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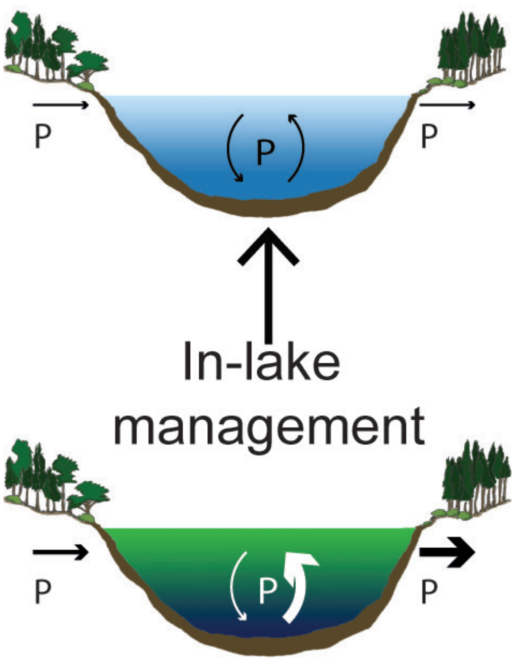
Restoration of Nutrient Rich Lakes

-Towards Better Understanding of Sediment Phosphorus Availability and Management

Oskar Agstam-Norlin



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Restoration of Nutrient Rich Lakes

Abstract

Lakes are important for many reasons as they provide valuable ecological and human services, such as drinking water and recreational use. Eutrophication, a result of excess nutrients (e.g. phosphorus (P)) in lakes, is a threat to these resources, causing impairment of water quality. Excess P loading to lakes accumulates in the sediment, consequently making sediment a potential source of P via release (internal loading). One way of counteracting effects caused by internal loading is to inactivate the pool of potentially available P in the sediment. Better information is needed for optimizing most in-lake P reduction methods, including aluminum (Al)-treatment. One of these areas is better knowledge about the availability of different P fractions, and which fractions to target with a specific dose of Al under certain environmental conditions such as bioturbation (e.g. sediment mixing by carp). We also need to deepen the knowledge about modern Al-treatment methods, with respect to both treatment techniques and dosing. Knowledge about factors affecting how long the positive effects from an Al-treatment last also needs to be improved. This thesis presents results concerning optimization of Al application methods, where a novel application method that injects Al into the sediment was evaluated and a model for optimal Al dose determination is presented. Factors affecting treatment longevity were evaluated, using historical water quality records and knowledge about a previously assumed recalcitrant P form being bioavailable due to bioturbation by benthic feeding fish like carp and bream. Al-treatment methods, including practical Al application methods as well as dosing methods are developing rapidly and being applied in the field, and further work is needed to keep up with evaluating the progress of lake restoration results using methods like Al-treatment.

Keywords: phosphorus (P), internal P loading, sediment, legacy P, eutrophication, lake restoration, aluminum (Al)-treatment

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Restaurering av näringsrika sjöar

Sammanfattning

God vattenkvalitet i sjöar skapar förutsättningar för viktiga ekosystemtjänster såsom dricksvatten och livsmedelsproduktion. Om sjöar blir övergödda på grund av fosforöverskott, leder det till en försämrad vattenkvalitet som t.ex. visar sig i form av algblomningar. Ett sätt att återskapa god vattenkvalitet till en övergödd sjö är att inaktivera överskottet av tillgänglig fosfor (P) som är lagrat i dess sediment. P som ackumulerats i sjöars sediment över flera decennier utgör källan för internbelastning, där sedimentfosfor ständigt frigörs och anrikar vattenmassan med näring. För att optimera restaureringsmetoder, däribland aluminiumbehandling som används för att inaktivera sedimentfosfor, krävs utökade kunskaper om associerad metodik. Det finns kunskapsluckor gällande vilka fraktioner av sedimentfosfor som kan frigöras från sedimentet och därmed utgöra en källa för internbelastning. Sådan kunskap är viktig eftersom vetskapen om den totala mängden fosfor som ska inaktiveras bland annat styr den dos av aluminium (Al) som bör tillsättas till en sjö för bästa resultat vid en Al-behandling. Tillgängligheten av specifika P-fraktioner kan också styras av processer som förändrar den kemiska miljön vid sedimentet, såsom sedimentomblandning orsakad av bottenlevande fisk. Kunskapsbasen gällande moderna och nyutvecklade praktiska Al-behandlingsmetoder behöver utökas. Utvärdering av faktorer som påverkar varaktigheten av Al-behandling är också viktig att utröna. Resultaten från studierna i denna doktorsavhandling presenterar ny kunskap som utökar förståelsen gällande en nyutvecklad teknik av Al-behandling där Al harvas ner i sedimentet istället för att, konventionellt, tillsättas vattenmassan i löst form och en anpassad Al-doseringsmodell har utvecklats och presenteras. Faktorer som påverkar varaktigheten av Al-behandling har utvärderats med hjälp av historiska data rörande vattenkvalitet. Vidare presenteras resultat som indikerar att en P-fraktion (kalciumbunden P) som tidigare ansetts vara icke-tillgänglig, kan vara en källa för internbelastning, under sedimentomrörning.

Nyckelord: fosfor, internbelastning, sediment, övergödning, sjörestaurering, aluminiumbehandling, aluminiumfällning

Dedication

To my girls.
Karin, Signe & Saga (&IA)

"I´m just a tiny researcher in the big world."
Said by my daughter Signe (2 years old)

"Jag är bara en liten forskare i den stora världen"
Sagt av min dotter Signe (2år)

Contents

List of publications

This thesis is based on the work contained in the following papers, referred to by Roman numerals in the text:

I. **Agstam-Norlin O**., Lannergård E. E., Rydin E., Futter N. M., Huser J. B. (2021). A 25-year retrospective analysis of factors influencing success of aluminum treatment for lake restoration. *Water Research*. 200 (117267).

II. **Agstam-Norlin O**., Lannergård E. E., Futter N. M., Huser J. B. (2020). Optimization of aluminum treatment efficiency to control internal phosphorus loading in eutrophic lakes. *Water Research*, 185 (116150).

III. **Agstam-Norlin O**., Bajer P.G., Huser J. B. Effects of bioturbation on sediment phosphorus fractions and active sediment depth. (manuscript)

Papers I-II are reproduced with the permission of the publisher.

The contribution of Oskar Agstam-Norlin to the papers included in this thesis was as follows:

I. Planned the study together with the last author and data retrieval together with the third author. Performed data analysis and paper writing with help from all co-authors.

II. Planned the study together with the last author. Field work was performed by the first author. The second and last co-author supported the study with laboratory work. All co-authors were involved in the data analysis and contributed to writing the paper.

III. All co-authors in this paper contributed to experimental design, construction of experimental material, data analysis and paper writing. Field sampling and laboratory work was performed by the first author.

Additional papers

In addition to the papers included in the thesis, the author has contributed to the following peer-reviewed publications:

Lannergård, E. E., **Agstam-Norlin, O**., Huser, B.J., Sandström, S., Rakovic, J., Futter, M.N. (2020). New insights into legacy phosphorus from fractionation of streambed sediment. *Journal of Geophysical Research: Biogeosciences,* 125, e2020JG005463

Peter, S., **Agstam-Norlin O**., Sobek S. (2017).Widespread release of dissolved organic carbon from anoxic boreal lake sediments. *Inland Waters*. 7 (2), 151-163

Abbreviations

Al	Aluminum
Ca	Calcium
Chl a	Chlorophyll a
OM	Organic matter
Fe	Iron
P	Phosphorus
P_{Pw}	Pore-water phosphorus
P_{Fe}	Iron bound P (Also including Manganese bound P)
P_{mob} (or Mob-P)	Mobile P (P_{Pw} + P_{Fe})
P_{Ca} (or Ca-P)	Calcium bound phosphorus
P_{org} (or Org-P)	Organic bound phosphorus
$P_{lab.org}$	Labile organic phosphorus
P_{Al} or (Al-P)	Aluminum bound phosphorus
SD	Secchi disc depth
TP	Total phosphorus
WFD	Water Framework Directive

1. Introduction

Lakes are important for many reasons as they provide vital ecosystem services such as drinking water, recreational uses, food supply and more. There are over 100000 lakes (> 1 ha) in Sweden (Huser and Fölster 2013, Sonesten 2013), but only 4 % of the lakes have been studied adequately enough to be able to quantitatively determine trophic state. Unfortunately there are severe threats to these resources, one of the main ones being caused by excess internal and external loading of nutrients. The excess input of nutrients can lead to eutrophication that can alter lake ecosystems and impair the natural benefits of lakes. About 2 % of the studied lakes were determined to be eutrophic, with total phosphorus (TP) concentrations exceeding 25µg/L (Huser and Fölster 2013). The high number of unclassified lakes in Sweden is concerning because the number of eutrophied lakes is critical both for local management and for meeting the requirements of the EU Water Framework Directive (WFD). To be able to manage eutrophication problems in lakes, there is a crucial need to understand the drivers behind eutrophication. External and internal loading of P often control the trophic state of lakes, but climate change (Jeppesen et al. 2011) and other in-lake factors such as sediment mixing (Huser et al. 2016a) may also alter nutrient cycling and availability and contribute to eutrophication.

1.1 Phosphorus cycling in lake sediment

1.1.1 Inorganic P fractions

The input of P to lakes (external loading) comes mainly from polluted industrial and municipal wastewater, as well as farmland fertilizers leaching from soils and runoff from urban areas. The management of these sources is thus the primary long term goal for overcoming eutrophication (Conley et al. 2009).

