of a model able to predict the optimal Al dose to maximize binding efficiency based on mobile sediment P mass and lake morphology. The predictive model can be used to evaluate cost-effectiveness and potential outcomes when planning Al-treatment using direct sediment application to restore water quality in eutrophic lakes.

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1. Introduction

Historical accumulation of phosphorus (P) in lake sediment generally originates from external sources in the surrounding catchment, including industrial and municipal wastewater, leaching from agricultural soils and runoff from urban areas. Controlling external P sources has been the primary long-term management strategy for overcoming lake eutrophication (Conley et al., 2009), however, focusing exclusively on external sources is often insufficient. Even if external inputs of P are reduced, the historical (legacy) P accumulated in lake sediment can contribute to elevated surface water nutrient concentrations for decades or longer (Sas, 1990). Different forms of sediment P have different internal loading potential. Internal (in-lake) release of legacy P is driven mainly by the mobile sediment P (P_{mob}) forms including porewater/easily exchangeable P and iron/manganese bound P (Paraskova et al.,

2013; Pilgrim et al., 2007); organic P can also contribute to the P_{mob} pool after mineralization of organic matter (Schütz et al., 2017).

There are numerous methods for managing internal P loading in lakes (Cooke et al., 2005), with the most common and cost-effective method being addition of metals salts, such as aluminum (Al), to improve sediment P binding capacity (Huser et al., 2016c). Binding of P by Al occurs naturally in soil and sediment and Al is commonly used in tertiary wastewater and drinking water treatment to reduce P concentrations and precipitate particulate matter. Since the 1960s, addition of Al-salts has been used as a restoration tool in hundreds of eutrophic lakes around the world (Huser et al., 2016b). Treatment longevity, however, has varied greatly. Huser et al. (2016b) analyzed data from 114 Al treated lakes and showed that the main factors affecting treatment longevity included Al dose, lake morphology, and the watershed to lake area ratio, with Al dose explaining the largest amount of variation. Although not examined due to lack of data, Huser et al. (2016b) suggested that analysis of the Al dose versus P_{mob} content might have improved the model

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developed for predicting treatment longevity.

The efficiency with which Al binds P likely contributes to treatment longevity, given that one of the main goals of an Al treatment (there are others, mostly precipitation of water column P) is to inactivate legacy P_{mob} . Al binding efficiency has varied by an order of magnitude in previous European and North American lake restoration projects, ranging from 2.1:1 to 21:1 (Al:Al bound P, molar basis) (Huser et al., 2011; Huser, 2012; Jensen et al., 2015; Lewandowski et al., 2003; Reitzel et al., 2005; Rydin et al., 2000; Rydin and Welch, 1999; Schütz et al., 2017). Greater doses of Al have generally resulted in less efficient P binding, i.e. higher ratios of Al added to Al bound P (Al: P_{Al}) (Huser, 2012). Furthermore the mass of available P_{mob} prior to treatment is highly correlated to binding efficiency, with low amounts of P_{mob} relative to Al dose resulting in less efficient Al binding (James, 2011).

Morphology is also important as lakes with steep sediment bed slopes have been shown to have higher Al: P_{Al} ratios (less efficient binding), whereas gradual bed slope lakes have had lower Al: P_{Al} ratios (more efficient binding) (Huser, 2012). Huser (2012) suggested that this difference was related to natural movement of the mineral aluminum hydroxide (Al(OH)₃-floc) from erosion zones of lakes to accumulation bottoms, and that the difference in transport rate and accumulation of Al(OH)₃-floc in deeper areas depended on lake morphology. This process was detected in Lake Harriet (US) as well, where Al added to the littoral erosion zone was translocated to the deeper, accumulation areas of the lake within 6 months (Huser, 2017). Steepness of the sediment bed slope in lakes can be quantified using the Osgood index, which is mean depth (m) divided by the square root of the lake surface area (km²). Cooke et al. (1993) suggested that lakes with gradual sediment bed slope (Osgood index < 6) would have more successful responses to Al treatment than lakes with steeper bed slopes (Osgood index > 6) given all other conditions being equal. Because the newly formed amorphous Al minerals start to crystalize following Al treatment, the potential for P binding decreases with time due to decreased mineral surface area (Berkowitz et al., 2006). Thus, the longer it takes for Al to bind P, the lower the binding efficiency (de Vicente et al., 2008b). If Al is added far in excess of P_{mob} , or excess Al accumulates in deeper areas of the lake, it will take longer to saturate Al binding sites, resulting in lower binding efficiency.

Other factors may also affect binding efficiency. Sediment mixing by benthic feeding fish may decrease the time needed for contact between Al and P and improve binding efficiency (Huser et al., 2016a). However, bioturbation by benthic invertebrates can have a limited overall effect on Al treatment effectiveness (Nogaro et al., 2016). Sorption competition between Al and other inorganic compounds that can complex with Al, e.g., silicates (de Vicente et al., 2008a), fluoride, sulfate (Roberson and Hem, 1967) can reduce P binding efficiency. Organic matter in general (Bloom, 1981; de Vicente et al., 2008a; Lind and Hem, 1975) and labile organic matter in particular (e.g. phytoplankton exudates and microbial transformed detritus) also compete with P for Al binding sites (Du et al., 2019). However, most forms of labile organic matter break down quickly and available Al mineral binding sites should sorb the P released (Reitzel et al., 2007).

This study was performed to improve predictions of P binding efficiency in Al treated eutrophic lakes. Twenty-two sediment cores were collected from sediment transport and accumulation zones in seven Al treated Swedish lakes. Five of the seven lakes were treated with methods where Al was directly added into lake sediment, instead of added to the water where amorphous Al(OH)₃-floc then precipitates and settles on to the sediment surface. Theoretically, direct sediment Al application should improve sediment binding efficiency as it distributes the newly formed Al mineral where P_{mob} is within the sediment profile. Lake morphology and sediment and

water chemistry were analyzed to identify factors related to binding efficiency (Al: P_{Al} ratios) and a predictive model was developed that can be used to maximize P binding efficiency.

2. Materials and methods

2.1. Study sites

All study lakes are situated in southeastern Sweden, within 30 km of Stockholm city (Fig. 1). Lake size and mean depth varied, ranging from 6 to 272 ha and 2–8.7 m, respectively (Table 1). All lakes were eutrophic and pH ranged from 8.0 to 8.8. (Table 1). The applied Al dose varied between 20 and 75 g m⁻² across the lakes and two different Al-salts were used: Poly aluminum chloride (PAC) and aluminum sulfate (Alum) (Table 2). Application technique differed between lakes as well (Table 3). PAC (pre hydrolyzed AlCl₃) was applied in liquid (l) form whereas Alum was applied in solid (s) form. In Lötsjön, Alum was added directly to the water where it sank into the sediment, whereas it was spread on the ice and allowed to dissolve during thaw in Långsjön b. Cores were collected from multiple depths (transport and accumulation bottoms) in all lakes. Accumulation bottoms were defined as the deepest part of the lake where surrounding sediment transport was directed. Transport bottoms represent the remaining parts of the lake. (Table 2).

2.2. Sediment sampling

A Willner gravity corer was used to collect intact sediment cores (generally the uppermost 30 cm) from the lakes. After collection, each core was sliced in the field at 1-cm intervals at sediment depths from 1 to 10 cm, and 2-cm intervals thereafter. All samples were stored no longer than 4 weeks in sealed containers, in the dark at 4 °C before analysis. In order to include spatial variability within each lake, and cover areas where different Al doses were applied, samples were collected at different locations and different water column depths (Table 2), representing both transport and accumulation bottoms (Håkanson and Jansson, 1983).

2.3. Laboratory analysis

Sequential extraction was used to characterize P fractions using a method originally developed by Psenner et al. (1988) and modified by Hupfer et al. (1995). The quantified fractions were: pore-water/easily exchangeable-, iron (Fe)/manganese (Mn) bound-, Al

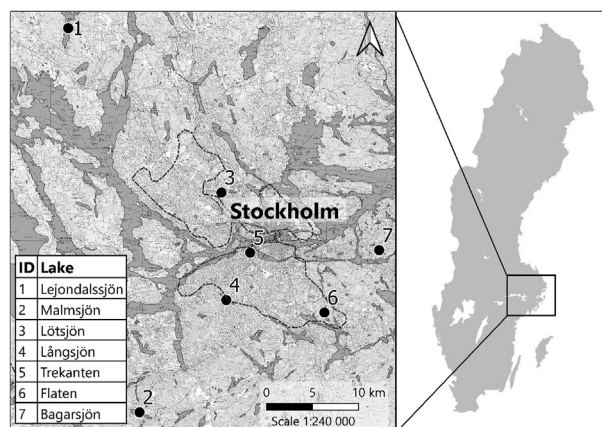


Fig. 1. Map showing position of the study lakes located within a 30 km radius of Stockholm city in Sweden.

Table 1

Morphological data and means for water chemical data (May–September, 2 years pre-treatment), ND = no data.

Lake	Max depth (m)	Mean depth (m)	Lake area (Ha)	pH	TP (mg L ⁻¹)	Conductivity (μS cm ⁻¹)	Alkalinity (mg L ⁻¹)	Chl a (μg L ⁻¹)	Secchi depth (m)
Bagarsjön	5.6	2.3	6	8.1	0.057	479	90.3	ND	3.0
Flaten	13.1	8.7	63	8.7	0.034	391	98.1	13.2	3.1
Lejondalssjön	14	7.5	272	8.2	0.046	ND	94.6	ND	2.8
Långsjön a	3	2	30	8.7	0.099	257	85.5	50.4	0.9
Långsjön b	3	2	30	ND	ND	ND	ND	ND	ND
Lötsjön	3.2	1.5	6	8	ND	ND	ND	ND	0.6
Malmsjön	6.8	4.7	89	8.8	0.131	260	70.8	25	1.0
Trekanten	6.6	3.6	14	8.2	0.072	320	116.6	25.4	2.7

Table 2

Information regarding applied Al dose, year of treatment and Al form used (solid form = (s), liquid form = (l)). Additional information on water depth where sediment cores were collected and number of cores collected for each lake. Note, two applications were conducted in Långsjön (Långsjön a, 2006 and Långsjön b, 1968/1971).

Lake (core ID)	Applied Al dose (g m ⁻²)	Al form	Treatment year	Sediment cores collected (N)	Sediment core collection depth (m)
Bagarsjön (1, 2, 3)	50	PAC (l)	1997	3	3, 4, 6
Flaten (1, 2)	54, 70	PAC (l)	2000	2	10, 13
Lejondalssjön (1, 2, 3)	25	PAC (l)	1991–1993	3	13, 14, 13
Långsjön a (1, 2)	50, 75	PAC (l)	2006	2	2, 3
Långsjön b (1)	20	Alum (l)	1968 & 1971	1	3
Lötsjön (1, 2, 3)	36	Alum (s)	1968–1979	3	2, 2, 2
Malmsjön (1, 2, 3, 4, 5)	60	PAC (l)	2007	5	4, 6, 6, 4, 3
Trekanten (1, 2, 3)	60	PAC (l)	2011	3	7, 5, 3

Table 3

Sediment chemical data for each core collected from all study lakes together with morphological data and information on treatment method. Detected Al dose represents the measured Al in the sediment as a result of Al treatment.