Some of the P that enters lakes accumulates in the lake sediment. Even if external inputs are controlled, this historical (legacy) P in the sediment will contribute to elevated nutrient concentrations in the water column well in to the future in most lakes via internal loading (Pilgrim et al. 2007, Sas 1990, Sondergaard et al. 2008). The in-lake P cycle is mainly driven by the mobilization dynamics of sediment P (Pilgrim et al. 2007), along with the different in-lake processes that govern the rate at which P is mobilized and released into the water column. Oxygen levels in lakes are important because the binding of P to elements such as iron (Fe), is sensitive to low oxygen conditions (anoxia) that lead to a decrease in the oxidation-reduction (redox) potential at the sediment-water interface. Anaerobic conditions can cause release of Fe bound P (P_{Fe}) from the sediment to the water column via reduction of ferric Fe (Fe III) to ferrous Fe (Fe II) (Ramm and Schepps 1997). Anoxia occurs when deep lakes stratify and diffusion of oxygen to the hypolimnion is limited, but can also occur in shallow lakes during calm periods when the water column stabilizes and respiration is high (e.g. night time). The process accelerates during warmer periods due to the consumption of oxygen as bacteria degrade organic matter in the water and sediment. Large amounts of P can be mobilized during these events and further diffuse from the sediment to the overlying water body. In-lake P dynamics are, to a large extent, governed by the potential for internal loading (Liboriussen et al. 2009, Nürnberg 2009).

However, to view internal loading of P as an exclusive result of anoxia is an over simplification. To understand internal P loading in a more complete manner, a more refined view is needed. In a review by Hupfer and Lewandowski (2008), it was suggested that the oxic state near the sediment water interface should be considered as one important driver, among many other influencing drivers behind internal P loading. Other influencing factors include: the amount and form of P binding metals, pH controlled release of P and mineralization of P in organic matter. Huser and Rydin (2005) showed the importance of P binding elements, such as aluminum (Al), which regulates P release from lake sediments and in a survey of 43 lakes by Kopacek et al. (2005) it was also shown that the P sorption capacity of lake sediment is increased by the availability of naturally occurring aluminum hydroxide ($Al(OH)_3$).

P release from sediment is also affected by pH because the solubility of Fe and Al increases at both low and high pH, whereas the solubility of calcium (Ca) minerals and P bound to them (P_{Ca}) decreases at low pH (Gomez et al. 1999). Elevated P_{Fe} and P_{Al} release during high pH conditions has been observed in several studies (Boers 1991, Gomez et al. 1999), which is generally caused by excessive photosynthetic activity/productivity in eutrophic systems (Boers 1991). P_{Ca}, which earlier has been viewed as recalcitrant (Andreiux 1997), has been shown to be labile (releasable) in lakes with fish farms, and release could be explained by low pH due to mineralization of large amounts of organic material (fish feed/excretion residue (Kassila et al. 2001)). A high rate of mineralization has been shown to decrease the sediment pH (Staudinger et al. 1990) via production of carbonic acid (CO_2/H_2CO_3), in some cases reaching pH 6 (Kassila et al. 2001) where dissolution of P_{Ca} has been shown by Gomez et al. (1999) to occur.

1.1.2 Organic P fraction

Often in the shadow of inorganic P contribution to internal loading, organic matter (OM) input to lake sediment can also contribute to elevated internal loading rates through the mineralization/degradation process of OM containing P (Paraskova et al. 2013). Mobilization of P from OM, through decomposition and mineralization of OM in the sediment (sediment diagenesis), varies based on oxygen conditions and has a positive correlation to higher temperatures (Gudasz et al. 2015, Sobek et al. 2017). It has been shown that aerobic conditions increase the mineralization rate, and thus P release from OM can be promoted by high oxygen levels (Moore et al. 1992).

1.2 Climate change and eutrophication

Both external and internal nutrient cycling processes in freshwater systems can be affected by climate change, e.g. P input to lakes is argued to increase by intensified storm events as well as enhanced soil temperature and melting of glaciers (Jeppesen et al. 2011). Elevated temperature can enhance the transportation rate of OM (including organic bound P (P_{org})) from the catchment to the lake (Larsen et al. 2011), and can decrease the efficiency of lake sediment P storage capacity via longer growing season and higher chance for oxygen depletion. The high OM content together with higher temperature in the sediment enhances respiration rates, which increases carbon utilization. This may also lead to more frequent anoxia at the sediment surface of lakes due to oxygen consumption by microbes (Moss et al. 2011), potentially increasing release of sediment P. In summary, climate change triggers and intensifies many factors that can lead to increased internal P loading and eutrophication of lakes.

1.3 Benthic fish impact on water quality and sediment P

Water quality and chemistry can be affected by benthic feeding fish, such as the common carp *(Cyprinus carpio)*, through two main pathways. First, physical disturbance of the sediment and pore-water can enhance the diffusion/transport rate of P to the water body. Second, larger amounts of the sediment (i.e. a greater depth) may be affected by aerobic mineralization of OM due to increased sediment mixing depth and thus aeration of formerly anoxic sediment (Fukuhara and Sakamoto 1987, Huser et al. 2016a).

The importance of benthic feeding fish effects on water quality and mobilization of P from lake sediment has been suggested for decades. Knowledge about benthic feeding fish mobilizing P by mixing sediment and via excretion, shows the regulating role benthic fish can have on lake nutrient cycling and thus lake water quality (Andersson et al. 1988, Morgan and Hicks 2012).

As stated, bioturbation increases the flux, or diffusion, of P between lake sediment and the overlying waterbody (Graneli 1978), partly due to oxygenation of formerly anoxic, deeper parts of the sediment, which allows for aerobic mineralization and thus an elevated release of sediment bound P (Fukuhara and Sakamoto 1987). P mobilization is thus related to the extent lake sediment is exposed to oxygen. Because bioturbation can increase the oxygenation of sediment, it can potentially affect other P fractions as well because the chemical milieu is changing. Oxygenation can prevent low redox conditions, thereby potentially supressing the release of P_{Fe} because this P form is generally controlled by redox state (Ramm and Schepps 1997). But contrary, bioturbation can enhance the microbial mineralization of OM and thus P_{org}, causing release of P (Huser et al. 2021, Ritvo et al. 2004).

Additionally, high mineralization rates have been shown to decrease pH in the sediment (Staudinger et al. 1990), to the point where P release from Ca has been shown to be significant (pH 6) (Gomez et al. 1999, Kassila et al. 2001). Furthermore, bioturbation to a deeper sediment depth has been shown to be closely connected to the potential for P mobilization, by increasing the total potentially available P mass and the potential for internal loading (Huser et al. 2016a).

The specific mixing depth that bioturbation by benthic feeding fish causes is thus likely an important factor for the overall mobilization rate of P from lake sediments (Adámek and Maršálek 2012). There is a general biomass dependence pattern of higher densities of carp promoting greater levels of total P (TP) in lake water (Chumchal et al. 2005). Specifically, it has been suggested that there is a fish size dependence related to P levels, where the size of carp is more important than the actual biomass (e.g. kg/ha). It has been argued that larger carp contribute to P mobilization via physical bioturbation to a greater extent, whereas smaller carp likely contribute to P mobilization mainly by excretion (Driver et al. 2005). Carp can increase the mixing depth of lake sediment up to 2.5 times (15 cm), and consequently increase the amount of P_{mob} in the sediment profile potentially available for release by up to 92% (Huser et al. 2016a).

1.4 Restoration methods to reduce internal loading

1.4.1 Reduction fishing, oxygenation and dredging

There are several restoration methods that have been developed to reduce eutrophication. Reduction fishing is one way of manipulating the food web by decreasing the density of targeted fish groups in lakes, such as planktivorous or benthic fish. The aim can be to increase zooplankton populations by reducing planktivorous fish and thus enhance the effectiveness of phytoplankton grazing pressure. Another method aims to reduce the population of benthic feeding fish in order to decrease sediment bioturbation and consequently reduce i.e. turbidity (Meijer et al. 1990) and lower the potential for P flux from the sediment (Huser et al. 2016a). In a study by Sondergaard et al. (2008), a large set of lakes was monitored during different degrees of reduction fishing, and they found that this method is a relatively efficient way of counteracting the effects of bioturbation on eutrophication. However, this is not considered as a one-time treatment, but rather a tool that has to be regularly used to maintain positive effects, and the effect is dependent on a high rate of fish removal (Sondergaard et al. 2008). Biomanipulation in this manner is a way of treating the symptoms of excess internal P loading and eutrophication.

To be able to target the source of the problem (i.e. excess nutrients), methods for the management of internal P loading have been developed. Oxygenation of hypolimnetic water is one way of counteracting anoxic conditions at the sediment-water interface and limiting P release caused by anoxia. Studies have shown that this method can dampen the accumulation of P in hypolimnetic water, but it is rather unclear if the overall water quality can be improved using this restoration method alone (Liboriussen et al. 2009). For oxygenation to be effective, the binding capacity of the sediment must be sufficient, and in some cases it may need to be supplemented by Al- or Fe-based minerals to be effective (Engstrom 2005).

Dredging of lake sediment is another method that physically removes P from the lake. In dredging, the most important factor to consider is the P content in the sediment profile. This information is needed to accurately decide the dredging depth so that the removal of the top sediment would not reveal a layer with similar, or even higher P levels and thus induce a reverse effect (Van der Does et al. 1992).

1.4.2 Phosphorus binding / inactivation by aluminum

Al-treatment of a lake binds P in lake water, but the main target is excess P in the sediment. When Al is added to lake water, Al^{+3} can bind directly to phosphate before $Al(OH)_3$-floc forms and precipitate. The second form of binding occurs via sorption to solid $Al(OH)_3$-floc that forms and settles on the sediment surface during water application, or is injected into the sediment matrix if that sediment treatment technique is used (Schütz et al. 2017). Here a sort of "buffer" of $Al(OH)_3$-floc at the sediment-water interface/sediment matrix develops, where the mineral binds P diffusing from deeper sediment layers over time. Liquid Al in aqueous conditions forms $Al(OH)_3$-floc through a series of hydrolysis reactions, the solid product $Al(OH)_3$-floc has the ability to efficiently bind P. The solid form is pH dependent which starts to form at pH > 4 and dominates at pH 6-8, whereas at lower pH (< 4) cationic dissolved Al forms dominates and at pH > 8 soluble anionic Al begins to increase. Outside the pH range of 6-8, the ability of the Al-complex to bind and inactivate P is reduced (Cooke et al. 2005). Sediment can buffer pH changes, and pH in sediment (compared to pH in the water column) may be 1-2 units lower (eutrophic lakes) or higher (acid lakes) than surface water pH (Jeffries et al. 1979).

1.5 The longevity of aluminum treatment

The longevity of Al-treatment of lakes is an important factor to consider when choosing this restoration method. Several studies report a rather quick reestablishment of pre-treatment conditions (a few months) while other studies report longevities of up to 40 years or more (Egemose et al. 2011, Garrison and Knauer 1984, Huser et al. 2011, Huser et al. 2016b, James et al. 1991, Welch and Cooke 1999). However it should be noted that longevity is mainly related to factors outside the binding of P by Al, and is generally controlled by how much external loading has been reduced. This is true for most in-lake measures. If external loading is greater than a natural, pre-impact level, internal loading will eventually return due to new sedimentation of P rich sediment on top of the treated layer.

There are several lake characteristics that can affect the longevity of Al-treatment of lakes. In an extensive study by Huser et al. (2016b) the longevity of Al-treatment of 114 lakes was analysed. Average longevity was reported to be 11 years with the range 0-45 years. However, among lakes that responded to treatment (defined as a >50% epilimnetic water TP decrease), an average longevity of 21 years was reported for deep (dimictic) lakes and 5.7 years for shallow (polymictic) lakes.

Lake morphology was one important factor in that study, most likely explained by previously stated differences in characteristics between shallow (polymictic) and deep (dimictic) lakes. Another factor heavily affecting the longevity of Al-treatment was watershed to lake area ratio (WA:LA) which is related to the relative importance of internal vs. external loads depending on this ratio. Nutrient availability in large lakes with small watersheds is more likely controlled by in-lake processes, instead of external loading, and vice versa.

Al dose was the most significant factor in treatment longevity. This makes sense as doses not sufficient to bind excess P_{mob}, or less efficient binding between Al and P (Huser 2012), may lead to a remaining pool of P_{mob} in the sediment that can continue to cause excess internal loading.

Benthic feeding fish in moderate to high biomass densities were shown to have a negative effect of the longevity of Al-treatment (Huser et al. 2016b), and the effect of carp on water column P is more pronounced in shallow lakes that do not stratify (Bajer and Sorensen 2015). In deep lakes and lakes were Al dosing was based on P_{mob} mass deeper in the sediment (deeper active sediment due to sediment mixing), however, the effect of benthic feeding fish on longevity was weaker (Huser et al. 2016b).

1.6 Al-treatment binding efficiency (Al to P_{Al})

The binding efficiency between Al and P in sediment likely affects the longevity of Al-treatment. The amount of P bound per unit Al after Al-treatment has varied by an order of magnitude in previous studies, with Al:P_{Al} ratios varying from 2:1 to 21:1 (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 1999a, Schütz et al. 2017). The underlying mechanism behind different binding efficiencies is in general controlled by the chance of Al to encounter P (in sediment or water) before the binding capacity of the mineral decreases due to crystallization (deVicente et al. 2008a) or other sorbents competing for binding sites. Specifically, the amount of P_{mob} in the sediment relative to Al dose will affect binding efficiency, because the chance of a small amount of Al to bind P when P is in excess is higher than vice versa (Le Chateliers principle) (James 2011). Therefore, greater, one-time doses of Al have generally resulted in lower binding efficiency and splitting doses has been suggested to improve binding efficiency (Huser 2012, Kuster et al. 2021).

Competing elements / compounds for sorption sites on the $Al(OH)_3$-floc may also lower binding efficiency. This includes silicates (de Vicente et al. 2008b), fluoride and sulphate (Roberson and Hem 1967). Also, organic matter in general (Bloom 1981, de Vicente et al. 2008b, Lind and Hem 1975), and especially labile organic matter (e.g. microbial transformed detritus and phytoplankton exudates) can compete for binding sites on the $Al(OH)_3$-floc

(Du et al. 2019). It should be noted that most forms of labile organic matter have a rapid break down and then release P that can sorb to available binding sites on the $Al(OH)_3$-floc (Reitzel et al. 2007).

Lake morphology has been shown to affect the amount of P bound by Al following Al-treatment. Lakes with steep sediment bed slope (where Al is added to the water column) generally have lower binding efficiency than gradual bed slope lakes. Huser (2012) suggested that this difference could be explained by the natural movement of $Al(OH)_3$-floc to accumulation zones of a lake (e.g. deep holes) and that the rate of transport depends on the steepness of the sediment bed slope. In Lake Harriet (US), this process was shown by Al addition to exclusively littoral zones of the lake that resulted in $Al(OH)_3$-floc accumulation in the deepest part of the lake within 6 months (Huser 2017). Natural sediment movement can translocate the intended dose of Al from a target location to another, potentially causing under dosing in one location and overdosing in another (Al in excess relative to P will result in lower binding efficiency).

The steepness of the sediment floor can be standardized using the Osgood index, which is the mean depth (m) divided by the square root of lake surface area (km^2) (Osgood 1988), and Cooke et al. (1993) suggested, with all other conditions being equal, that lakes with steep bed slopes (Osgood index > 6) would have less successful results of Al-treatment compared to gradual bed slope lakes (Osgood index < 6). Further, the time between $Al(OH)_3$-floc formation and when Al encounters and binds with P in the sediment is of essence, because following Al-treatment, the $Al(OH)_3$-floc starts to crystallize and binding sites are reduced due to decreased mineral surface area (Berkowitz et al. 2006). The longer it takes for Al to encounter P, the lower the binding efficiency (deVicente et al. 2008a), as noted above.

Sediment mixing/bioturbation can potentially increase binding efficiency, because it can reduce the time needed for Al to bind P (Huser et al. 2016a). However it has been shown that bioturbation by benthic invertebrates has a limited effect on binding efficiency of Al and P after Al-treatment (Nogaro et al. 2016). Apart from the above proposed controlling factors of longevity, it should be stated again that longevity is generally controlled by the extent of external loading after treatment, assuming an adequate dose had been added to the sediment. If external loading is not controlled, the input of P will eventually overwhelm the effects of Al-treatment even though the sediment (legacy) P at the time of treatment has been fully inactivated.

1.7 Aluminum dosing procedures

The dosing procedure used, when applying Al for P inactivation, has been shown to be of great importance to Al-treatment longevity (Huser et al. 2016b). Al-treatments and dosing calculations have been conducted for at least five decades and throughout this time they have been improved due to scientific progress. Al dosing was first based on measures of alkalinity in lake water, and the Al dose was set to the amount that could be added without reducing pH in the lake water below pH 6. P in sediment or water was not considered in any way (Kennedy and Cooke 1982). Dosing according to these restrictions has probably led to inaccurate Al doses resulting in underdosing (Huser et al. 2016b). In the 1990´s a new approach to Al-treatment was developed, using the measure of yearly internal loading rate measured in the lake water to adjust the Al dose. The problem with this approach is that it only accounted for a specific internal loading rate during one year, even though the sediment contains many years' worth of potential internal P loadings (Kennedy et al 1987). That is, not all P_{mob} is released from the sediment in one year. Due to increased analytical possibilities using P fractionation methods such as Psenner et al. (1988), the quantification of specific P pools in lake sediment was possible. Several dosing methods have been developed based on sediment P available for release, and approximately ten years later Rydin and Welch (1999) developed a modified Al-treatment dosing procedure based on sediment P_{mob} (pore-water P (P_{Pw}) + (P_{Fe})) mass in the top 4 cm of the sediment. In 2014, a dynamic model for Al-dosing was developed by Huser and Pilgrim (2014), where the dose of Al can be calculated in order to target a specific goal for internal loading reduction. This can serve as a useful tool in lake management, because zero internal loading might not be "natural" in all cases.

2. Aims and objectives

The general aims of this thesis were to gain a better understanding of sediment processes related to quantifying bioavailable forms of sediment P since the knowledge of the amount of bioavailable or potentially releasable P in the sediment is a fundamental factor for successful lake restoration. Furthermore, another aim was to increase the knowledge concerning P inactivation by Al-treatment to allow for optimization of a newly developed sediment injection treatment method.

The specific objectives were to:

- Investigate the results of Al-treatment among a set of Swedish lakes previously treated with Al and identify controlling factors of longevity and effectiveness.

- Improve predictions of P binding efficiency (the amount of P bound per unit of Al added) in eutrophic Al-treated lakes using a novel Al application method where Al is injected into the sediment matrix instead of applied to the water column.

- Investigate the effect of sediment mixing/bioturbation on P fractions and the active sediment layer depth.

3. Materials and methods

3.1 General study procedures

3.1.1 Paper I: Factors affecting Al-treatment

The study involving the retrospective analysis of factors influencing success of Al-treatment for lake restoration was based on retrieving and analysing historical lake water quality data from municipalities and county boards of Sweden. Six lakes within a radius of 30 km from Stockholm city were included (Figure 1). The dataset included lakes with various ratios of watershed area to lake area (WA:LA), different Al application techniques, varying Al doses and Al forms applied ($AlSO_4$ (liquid and solid) or PAC) and lake bathymetry. The dataset included nutrient related water quality data of various quantity and quality including at least yearly august data points of surface water total phosphorus (TP), and at most monthly (May to August) data points for TP, chlorophyll a (Chl a) and secchi disc depth (SD) including vertical water column TP samples at one meter interval (most cases). Historical trends of the variables TP, Chl a, SD and internal loading rate (Li) were investigated with respect to effect size of changes to nutrient related water quality variables and longevity of Al-treatment.