Lake (Core ID)	Treatment method	Osgood index	Detected Al dose (g m ⁻²)	P _{Al} (g m ⁻²)	Al:P _{Al}	P _{mob} (g m ⁻²)	P _{lab.org} (g m ⁻²)
Långsjön a (1)	Sediment	3.7	27.7	2.1	13.4	3.6	3.5
Långsjön a (2)			17.6	1.4	12.5	2.0	2.7
Långsjön b (1)	Water		9.9	0.9	10.6	2.2	1.7
Lejondalssjön (1)	Water	4.6	17.9	1.6	10.9	4.7	1.7
Lejondalssjön (2)			27.3	2.1	12.7	9.8	3.6
Lejondalssjön (3)			27.8	2.7	10.1	7.5	5.6
Malmsjön (1)	Sediment	5.0	26.0	1.8	14.4	2.5	2.3
Malmsjön (2)			36.3	2.8	12.8	3.8	1.7
Malmsjön (3)			50.9	3.3	15.6	4.4	2.0
Malmsjön (4)			50.0	3.1	16.0	4.3	3.6
Malmsjön (5)			25.0	1.9	12.9	2.7	5.4
Lötsjön (1)	Sediment	6.1	51.8	7.8	6.6	11.2	2.5
Lötsjön (2)			73.9	15.9	4.7	20.6	10.0
Lötsjön (3)			79.7	13.3	6.0	16.2	7.8
Bagarsjön (1)	Water	8.8	11.8	0.9	13.7	1.5	1.1
Bagarsjön (2)			108.2	6.2	17.5	7.4	2.6
Bagarsjön (3)			84.6	5.7	14.9	7.0	2.0
Trekanten (1)	Sediment	9.5	140.2	11.7	12.0	14.7	12.3
Trekanten (2)			54.1	5.2	10.4	6.4	1.2
Trekanten (3)			26.5	3.7	7.3	4.6	1.6
Flaten (1)	Sediment	11.0	41.1	5.1	8.1	5.7	1.1
Flaten (2)			34.6	3.3	10.6	4.1	2.9

bound-, organic, and calcium (Ca) bound P. Analysis of soluble reactive P (SRP) in the extracts was performed using the molybdate blue method (Murphy and Riley, 1962). Sediment Al was extracted using acid ammonium oxalate according to the protocol of Jan et al. (2013) and references therein. Al concentrations were determined with inductively coupled plasma atomic emission spectrometry (ICP-AES) at a wavelength of 396.15 nm. Sediment density was estimated following loss on ignition at 550 °C for 2 h and water content was determined after 24 h storage at -20 °C followed by freeze drying (Håkanson and Jansson, 1983).

2.4. Calculations and statistical analysis

Background concentrations of Al and P_{Al} (calculated using sediment layers unaffected by Al treatment) were subtracted from Al and P_{Al} concentrations in the treated layer to determine the total mass of Al and P_{Al} resulting from treatment. The Al:P_{Al} molar ratio was calculated as the sum of excess Al (i.e. above background) divided by the mass of P_{Al} formed in the sediment due to treatment.

The amount of labile organic P (P_{lab.org}) was determined by subtracting background concentrations deeper in the sediment

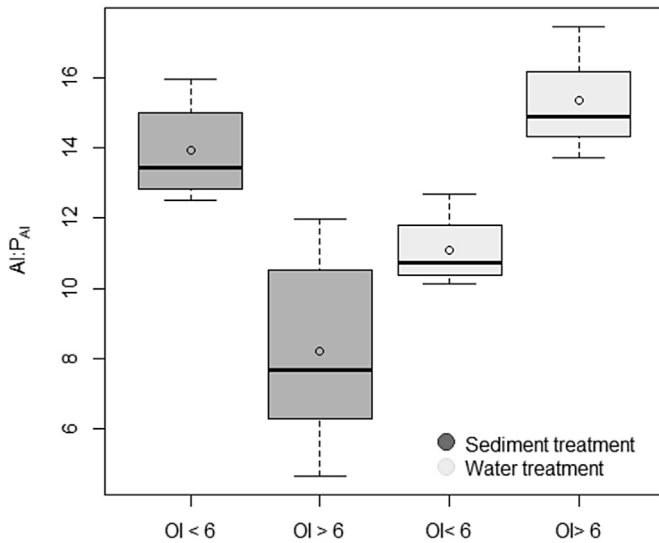


Fig. 2. Boxplot showing Al:P_{Al} ratios for individual cores grouped by Al treatment method (sediment vs. water) and lake morphology (Osgood index <6 or >6). Solid lines and circles within the boxplots represents median and mean values, respectively.

(where only recalcitrant forms of organic P are assumed to remain) from the total organic P fraction. Pre-treatment P_{mob} , defined as the sum of porewater/easily exchangeable P and Fe bound P, was estimated by summing the P_{Al} formed from P_{mob} after treatment and the remaining P_{mob} in the sediment profile above and within the treatment layers. The lake morphology (bed slope) parameter was determined according to the Osgood index: $= Z_m/A^{-0.5}$, where Z_m is the mean water depth (m) and A is lake surface area (km^2) (Osgood, 1988). JMP statistical software (SAS institute Inc., version 11.0.0) was used for all statistical analyses. One-way ANOVA following Tukey's (HSD) post hoc test was used to investigate the significance of differences between binding efficiency (Al:P_{Al}), grouped by treatment type (sediment vs. water application) and lake morphology (Osgood index < or > than 6). Stepwise multiple linear regression (MLR) with forward selection was conducted to explain the variation in Al:P_{Al} with predictor variables represented by water and sediment chemical data along with lake morphology index (Tables 1–3). Predictors improving model fit were included at the significance level of $p \leq 0.05$, and variables with high bivariate correlations (>0.8) were excluded from the analysis to increase matrix stability.