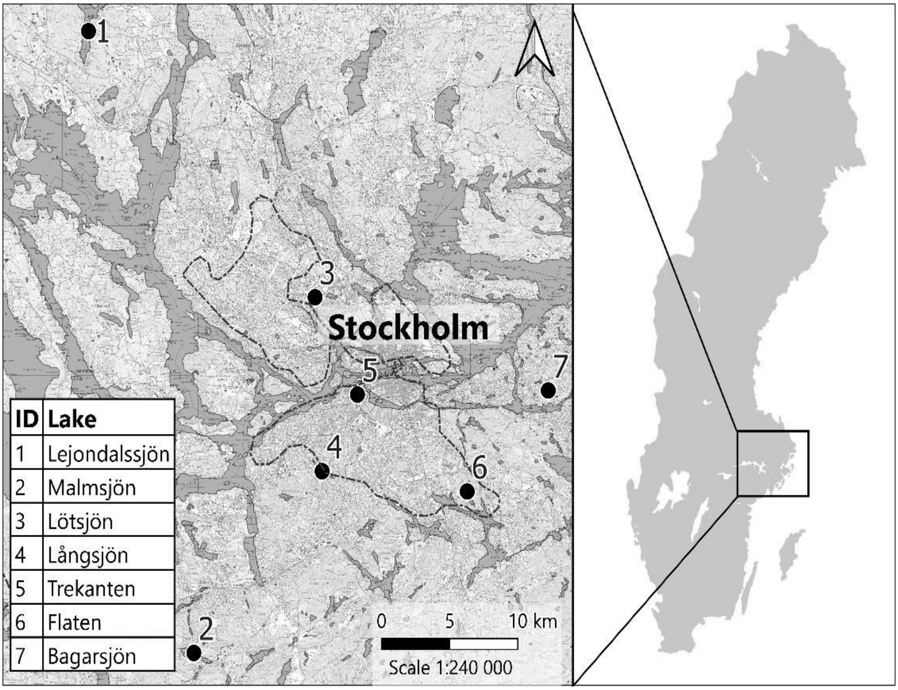

Figure 1. Location of the study lakes for Paper I & II. Lake Lötsjön is not included in Paper I due to lack of water quality data.

3.1.2 Paper II: Optimizing Al-application methods

The paper concerning optimization of Al-treatment efficiency to control sediment P release in previously eutrophic lakes was based on sediment from seven lakes (Figure 1) located within 30 km radius of Stockholm city. The sediment samples were analysed for total Al and P_{Al} originating from Al-treatment. The ratios of P bound per unit of Al (i.e. binding efficiency or Al:P_{Al}) for several locations in each lake were compared to different lake characteristics and Al-treatment variations (treatment type and dose) among lakes. This was done using stepwise multiple linear regression to find the controlling factors of binding efficiency within this data set.

3.1.3 Paper III: Sediment mixing depth and P fractions

The third paper concerns sediment mixing by e.g. carp (*Cyprinus carpio*). Bioturbation effects on P fractions and sediment mixing depth were studied at a small pond (0.45 ha) at SLU campus area in Uppsala (coordinates: 59.814436, 17.666198, Figure 2). The pond is eutrophic (mean growing season TP = 69 µg/L, phosphate = 7 µg/L) and has a generally homogenous bathymetry with a maximum depth of 2 m and mean depth of 1 m. Growing season turbidity averages 31 FNU, Chl a 43 µg/L and total nitrogen (TN) 592 µg/L.

The sediment is dense (upper most 10 cm layers mean dry bulk density=0.3g/cm^3), with slightly softer sediment at the surficial layers containing more organic matter, especially at maximum depth areas. After the pond was constructed (1970´s), carp were added and have been visually observed for 6 consecutive years with (10-15) adult carp (ca 3 kg and 40 cm in length) being visible at the surface. Additionally, test fishing for small sized fish, using benthic multi mesh gill nets (European standard (SS-EN 14757:2015) was performed in 2021 and showed the presence of Roach (*Rutilus rutilus*), Common Carp (*Cyprinus carpio*), Crucian Carp (*Carassius carassius*) and White Bream (*Blicca bjoerkna*). The mean weights were; 10, 57, 19 and 26 g, respectively and the mean lengths were 101, 163, 110 and 104 mm, respectively.

To assess the effects of carp sediment mixing, 6 exclosures was built and installed in the pond in order to exclude the effect of sediment mixing in these areas. The exclosures were 2 x 2 m wide and 2.5 m deep and wrapped with plastic netting with the mesh size of 2 x 3 cm. The exclosures were pushed approximately 30 cm into the sediment to prevent carp from burrowing in. Mixing depth was determined by sprinkling clean, transparent quartz sand evenly over the sediment surface, and at the end of the experiment tracing the quartz sand in the vertical profile of the sediment comparing areas inside the exclosures to areas where carp could forage. This was done by taking intact sediment cores, slicing them at a 1-cm interval, and assessing the distribution of the sand in the samples. Samples were collected inside and outside the exclosures to be able to compare differences in mixing depth and sediment P fractions in areas with and without carp foraging.

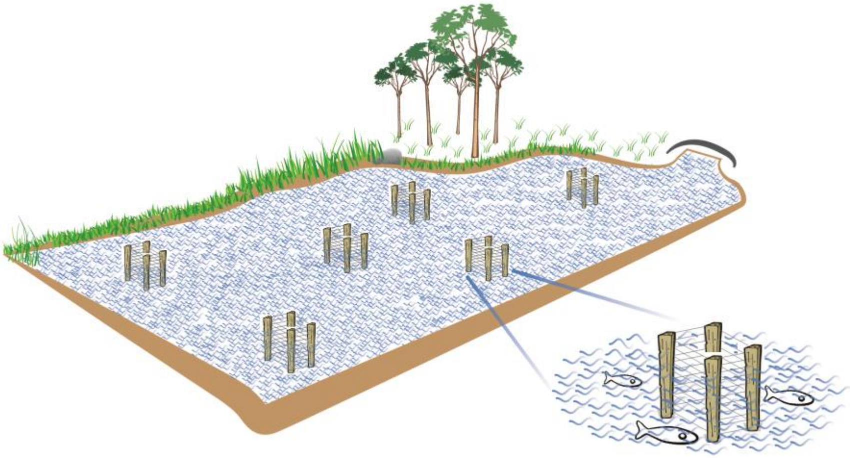

Figure 2. Conceptual sketch of study site for paper III.

3.2 Sediment sampling

In the study behind paper II, sediment cores from different locations of seven Swedish lakes were taken. The location of the sampled cores was based on the bathymetry of the lake to capture several depth zones of the sediment representing accumulation and transport bottoms. A Willner gravity corer was used to collect intact sediment cores, which were further sliced in to 1-cm slices from 0-10 cm depth, and 2-cm slices thereafter. In the study behind paper III, the same sampling procedure was applied, but one sediment core was instead taken inside each exclosure, and a corresponding number of cores outside the exclosures. All samples were stored in dark at 4°C for no longer than 4 week after sampling.

3.3 Laboratory analysis

3.3.1 Phosphorus fractionation

Quantification of different P fractions in lake sediment was done using sequential extraction based on the method developed by Psenner et al. (1988) and modified by Hupfer et al. (1995). This is an operationally defined method based on using different chemical treatments of the same sediment sample in a specific order, giving the possibility to separate and quantify different fractions of P corresponding to “pore-water-P (P_{Pw})”, “iron bound-P (and manganese bound-P)” (P_{Fe}), “aluminum bound-P” (P_{Al}), “organic P” (P_{org}) and “calcium bond-P” (P_{Ca}). Fractions are released after addition of different chemicals, and in the case of P_{org}, digestion under pressure. Both ammonium chloride (1 M, 2 h) and double deionized water (2 h, 20°C) have been used to release the fraction termed P_{Pw}; herein we used double deionized water. P_{Fe} is released through treatment with buffered sodium dithionite (BD) (0.11 M, 1 h). Further, P_{Al} is mobilized using NaOH (0.1 M, 16 h). This fraction of P is further digested in an autoclave at 120°C for 30 min, the difference between P_{Al} and the digested P_{Al} extract corresponds to P_{org}. P_{Ca} is then extracted through a treatment with hydrochloric acid (0.5 M, 24 h). For each step in the fractionation routine, a liquid sample containing mobilized P (PO_4^{3-}) is preserved and further analyzed according to the molybdate blue method using a spectrophotometer (Murphy and Riley 1962). Sediment water content for each slice/sample was determined after 24 h storage at -20°C followed by freeze drying at -50°C for 4 days. Sediment density was estimated using loss on ignition at 550°C for 2 h (Håkanson and Jansson 1983).

3.3.2 Sediment aluminum extraction and analysis

In paper II, the total amount of Al from Al-treatment was compared with the amount of P_{Al} formed in the same sample. Acid ammonium oxalate extraction was used to target the more amorphous form of Al to reduce masking of crystalline Al forms with origins elsewhere. The extraction was performed as described by Jan et al. (2013) and references therein where 16.2 g ammonium oxalate was mixed with 10.8 g oxalic acid dehydrate in one litre of distilled water. Sediment samples were extracted for 2 h in vials protected from light. The extracts were analysed for Al using inductively coupled plasma atomic emission spectrometry (ICP-AES) on the wavelength of 396.15 nm.