3. Results

3.1. General results

Elevated levels of Al and P_{Al} were found in all sediment cores at depths varying from the surface down to 26 cm. Elevated P_{Al} mass ranged from 0.9 to 15.9 $g\ m^{-2}$ above background values while Al mass (detected Al dose) varied between 9.9 and 140.2 $g\ m^{-2}$ (Table 3).

Al:P_{Al} ratios varied between 4.7 and 17.5 among the study lakes (Table 3). Ratios differed significantly ($F(3, 18) = 15.2$, $p < 0.0001$) when grouped by Al application method (water vs. sediment) and lake morphology (Osgood index < or > 6). Steep bed slope lakes treated with sediment Al injection or solid Alum application to sediment had significantly higher binding efficiency (mean Al:P_{Al} = 8.2 ± 2.6) than gradual bed slope lakes treated with the same Al application methods (mean Al:P_{Al} = 13.9 ± 1.4 ; $p < 0.001$) (Statistical details in Tables S1–S10). The highest ratios were

generally found in the steep bed slope Lake Bagarsjön where Al was applied to the water column (mean Al:P_{Al} = 15.4 ± 1.9) and were significantly greater compared to steep bed slope lakes receiving sediment treatment ($p < 0.001$). Gradual bed slope lakes did not differ based on treatment method ($p = 0.13$). Furthermore, significant differences in binding efficiency between lake morphology types were found when looking at specific treatment types. When Al was added to the water column, the difference between lake type was also significant ($p < 0.05$), but binding efficiency was instead greater in the gradual bed slope lake (Fig. 2).

3.2. Model development

3.2.1. All lakes

Stepwise MLR was conducted using morphology and water chemical data as well as applied Al dose, detected Al dose, P_{mob} , and $P_{lab.org}$ (Tables 1–3) as predictor variables for explaining variation in Al:P_{Al}. Variables with high bivariate correlations (>0.8) were excluded from the analysis to increase matrix stability. The final MLR model explaining variation in Al binding efficiency (Al:P_{Al}) included P_{mob} ($p < 0.0001$), detected Al dose ($p < 0.0001$) and Osgood index ($p < 0.01$) as significant factors. P_{mob} , detected Al dose and Osgood index explained 28%, 30% and 13% of the variation, respectively, resulting in a model ($r^2_{adj} = 0.71$, $p < 0.0001$, $DF = 21, VIF = 1.88, 2.25, 1.28$) with the following parameters (Eq. (1)):

$$(Al:P_{Al} = 15.70 - 0.79 \times P_{mob} + 0.10 \times \text{detected Al dose} - 0.55 \times \text{Osgood index}) \quad (1)$$

3.2.2. Sediment treated lakes

An additional stepwise MLR was conducted using only lakes treated with sediment injection or solid Alum application (Table 3). The MLR explaining variation in Al binding efficiency (Al:P_{Al}) among sediment treated lakes included P_{mob} ($p < 0.0001$), detected Al dose ($p < 0.0001$) and Osgood index ($p < 0.001$) as significant factors, explaining 45%, 19% and 23% of the variation, respectively (Fig. 3). The resulting model (Eq. (2)) explained a greater amount of variation ($r^2_{adj} = 0.87$, $p < 0.0001$, $DF = 14$, $VIF = 2.46, 2.62, 1.11$) compared to the model including both water and sediment treated lakes:

$$(Al:P_{Al} = 15.93 - 0.82 \times P_{mob} + 0.11 \times \text{detected Al dose} - 0.66 \times \text{Osgood index}) \quad (2)$$

Eq. (2) was rearranged in order to predict Al dose based on desired binding efficiency (Al:P_{Al}), measured P_{mob} and Osgood index (Eq. (3)). To demonstrate this model generalization, Al:P_{Al} was fixed at 10, P_{mob} ranged between 0 to maximum 20 $g\ m^{-2}$ and the Osgood index was set at 3, 6 and 9 to represent gradual, medium, and steep bed slopes (Fig. 4). The significance of the results presented in Fig. 4 is further evaluated in the discussion section.

$$(Al\ dose = 1.1 \times Al:P_{Al} + 8.2 \times P_{mob} + 6.6 \times \text{Osgood index} - 159)(3)$$

4. Discussion

4.1. Comparison to previous studies

Ratios of Al:P_{Al} in this study (4.7–17.5) were in the range of what has previously been reported (Huser et al., 2011; Huser 2012, 2017;

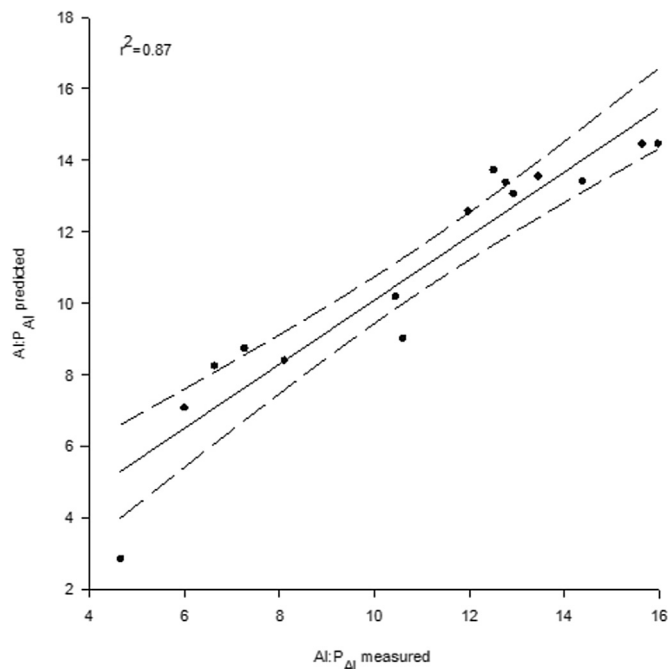


Fig. 3. Measured versus predicted values of Al:P_{Al} for sediment treated lakes, described by the model $\text{Al:P}_{\text{Al}} = 15.93 - 0.82 \times P_{\text{mob}} + 0.11 \times \text{detected Al dose} - 0.66 \times \text{Osgood index}$. Dashed lines represent 95% confidence intervals.