3.3.3 Sediment mixing depth analysis

A total of 500 kg clean transparent quartz sand (size ~1mm) was sprinkled and evenly distributed on the sediment in the pond at the beginning of the study (2016-06-04). During fall (2016-10-05), intact sediment cores were collected and sliced, one core per exclosure (n = 6) and six cores outside the exclosures. The samples were sieved (mesh size = 0.5 mm) and the number of sand grains at every layer in the vertical profile was noted. In order to estimate sedimentation rate in the exclosures, 4 sediment traps were strapped to the sides of exclosures. The sediment traps were constructed with plastic tubes (diameter = 64mm) with closed bottoms. The sedimentation rate was determined as the height of collected sediment during the study time frame, and was used to estimate the amount of sediment burial on top of original sediment surface in the exclosures.

3.4 Calculations and statistics

3.4.1 Paper I

The effect of Al-treatment was based on percent decrease of any measured water quality related parameter compared to pre-treatment. Pre- and post-treatment comparisons were based on 4-year periods to reduce the effect of natural, interannual variation. Treatment longevity was determined as the year where the annual mean (or data point for the lake with August only sampling) of surface water TP measurements (or estimation using linear extrapolation when end of longevity was not reached) exceeded one standard error of the mean (SEM) below the average of 4 years pre-treatment TP. In cases where no deterioration of post treatment water quality was found, the longevity prediction equation (LPEq) of Huser et al. (2016) was used.
Principal component analysis (PCA) was used to explore factors affecting Al-treatment longevity. Internal loading rates (Li) were calculated for dimictic, stratified lakes that included vertical water column profile measurements of TP (Lejondalssjön, Flaten and Trekanten). To calculate Li, the height of hypolimnetic water was determined using the temperature profile. Below the thermocline (i.e. the hypolimnion) TP concentration was multiplied by water volume at each meter depth interval in the lake (surface and bottom water for Lejondalssjön pre-treatment period). The seasonal increase of hypolimnetic TP mass with surface water TP subtracted corresponds to partial net internal loading rate: $mg/m^2/day$ (Nürnberg 2009).

3.4.2 Paper II

Several variables for sediment chemistry were derived and calculated from P fractionation and Al analysis: Al, P_{Al}, $P_{lab.org}$ (labile organic P) and estimation of pre-treatment P_{mob}. To determine the total mass of Al and P_{Al} originating from solely the Al-treatment, background concentrations (layers unaffected by Al-treatment) were subtracted from the Al and P_{Al} in the sediment profiles. The sum of excess Al (i.e. above background mass) was divided by the sum of P_{Al} formed by treatment (i.e. above background) to calculate the binding efficiency ratio Al:P_{Al}. $P_{lab.org}$ was estimated in similar manner where deeper layers of sediment with stabile background concentrations of P_{org} were considered as recalcitrant forms and therefore subtracted from the concentrations in the upper sediment profile, leaving an estimate of $P_{lab.org}$. Pre-treatment P_{mob} was estimated by summing the remaining P_{mob} in the sediment layers above and within layers affected by Al-treatment with the P_{Al} formed from P_{mob} after treatment. Lake morphology (steepness of sediment bed slope) was estimated using Osgood index as a slope factor, which was calculated as: $Z_m/A^{\wedge -0.5}$ where "Z_m" is mean depth and "A" corresponds to lake surface area (km^2) (Osgood 1988). Stepwise multiple linear regressions was conducted using JMP software (SAS institute inc. version 11.0.0) to find predictor variables explaining binding efficiency (Al:P_{Al}). Variables (Paper II: Tables 1-3) were included at a significance level of < 0.05. In order to preserve matrix stability, variables with high bivariate correlations (> 0.8) were excluded from the analysis. To explore the effect of treatment method (water vs. sediment treatment) in lakes with steep or gradual bed slope, we performed a one-way ANOVA test following Tukey´s post hoc test.

3.4.3 Paper III

When comparing sediment mixing depth inside and outside exclosures, (i.e. sediment mixing by carp or not) we used a breaking point defined as: maximum mixing depth is represented by the number of layers (1 layer=1cm) where >95% of the tracer sand grains were found in the average vertical sediment core profile. Because major sedimentation on the surface of sediment in the exclosures was expected, sediment traps were used to calculate the additional layers of sediment deposited on top of original sediment surface in the exclosures. Wilcoxon´s rank sum test was used for comparison of changes in P mass in the different P fractions due to sediment mixing or lack of sediment mixing. Two different comparisons were conducted. One was the comparison of the cumulative mass of different P fractions in the upper most 10 cm of sediment in exclosures versus areas with carp present. The second was a comparison of P_{mob} in the active sediment layer i.e. layers where sediment was mixed in exclosures and outside.

4. Results and Discussion

4.1 Optimizing lake restoration

There are a number of important steps to consider in order to successfully and sustainably reduce P and achieve good water quality in eutrophic lakes. All lake restoration projects should start with understanding the lake´s P cycling dynamics, including internal and external loading. For this, accurate lake water quality monitoring is crucial, as shown in Paper I where the data needed to determine success of Al-treatment is 100% controlled by water monitoring work performed before and after treatment. When understanding where water quality issues begin, it is then possible to address sources and determine the optimal restoration tool or tools. If internal loading is a substantial nutrient source, tools such as Al-treatment can be used, but first the amount of and method of Al application have to be properly determined as longevity and effectiveness relies highly on these factors. (Paper I & II).

4.1.1 Optimizing Al dose to inactivate P

The work in this thesis showed that, in accordance to previous work (Huser et al. 2016b), Al dose is important for both effectiveness of treatment and longevity together with binding efficiency of Al and P in sediment following Al-treatment. Longevity of Al-treatment among the studied lakes varied between 7 and > 47 years, which is in line with previous studies where longevity of positive effects lasted from a few months up to 40 years or more (Egemose et al. 2011, Garrison and Knauer 1984, Huser et al. 2011, Huser et al. 2016b, James et al. 1991, Welch and Cooke 1999) (Figures 1, 3, 5, 7, 8 and 9 in Paper I). Using PCA to explore structure and correlations between longevity and in-lake factors together with Al dose revealed structures in the data set that are in line with current understanding. As reported by Huser et al. (2016b), longevity showed positive correlations to Al dose and lake type (Osgood index indicating dimictic versus polymictic) and a negative correlation to WA:LA, meaning that the larger watershed relative to lake

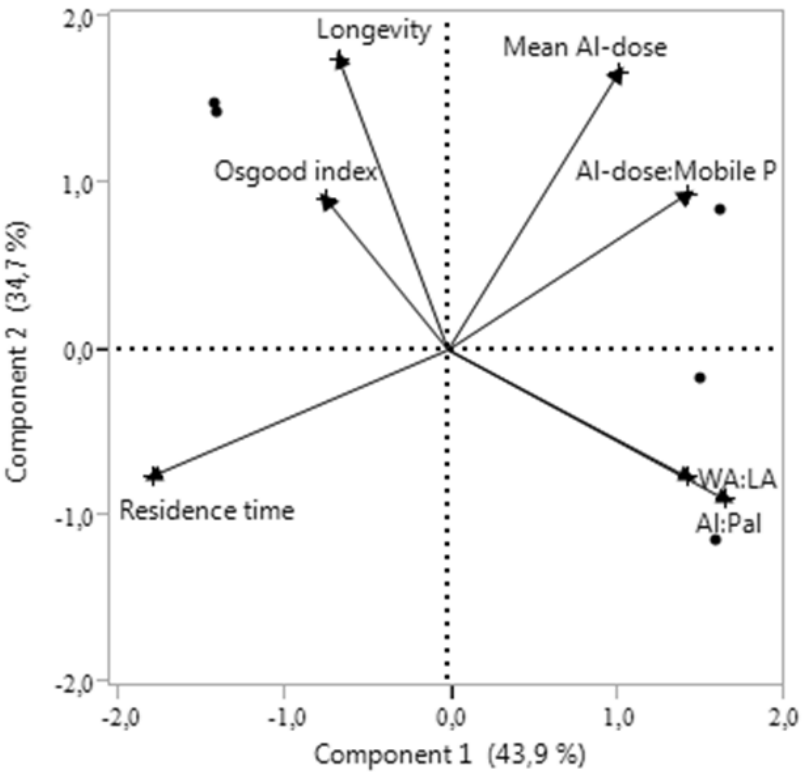

Figure 3. Biplot from principal component analysis on variables from Table 1 (Paper I), explaining 79% of the total variation in treatment longevity.

area, the more important external sources will be on water quality, and vice versa. Binding ratio ($Al:P_{Al}$) had a negative correlation to longevity, i.e. as $Al:P_{Al}$ decreases (binding efficiency increases) the longevity increases (Figure 3). This effect has not been shown previously. It should be noted that PCA does not serve as a tool for prediction, rather it is method of describing structures in a certain data set. Therefore, it is not possible to apply these findings to other lakes, but it is an important tool showing which factors are important or related.