Jensen et al., 2015; Lewandowski et al., 2003; Reitzel et al., 2005; Rydin et al., 2000; Rydin and Welch, 1999; Schütz et al., 2017). The variation of Al:P_{Al} ratios between lakes in this study was similar to those reported by (Huser, 2012) in six Al treated lakes in Minneapolis (US), whereas it was contradictory to the generally consistent ratios (mean of 10.7, range from 9.8 to 11.5) reported by Rydin et al. (2000) in six lakes in Washington (US).

4.2. Effect of Al applied and P_{mob} content on binding efficiency

Lewandowski et al. (2003) found consistent, low Al:P_{Al} ratios of 2.1 and 2.2 in Lake Süssersee (Germany) where low doses of Al were added annually over 16 years. Huser (2017) also reported a similarly low ratio (2:1) after a low dose treatment (11 g m⁻²) in Lake Harriet (US). Low dose treatments can generate higher binding efficiency (lower Al:P_{Al} ratio) due to the increased chance of Al encountering P before crystallization affects binding efficiency (de Vicente et al., 2008b). A similar situation is apparent among the study lakes herein: Lötsjön was treated with multiple low doses (multiple applications over 9 years, 36 g m⁻² in total). This resulted in Al:P_{Al} ratios as low as 4.7, which was the lowest ratio (i.e. best binding efficiency) detected in this study. In addition to the low dose applied, Lötsjön also had the highest amount of P_{mob} available before treatment (20.6 g m⁻², Table 3). This would also theoretically increase binding efficiency due to the low amount of Al (sorbent) relative to the amount of P_{mob} (sorbate, i.e., Le Chateliers principle).

In contrast, Malmsjön received a relatively higher Al dose (60 g m⁻², single application) with a lower amount of pre-treatment sediment P_{mob} (mean 3.5 g m⁻², Table 1, Table 3), resulting in one of the highest ratios in the study (mean 14.3). Bagarsjön also had high Al:P_{Al} ratios and received a similar dose to Malmsjön (50 g m⁻², single application), but P_{mob} availability was greater (mean 5.3 g m⁻²) compared to Malmsjön (Table 2, Table 3). This would theoretically result in a higher binding efficiency (lower Al:P_{Al} ratio), but this was not the case. Although patterns in binding efficiency, to some extent, can be explained by the relative amount

of Al added to available P_{mob}, other factors also affect binding efficiency, e.g., lake morphology and Al application technique.

4.3. Effects of lake morphology and treatment method on binding efficiency

After Al application, horizontal movement of the Al(OH)₃-floc towards deeper accumulation zones can occur as a consequence of the relatively low density of the amorphous mineral, similar to that of organic rich, low density sediment (Egemose et al., 2010; Huser, 2012). Huser (2012) demonstrated this in a study of six Minneapolis (US) lakes receiving water application of liquid Alum where steep bed slope lakes had lower binding efficiency compared to gradual bed slope lakes. However, the results from this study showed the opposite, with a negative correlation between Al:P_{Al} and Osgood index, where steep bed slope lakes (Osgood index > 6) generally had lower Al:P_{Al} (i.e. greater binding efficiency).

The main difference between the Al treatments reported by Huser (2012) and those reported here was the Al application method, i.e. sediment Al injection or solid Alum application was used in a majority of the studied lakes. These application methods can result in Al being distributed in the vertical sediment profile (generally the uppermost 10 cm) instead of precipitating in the water column (water treatment) and settling to the sediment surface where time is needed for natural incorporation of the Al mineral into surficial sediment (Fig. 5). Although not previously studied, application of Alum sediment pellets likely works in the same manner in lakes with low-density, surficial sediment as demonstrated in this study. For instance, Lötsjön had low surficial (mean 0–10 cm) sediment density (1.03 g cm⁻³) whereas Alum pellets have a nearly threefold higher density (2.7 g cm⁻³).

Sediment injection and solid Alum pellet application can distribute the Al(OH)₃-floc deeper in the sediment compared to water application, which would reduce horizontal transport at the sediment surface. Sediment treatment should increase the chance for Al to encounter P_{mob}, as Al is distributed within the sediment matrix where P_{mob} is available and binding can occur before further crystallization and reduction in mineral surface area occurs. Additionally, the Al(OH)₃-floc can then follow sediment as it is naturally translocated to deeper areas of the lake, increasing the chance for Al to encounter P_{mob} at new locations of the sediment (Huser, 2017). The transport rate of natural sediment is generally higher in lakes with steep bed slope (Håkanson and Jansson, 1983), accelerating the possibility of Al encountering P_{mob} in the sediment before crystallization reduces the surface area of the amorphous Al mineral and decreases potential binding sites (Berkowitz et al., 2005; de Vicente et al., 2008b).

4.4. Other factors affecting binding efficiency of Al in lakes

Although the MLR model explained 87% of the variation in binding efficiency of Al in sediment treated lakes, other factors may also affect binding between Al and P. For example, Du et al. (2019) showed that dissolved labile organic matter competition for Al binding sites may be a factor controlling Al:P_{Al}, however this was not analyzed in our study. Instead, we analyzed labile organic P in sediment expressed as the non-recalcitrant fraction of Org-P, which had no significant effect on the model. Sediment resuspension and mixing caused by benthic feeding fish (e.g. common carp) (Breukelaar et al., 1994; Driver et al., 2005; Huser et al., 2016a,b) might also affect binding efficiency via increased chance for contact between Al and P (Huser et al., 2016a). However, Nogaro et al. (2016) showed that bioturbation caused by benthic invertebrates had limited effect on treatment efficiency.

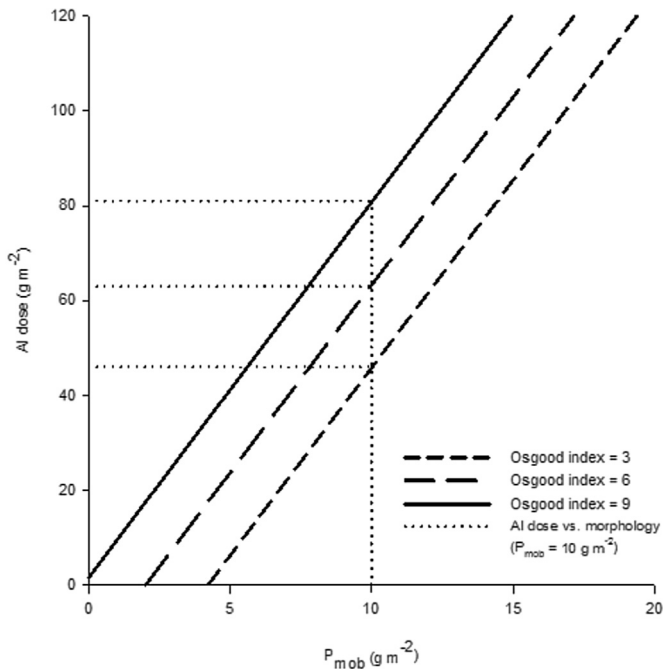


Fig. 4. Al dose allowed to achieve $Al:P_{Al} = 10$ using sediment Al application in three hypothetical lakes with Osgood index at 3, 6 and 9 and a range of sediment P_{mob} mass. Dotted line indicates doses for varying Osgood index with P_{mob} fixed at 10 g m^{-2} .

4.5. Maximizing binding efficiency – implications for treatment effectiveness

Equation (3) can be used to calculate the required Al dose to optimize binding efficiency depending on sediment P_{mob} mass and lake morphology. The conceptual graph (Fig. 4) demonstrates how to estimate an Al dose with a fixed ratio of $Al:P_{Al}$ at 10, a range of P_{mob} from 0 to 20 g m^{-2} , and an Osgood index of 3, 6 and 9. For example, a gradual bed slope (Osgood index = 3) where sediment translocation is relatively low, and a P_{mob} mass of 10 g m^{-2} cannot attain an $Al:P_{Al}$ ratio of 10 at an Al dose higher than 46 g m^{-2} . However, in a system where the bed slope is steeper (Osgood = 9), natural sediment movement can increase the chance of Al encountering P_{mob} during natural translocation of sediment, which allows for a dose of up to 81 g m^{-2} while still being able to attain an $Al:P_{Al}$ ratio of 10. By considering the findings in this study when planning Al-treatment, it is possible to increase cost efficiency and treatment effectiveness by optimizing Al dose according to the model (Eq. (3)). It should be noted that these relationships only apply to lakes where Al is either injected into the sediment or when pellets are used that can sink through low density, surficial sediment often found in eutrophic lakes.

4.6. Other considerations

The study results were strongly influenced by the type of Al addition method used. This is the main reason why our results generally contradict those in previous studies where water column Al applications were used, i.e., Huser (2012). The opposing results are due to differences in Al binding efficiency when different methods are used. Thus, the model presented here (Eq. (3)) should only be used to evaluate cases where Al is applied directly to the sediment.

Another factor that should be considered is that buffered, or pre-hydrolyzed polyaluminum chloride (PAC) was used in all lakes

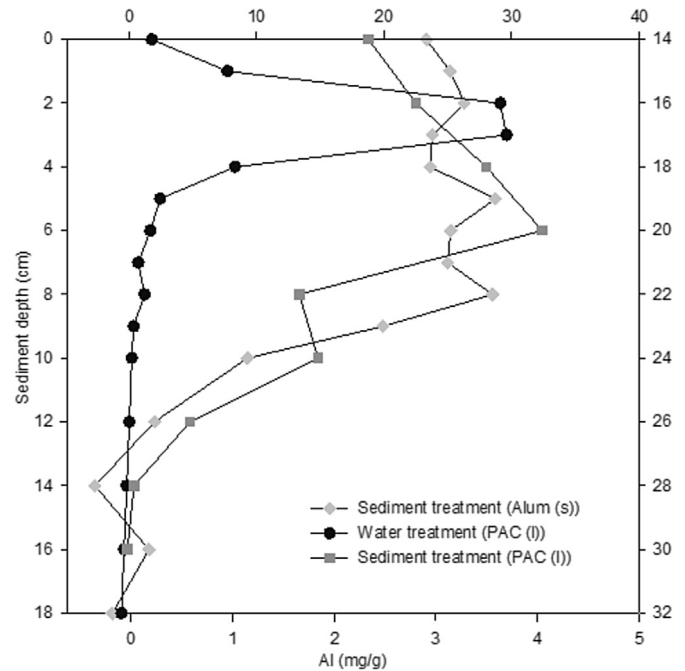


Fig. 5. Cores from two lakes where sediment treatment was used are shown. Lötsjön (Sediment treatment, Alum (s)) and Malm sjön (Sediment treatment, PAC (I)). Due to the differences in treatment age, the depth range of Lötsjön was adjusted to match the treatment date of Malm sjön (30 years difference in treatment age). Bagarsjön (Water treatment, PAC (I)), where Al was added to the water, is shown for comparison.