It may seem obvious that binding efficiency is an important factor for treatment longevity, even though this is the first work to show that. The ratio of Al:P_{Al} has been shown to vary by an order of magnitude between different Al-treatments (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). There are several factors that can affect

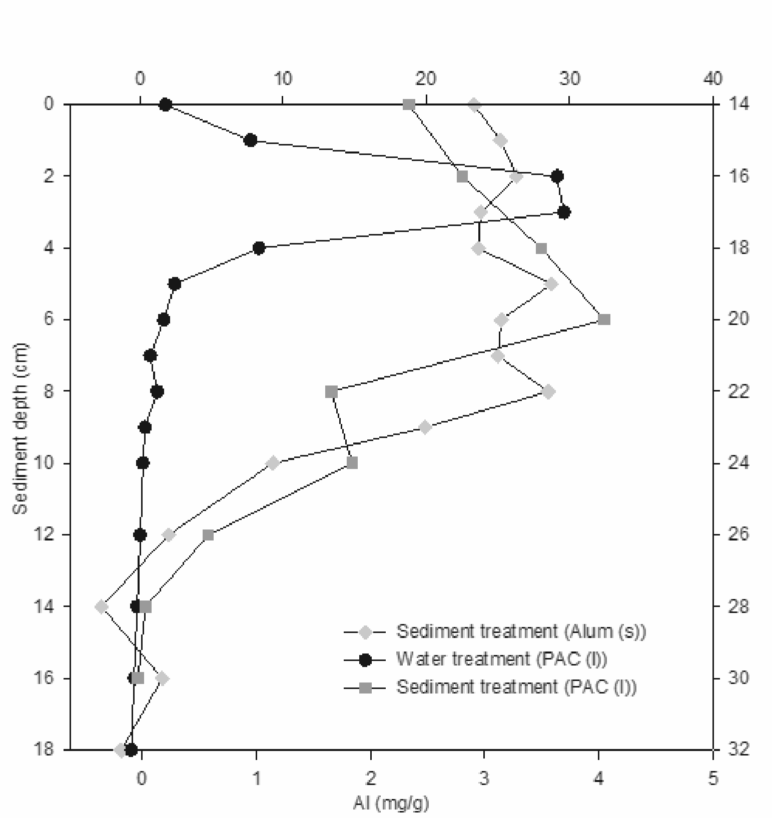

Figure 4. Cores from two lakes where sediment treatment was used are shown. Lötsjön (Sediment treatment, Alum (s)) and Malmsjön (Sediment treatment, PAC (l)). Due to the differences in treatment age, the depth range of Lötsjön (right-hand axis) was adjusted to match the treatment date of Malmsjön (30 years difference in treatment age). Bagarsjön (Water treatment, PAC (l)), where Al was added to the water is shown for comparison.

binding efficiency, such as Al dose and lake morphology, which Huser (2012) described and further developed an Al dosing method based on these factors. Steeply sloping sediment bed slopes resulted in excess accumulation of Al in the deeper parts of the lake, and thus the steeper the slope, the lower the binding efficiency. That study was done on lakes where Al was added to the water column, where the $Al(OH)_3$-floc normally accumulates in surficial sediment layers, and in steep bed slope lakes tends to then be transported to accumulate in deep areas. However, a newly developed Al application method was used for the majority of the lakes studied in this thesis (Paper II) which targets the Al dose directly into the sediment matrix by injecting the Al product (Schütz et al. 2017). For comparison purposes, profiles for Al in lake sediment treated using water and sediment treatment are shown in Figure 4. Our study showed the opposite response compared to previous

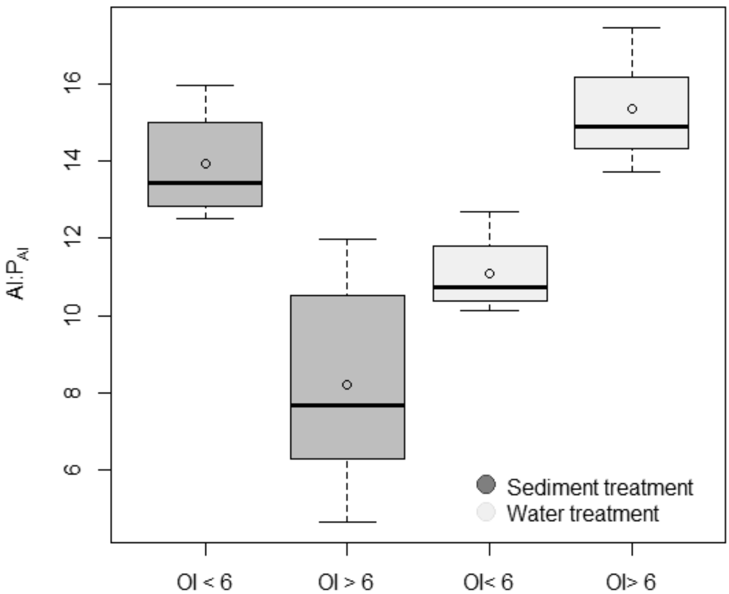

Figure 5. Boxplot showing Al:Al-P or $Al:P_{Al}$ ratios for individual sediment cores grouped by Al-treatment method (sediment vs. water) and lake morphology (Osgood index <6 or >6). Solid lines and circles within the boxplots represents median and mean values, respectively.

work with respect to lake morphology. Steeper sediment bed slopes (Osgood index > 6) increased binding efficiency (Figure 5) to an average of $Al:P_{Al}$ (or Al:Al-P) = 8.2 ± 2.6, whereas gradual bed slope lakes (Osgood index < 6) averaged 13.9±1.4.

This is likely explained by the chance for Al to encounter P before crystallization of the complex reduces P binding sites. As sediment naturally moves down slope towards the deeper parts of lakes, Al injected into the sediment matrix at depth (instead of added to the water and precipitated) constantly relocates within the sediment as it moves naturally, increasing the chance for P binding by Al. Using stepwise multiple linear regression (MLR), a model was developed to refine Al dosing regarding the injection application method of Al where the detected Al dose and the available P_{mob} in the sediment together with lake morphology (Osgood index) explained 87% of the variation for binding efficiency (Figure 6).

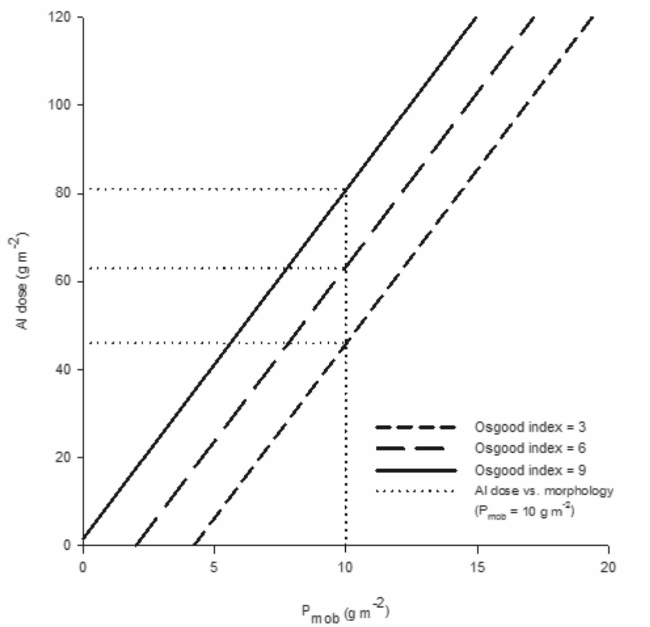

Figure 6. Al dose allowed to achieve $Al:P_{Al}$ = 10 using sediment Al application in three hypothetical lakes with Osgood index at 3, 6 and 9 and a range of sediment P_{mob} mass. Dotted line indicates doses for varying Osgood index with P_{mob} fixed at 10g/m^2. Model equation: Al dose= 1.1 × $Al:P_{Al}$ + 8.2 × P_{mob} + 6.6 × Osgood index.

4.1.2 Which P fractions are mobile?

In order to determine an optimal dose of Al needed to inactivate the targeted amount of P in eutrophic lake sediment for lake restoration, extended knowledge concerning the potential availability of P fractions is needed. Historically, P_{mob} has been accounted for and in some cases P_{org} or $P_{lab.org}$ to constitute the potentially "mobile" fraction of sediment P with respect to P inactivation. However, in this thesis (Paper III) we can show that under some circumstances, another P fraction (P_{Ca}) may be potentially available for release. P fractions in sediment that may become available for release are controlled by the chemical milieu where oxygen state can regulate release of P_{Fe} and mineralization of organic matter can release P_{org} and $P_{lab.org}$. Low and high pH can cause dissolution of P_{Al} and P_{Fe} and low pH can cause dissolution of P_{Ca}, causing release of sediment P.

Bioturbation or sediment mixing caused by benthic feeding fish seems to alter the sediment environment. In paper III we investigated benthic fish bioturbation effects on P fractions and could show that the P_{Ca} fraction, formerly thought to be recalcitrant in field conditions (Andreiux 1997), can be important for internal loading in some cases. When sediment mixing by carp was stopped during the exclosure experiment, the only fraction significantly affected by the absence of bioturbation was P_{Ca}, which increased by 19% (Figure 7). The magnitude of P loss is similar to that found in a study by Kassila et al. (2001) where 22% P_{Ca} loss from sediment was recorded due to pH decrease caused by accelerated mineralization of organic matter in a fish farm environment. As a result of organic matter mineralization, pH can decrease via production of CO_2/H_2CO_3 (Carbonic acid) (Staudinger et al. 1990). It has been shown that already at pH 6, dissolution of P_{Ca} is substantial (Kassila et al. 2001).

However, other P fractions did not significantly change due to exclusion of carp bioturbation, which was unexpected and can probably be explained by the time frame of the study (4 months). In a rather similar field study published by Huser et al. (2021), P_{mob} and P_{org} increased by 45 to 120% and

38% in surficial sediment respectively, but this was shown 9 years after complete removal of carp.