except Lötsjön and Långsjön 2b (Table 2). While the dataset reported herein was too small to draw any conclusions between types of Al-salt used, it is possible that pre-hydrolyzed forms of Al result in lower binding efficiency, as hypothesized by Schütz et al. (2017). Hydrolysis reactions occur when Al is applied to water (or sediment porewater) and several monomeric Al species form before the solid-phase $Al(OH)_3$ mineral forms and precipitates. Buffered PAC compounds, on the other hand, come 'pre-hydrolyzed' with OH and thus the hydrolysis that occurs with Al is partially complete. Direct $AlPO_4$ formation, which has a theoretical 1:1 binding of Al to P, is thus limited when using PAC forms. Although this type of binding between Al and P is only dominant at high phosphate concentrations (Jenkins et al., 1971), it may occur when sediment porewater phosphate concentrations are much higher relative to those found in the water column in eutrophic lakes (Enell and Lövgren, 1988).

5. Conclusions

The results of this study indicate that P binding efficiency following Al treatment is regulated by Al added relative to the amount of legacy P in sediment (i.e. P_{mob}) and lake morphology (Osgood index). The main underlying mechanism is connected to the potential for Al binding of P_{mob} in sediment before crystallization of the amorphous Al mineral occurs and surface area/binding sites decrease. Elevated Al doses relative to sediment P_{mob} will generally reduce binding efficiency, whereas sediment injection of Al into the sediment (or solid Alum application) can improve binding efficiency, especially in lakes with steep sediment bed slopes. With sediment treatment, Al is distributed vertically in the sediment at the moment of treatment. This, along with natural movement of the sediment, increases binding efficiency by increasing the chance of Al encountering P_{mob} before crystallization causes a decrease in surface area of the mineral. The model developed in this study can be used to predict the optimal Al dose

needed to achieve a specific binding efficiency, thereby maximizing cost-efficiency and effectiveness of sediment Al treatment.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.watres.2020.116150>.