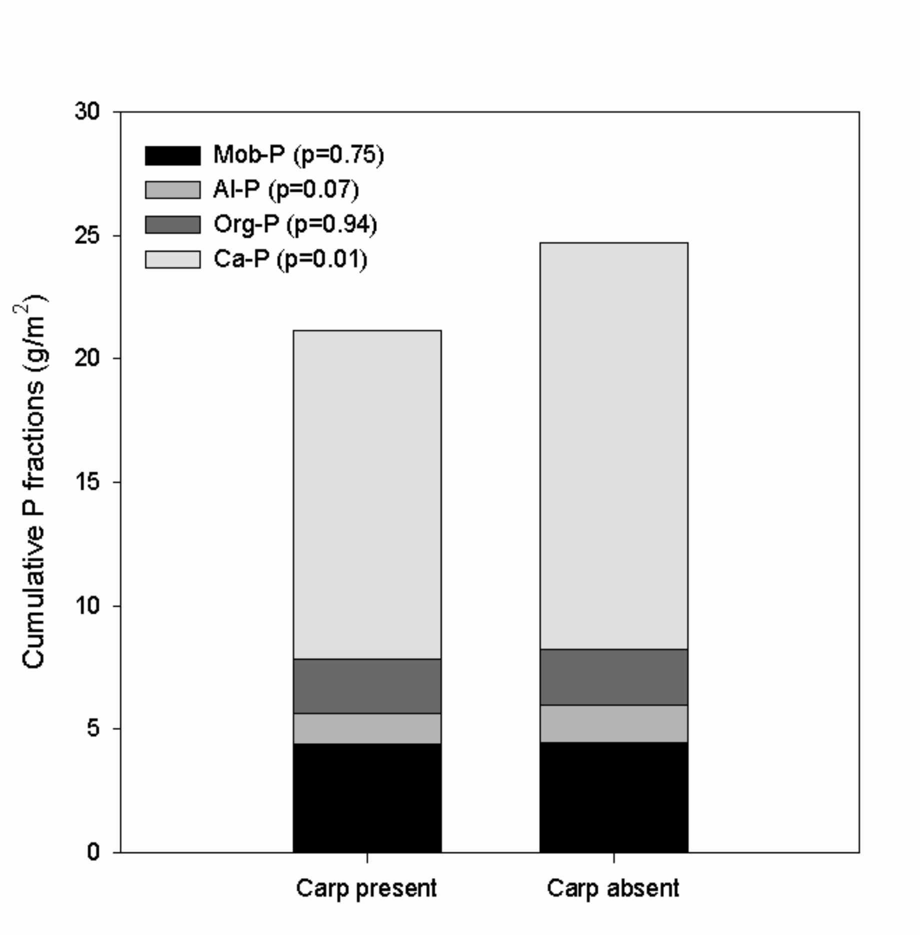

Figure 7. Cumulative amount of sediment phosphorus fractions inside and outside fish exclosures in the upper most 10 cm of sediment profiles with carp present and absent. P-values from Wilcoxon's rank sum test are showed in brackets.

4.1.3 The depth of active sediment due to sediment mixing

In the study behind paper III in this thesis, a new method of sediment mixing determination was applied. Similar to fluorescent sand tracer used in a study

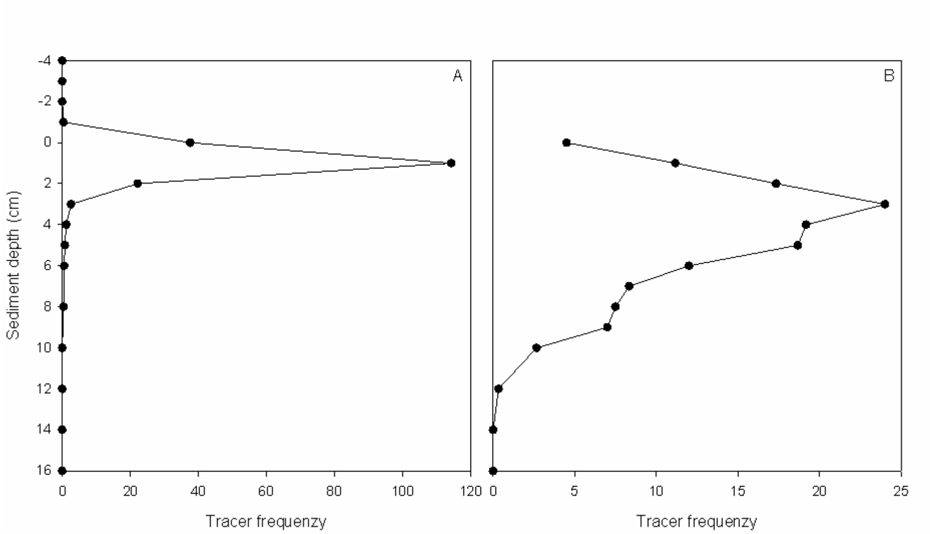

Figure 8. Mean distribution of transparent quartz sand grains (Tracer) found in vertical sediment profiles within fish exclosures (A, Carp absent) and in the pond (B, Carp present). Sediment depth = 0cm represents the original sediment surface level. A sedimentation rate of 4.4±1 cm was determined for the exclosures.

by Ritvo et al. (2004), transparent quartz sand grains were used to create a footprint of benthic feeding fish bioturbation during the growing season when they are most active. The intact sediment cores taken inside and outside the fish exclosures revealed that > 95% of the tracer sand grains were, on average, found in the top 3 cm of sediment depth where fish were excluded, and in the top 10 cm where carp and other fish were present (Figure 8). The sedimentation rate was 4.4 ± 1 cm during the experiment time frame, which is rather high but logical due to the constant mixing of sediment in the pond. Compared to the few studies conducted (to date) concerning sediment mixing depth, our results are intermediate or between those found recently. Ritvo et al. (2004) showed a mixing depth of 3 cm in high density sediment (bulk density = 0.71 g dry sediment/cm^3) with a high biomass of small sized carp (mean weight 650 ± 50 g, biomass density = 7584 kg/ha) in small ponds, whereas (Huser et al. 2016a) found a mixing depth of up to 15 cm with large bodied carp but lower overall biomass density (mean weight = 3.4 kg, 180 kg/ha) in low density sediment (dry bulk density = 0.16 g/m^3). In the

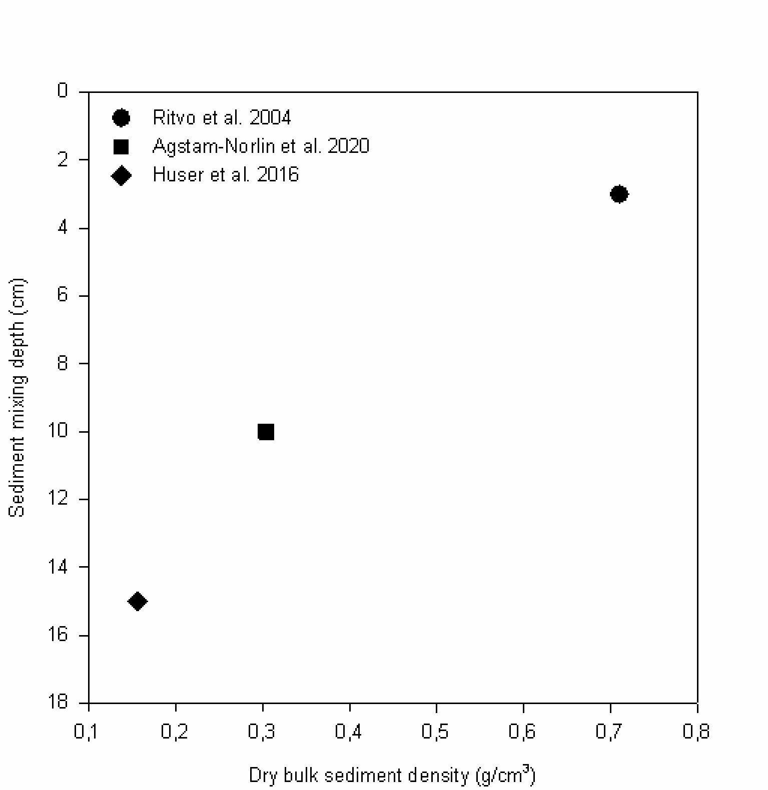

Figure 9. Graphic visualization of mean mixing depth and mean dry bulk sediment density (g/cm^3) from three available studies regarding sediment mixing depth caused by benthic fish.

sediment sampled as part of the study presented in paper III, the dry bulk density was 0.30 g/cm^3, which is intermediate compared to the other studies. Even though only three studies are available for comparison, a comparison of mixing depth versus sediment density is clear, whereas biomass (kg/ha) did not follow any pattern (Figure 9). As stated above, there is very little information on sediment mixing depth and the potential effects of carp biomass, fish size or sediment density. Therefore, further research in this subject is clearly needed to be able to understand benthic feeding fish effects on sediment mixing depth, in addition to sediment P release.
However, it seems highly likely that benthic feeding fish cause increased sediment mixing depth and consequently a larger potential mass of sediment and P that is exposed and connected to the water column. Huser et al. (2016a) showed that nearly twofold (up to 92%) more P_{mob} was potentially available

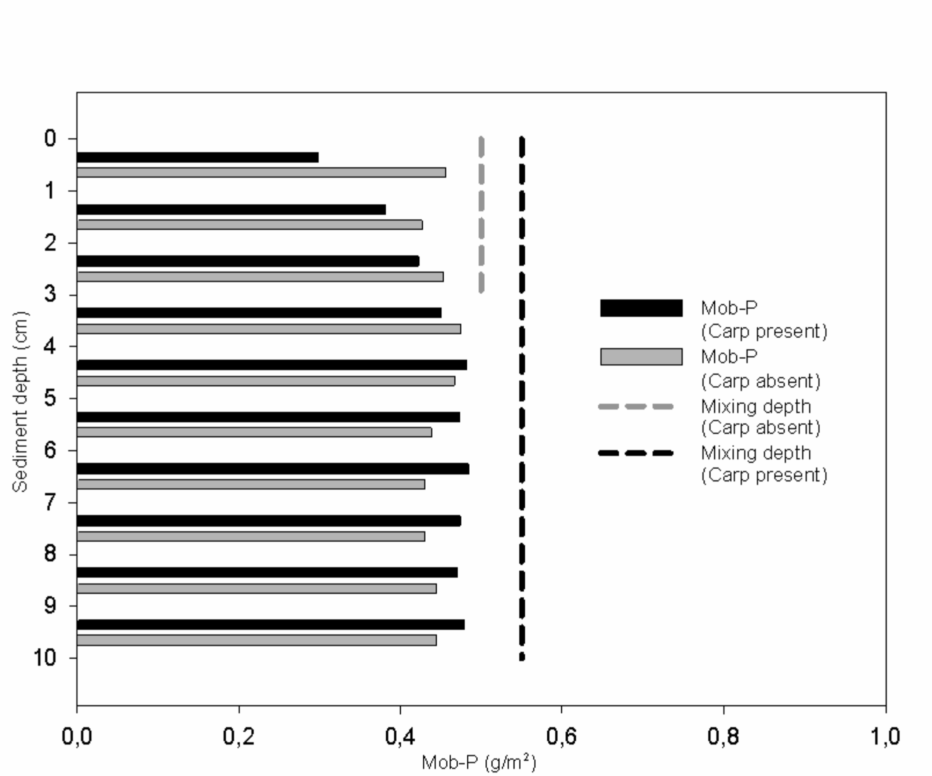

Figure 10. Mobile phosphorus in each layer of sediment inside and outside fish exclosures. Dashed lines indicate mixing depth (active sediment depth).