References

- Berkowitz, J., Anderson, M.A., Amrhein, C., 2006. Influence of aging on phosphorus sorption to alum floc in lake water. *Water Res.* 40 (5), 911–916.
- Berkowitz, J., Anderson, M.A., Graham, R.C., 2005. Laboratory investigation of aluminum solubility and solid-phase properties following alum treatment of lake waters. *Water Res.* 39 (16), 3918–3928.
- Bloom, P.R., 1981. Phosphorus adsorption by an aluminum-peat complex. *Soil Sci. Soc. Am. J.* 45 (2), 267–272.
- Breukelaar, A.W., Lammens, E., Breteler, J.G.P.K., Tatrai, I., 1994. Effects of benthivorous bream (*abramis brama*) and carp (*cyprinus carpio*) on sediment resuspension and concentrations of nutrients and chlorophyll a. *Freshw. Biol.* 32 (1), 113–121.
- Conley, D.J., Pearl, H.W., Howarth, P.W., Boesch, D.F., Seitzinger, S.P., Havens, K.E., Lancelot, C., Likens, G.E., 2009. Controlling eutrophication: nitrogen and phosphorus. *Science* 323, 1014–1015.
- Cooke, D.W., Welch, E.B., Peterson, S.A., Nichols, S.A., 2005. Restoration and Management of Lakes and Reservoirs. CRC Press, Boca Raton.
- Cooke, G.D., Welch, E.B., Martin, A.B., Fulmer, D.G., Hyde, J.B., Schriever, G.D., 1993. Effectiveness of Al, Ca, and Fe salts for control of internal phosphorus loading in shallow and deep lakes. *Hydrobiologia* 253, 323–335.
- de Vicente, I., Huang, P., Andersen, F.O., Jensen, H.S., 2008b. Phosphate adsorption by fresh and aged aluminum hydroxide. *ES T (Environ. Sci. Technol.)* 42 (17), 6650–6655.
- de Vicente, I., Jensen, H.S., Andersen, F.O., 2008a. Factors affecting phosphate adsorption to aluminum in lake water: implications for lake restoration. *Sci. Total Environ.* 389 (1), 29–36.
- Driver, P.D., Closs, G.P., Koen, T., 2005. The effects of size and density of carp (*cyprinus carpio* L.) on water quality in an experimental pond. *Arch. Hydrobiol.* 163 (1), 117–131.
- Du, Y., Zhang, Q., Liu, Z., He, H., Lürling, M., Chen, M., Zhang, Y., 2019. Composition of dissolved organic matter controls interactions with La and Al ions: implications for phosphorus immobilization in eutrophic lakes. *Environ. Pollut.* 248, 36–47.
- Egemose, S., Reitzel, K., Andersen, F.O., Flindt, M.R., 2010. Chemical lake restoration products: sediment stability and phosphorus dynamics. *Environ. Sci. Technol.* 44 (3), 985–991.
- Enell, M., Lövgren, S., 1988. Phosphorus in interstitial water: methods and dynamics. *Hydrobiologia* 170, 103–132.
- Hupfer, M., Gächter, R., Giovanoli, R., 1995. Transportation of phosphorus species in settling seston and during early sediment diagenesis. *Aquat. Sci.* 57 (4), 305–324.
- Huser, B.J., Bajer, P.G., Chizinski, C.J., Sorensen, P.W., 2016a. Effects of common carp (*cyprinus carpio*) on sediment mixing depth and mobile phosphorus mass in the active sediment layer of a shallow lake. *Hydrobiologia* 763, 23–33.
- Huser, B.J., Brezonik, P., Newman, R., 2011. Effects of alum treatment on water quality and sediment in the Minneapolis Chain of Lakes, Minnesota, USA. *Lake Reservoir Manag.* 27 (3), 220–228.
- Huser, B.J., 2012. Variability in phosphorus binding by aluminum in alum treated lakes explained by lake morphology and aluminum dose. *Water Res.* 46 (15), 4697–4704.
- Huser, B.J., 2017. Aluminum application to restore water quality in eutrophic lakes: maximizing binding efficiency between aluminum and phosphorus. *Lake Reservoir Manag.* 33 (2), 143–151.
- Huser, B.J., Egemose, S., Harper, H., Hupfer, M., Jensen, H., Pilgrim, K.M., Reitzel, K., Rydin, E., Futter, M., 2016b. Longevity and effectiveness of aluminum addition to reduce sediment phosphorus release and restore lake water quality. *Water Res.* 97, 122–132.
- Håkanson, L., Jansson, M., 1983. *Principals of Lake Sedimentology*. Springer-Verlag, Berlin.
- Huser, B.J., Futter, M., Lee, J.T., Perniel, M., 2016c. In-lake measures for phosphorus control: the most feasible and cost-effective solution for long-term management of water quality in urban lakes. *Water Res.* 97, 142–152.
- James, W.F., 2011. Variations in the aluminum:phosphorus binding ratio and alum dosage considerations for Half Moon Lake, Wisconsin. *Lake Reservoir Manag.* 27 (2), 128–137.
- Jan, J., Borovec, J., Kopacek, J., Hejzlar, J., 2013. What do results of common sequential fractionation and single-step extractions tell us about P binding with Fe and Al compounds in non-calcareous sediments? *Water Res.* 47 (2), 547–557.
- Jenkins, D., Ferguson, J.F., Menar, A.B., 1971. Chemical processes for phosphate removal. *Water Res.* 5 (7), 369–389.
- Jensen, H.S., Reitzel, K., Egemose, S., 2015. Evaluation of aluminum treatment efficiency on water quality and internal phosphorus cycling in six Danish lakes. *Hydrobiologia* 751 (1), 189–199.
- Lewandowski, J., Schauser, I., Hupfer, M., 2003. Long term effects of phosphorus precipitations with alum in hypereutrophic Lake Süsser See (Germany). *Water Res.* 37 (13), 3194–3204.
- Lind, C.J., Hem, J.D., 1975. Effects of organic solutes on chemical reactions of aluminum. *U.S. Geol. Survey* 1827 (G).
- Murphy, J., Riley, J.P., 1962. A modified single solution method for determination of phosphate in natural waters. *Anal. Chim. Acta* 27, 31–36.
- Nogaro, G., Harris, A.M., Steinman, A.D., 2016. Alum application, invertebrate bio-turbation, and sediment characteristics interact to affect phosphorus exchange in eutrophic ecosystems. *Freshw. Sci.* 35 (2), 597–610.
- Osgood, R.A., 1988. Lake mixis and internal phosphorus dynamics. *Arch. Hydrobiol.* 113 (4), 629–638.
- Paraskova, J.V., Rydin, E., Sjöberg, P.J., 2013. Extraction and quantification of phosphorus derived from DNA and lipids in environmental samples. *Talanta* 115, 336–341.
- Pilgrim, K.M., Huser, B.J., Brezonik, P.L., 2007. A method for comparative evaluation of whole-lake and inflow alum treatment. *Water Res.* 41 (6), 1215–1224.
- Psenner, R., Boström, B., Dinka, M., Pettersson, K., Pucsko, R., Sager, M., 1988. Fractionation of phosphorus in suspended matter and sediment. *Arch. Hydrobiol. Suppl.* 30, 98–103.
- Reitzel, K., Ahlgren, J., DeBrabandere, H., Waldeback, M., Gogoll, A., Tranvik, L., Rydin, E., 2007. Degradation rates of organic phosphorus in lake sediment. *Biogeochemistry* 82 (1), 15–28.
- Reitzel, K., Hansen, J., Andersen, F.O., Hansen, K.S., Jensen, H.S., 2005. Lake restoration by dosing aluminum relative to mobile phosphorus in the sediment. *Environ. Sci. Technol.* 39 (11), 4134–4140.
- Roberson, C.E., Hem, J.D., 1967. Solubility of Aluminum in the Presence of Hydroxide, Fluoride, and Sulphate. *U.S. Geologic Survey*.
- Rydin, E., Huser, B., Welch, E.B., 2000. Amount of phosphorus inactivated by alum treatments in Washington lakes. *Limnol. Oceanogr.* 45 (1), 226–230.
- Rydin, E., Welch, E.B., 1999. Dosing Alum to Wisconsin Lake Sediments Based on *in vitro* formation of aluminum bound phosphate. *Lake Reservoir Manag.* 15 (4), 324–331.
- Sas, H., 1990. Lake restoration by reduction of nutrient loading: expectations, experiences, extrapolations. *Int. Assoc. Theor. Appl. Limnol. Proc.* 24 (1), 247–251.
- Schütz, J., Rydin, E., Huser, B.J., 2017. A newly developed injection method for aluminum treatment in eutrophic lakes: effects on water quality and phosphorus binding efficiency. *Lake Reservoir Manag.* 33 (2), 152–162.