for internal loading from sediment in a field study of carp in the US. Herein we showed that in our study system, the potentially available P_{mob} pool increased by almost threefold due to increased sediment mixing depth (Figure 10). Whether the increased potential for internal P loading, caused by increased mass of sediment P exposed or connected to the water column, has any actual effect on in-lake P cycling has not yet been quantified, however likely it seems. Therefore, more research is needed in this area as well. Knowledge about the forms and mass of P in sediment, sediment density, and the effects of bioturbation/sediment mixing on these and how they affect a water body is crucial, both for understanding in-lake P dynamics as well as assessing the appropriate restoration tools needed for successful lake restoration.

5. Conclusions and outlook

The work in this thesis, together with our current understanding about lake restoration using Al, strengthens the knowledge base regarding controlling factors with respect to longevity and efficiency of treatment. Al dose has earlier been suggested to control the success of Al-treatment, and we confirmed this by showing how Al dose is a crucial factor to consider when restoring lakes using Al-treatment in Swedish lakes. The magnitude of P decrease in surface water immediately after treatment, and the longevity of positive treatment effects over time increased with the amount of Al added to a certain lake. However, variability of effectiveness and longevity, even when higher doses have been used, can occur due to other in-lake factors controlling Al-treatment success, such as variation in fish species community and binding efficiency. We showed that benthic feeding fish, such as carp, increase the amount of P potentially available for release from sediment to water by increasing the active sediment layer by up to threefold. In such cases, an Al dose might need to be adjusted due to a larger pool of available P. Additionally, we showed that P_{Ca}, previously thought to be recalcitrant, can be affected by bioturbation (sediment mixing), causing release of P from Ca potentially resulting in P released to lake water. Further research in the area of bioavailability of recalcitrant P forms (i.e. P_{Ca}) is highlighted since the immobility, in certain conditions, of such P forms is now questioned.

Apart from Al dose being an important factor controlling treatment effectiveness and longevity, we showed that the method of Al application used might also control the efficiency of binding between Al and P. Among the lakes studied in Paper II, we found that binding efficiency has a strong effect on treatment longevity. For lakes with steeply sloping sediment beds, where $Al(OH)_3$-floc transport to deeper areas is suspected, we found that by injecting Al into the sediment matrix, instead of applying it to the water that has been done historically, that the binding efficiency increased, making this novel application method more efficient in certain lakes. Variation in binding efficiency was also explained by the amount of P_{mob} available in the sediment relative to the amount of added Al, where sediment containing larger amounts of P_{mob} with the same Al dose were found to have greater binding efficiency (e.g. Le Chateliers principle).

To increase the chance for successful and sustainable lake restoration, it is essential to understand which forms of P are available under varying conditions. How to quantify the total pool of potentially releasable/available sediment P is key. This can include forms of P that have earlier been regarded as recalcitrant as we showed in Paper III. Further, the Al dose needs to be large enough to inactivate this pool of P, but not in excess, which can lead to low binding efficiency. With the use of our model, it is now possible to design a maximum Al dose that can be added to achieve a certain binding efficiency. This may result in multiple, smaller Al-treatments, instead of the entire dose being added at once, which is an ongoing practice. Even the choice of application method should be considered carefully. Depending on lake characteristics, the operational technique for Al application should be selected in order to maximize binding efficiency (Paper II), which together with other factors is tightly connected to efficiency and longevity of Al-treatment (Paper I). The overall results from this study advance our knowledge on sediment P forms and Al-treatment application methods which should increase the chances for sustainable lake restoration in the future.

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Popular science summary

The natural environment provides ecosystem services for us that are important to protect. Especially water, the foundation of life. We need to have access to drinking water, some of us find pleasure in having a swim in a clean lake and many people eat fish as part of their diet. In some lakes such services have been impaired due to decades of phosphorus input, leading to eutrophication. Even if the external inputs of phosphorus are controlled by factors like better wastewater treatment and restored wetlands, most lakes do not recover naturally. This is because decades of excess phosphorus inputs to lakes have accumulated in the lake´s sediment. Over the season, this P is released from the sediment to the water column, creating a vast supply of fuel (phosphorus), which causes algal blooms that in turn degrade water quality. Dead bottoms with no oxygen and fish kills are some symptoms of this process. However, there are methods that can be used to restore lake water quality in such situations. One method is to inactivate phosphorus in the sediment with minerals in order to cancel the fuel driving eutrophication. Aluminum treatment has been used for decades for this purpose, and has sometimes shown great effect. This thesis explores and develops knowledge in how to use this restoration tool in the most efficient manner. Both expanding knowledge in practical Al application procedures, but also expanding the knowledge about what types of phosphorus can be released from the sediment and cause problems. Further it contributes to the knowledge about factors influencing how long an aluminum treatment will last. By adding the aluminum mineral directly into the sediment matrix, instead of adding it to the water (the traditional method), treatment efficiency can be increased in certain lake types. Taking into account factors affecting longevity and efficiency of treatment, such as aluminum dose, the amount of mobile sediment phosphorus, presence of bottom feeding fish, and lake type it is possible to optimize the effect of this restoration tool. The knowledge gained in the studies included in this thesis will lead to more effective and sustainable lake restoration in the future.

Populärvetenskaplig sammanfattning

Sjöar tillhandahåller en mängd ekosystemtjänster som är viktiga för oss människor. Från sjöar med klart och rent vatten får vi ekosystemtjänster såsom möjligheten att hämta dricksvatten och rekreation i form av att kunna ta en simtur eller att äta en egenfångad fisk till middag. I en del sjöar har dessa ekosystemtjänster försämrats på grund av kontinuerlig tillförsel av fosfor (P) under flera decennier. Fosfor utgör bränsle för växtplankton bland annat, vilket ger upphov till övergödda sjöar med bland annat algblomningar som följd. I de sjöar där fosfor ansamlats i bottensedimentet under decennier hjälper det oftast inte att tillförseln av fosfor åtgärdas, genom exempelvis förbättrade avlopp, på grund av den fosfor som under lång tid ansamlats i sjöns bottensediment. I dessa fall kan man oftast räkna med att sjöarna inte tillfrisknar naturligt inom en rimlig tidsram eftersom den fosfor som ansamlats i sedimentet frigörs från bottensedimentet till sjöns vattenmassa. I sådana situationer finns det restaureringsmetoder som kan användas för att förbättra vattenkvaliteten. Denna avhandling utvecklar kunskapen om hur verktyg för sjörestaurering kan användas på bästa sätt. Ett sätt att inaktivera det överskott av fosfor som finns i sedimentet är att tillföra aluminum (Al) som binder fosfor och gör det otillgängligt för exempelvis växtplankton. Så kallad Al-behandling har använts i över 50 år och har visat sig vara effektivt. Kunskapsbasen om hur man effektiviserar Al-behandlingen med avseende på den praktiska appliceringsmetoden utökas. Även vetskapen om vilka former av fosfor som bör inaktiveras förbättras. En kunskapsutökning angående faktorer som påverkar varaktigheten och effektiviteten av Al-behandlingen presenteras i denna avhandling. Genom att använda en appliceringsmetod där Al harvas ner direkt i bottensedimentet, istället för att Al tillförs till vattenmassan, kan vi öka effektiviteten av aluminiumbehandlingen i sjöar med brant sluttande sedimentbottnar. Denna avhandling visar även att det är viktigt att rätt mängd Al används till en viss mängd P och att vissa former av fosfor som tidigare ansetts som immobila, under vissa förutsättningar kan bli mobila och borde inkluderas i de beräkningar av mängden fosfor som en viss aluminiumdos ska inaktivera. Effektiviteten kan även ökas genom att anpassa aluminiumdosen med avseende på tillgängligt mobilt fosfor i sedimentet.

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A 25-year retrospective analysis of factors influencing success of aluminum treatment for lake restoration

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ABSTRACT

For more than 50 years, aluminum (Al)-salts have been used with varying degrees of success to inactivate excess mobile phosphorus (P) in lake sediments and restore lake water quality. Here, we analyzed the factors influencing effectiveness and longevity of Al-treatments performed in six Swedish lakes over the past 25 years. Trends in post-treatment measurements of total phosphorus (TP), Chlorophyll a (Chl_a), Secchi disk depth (SD) and internal P loading rates (Li) were analyzed and compared to pre-treatment conditions. All measured water quality parameters improved significantly during at least the first 4 years post-treatment and determination of direct effects of Al-treatment on sediment P release (Li) was possible for three lakes. Improvements in TP (-29 to -80%), Chl_a (-50 to -78%), SD (7 to 121%) and Li (-68 to -94%) were observed. Treatment longevity, determined via decreases in surface water TP after treatment, varied from 7 to >47 years. Lake type, Al dose, and relative watershed area were related to longevity. In addition, greater binding efficiency between Al and P was positively related to treatment longevity, which has not previously been shown. Our findings also demonstrate that adequate, long-term monitoring programs, including proper determination of external loads, are crucial to document the effect of Al-treatment on sediment P release and lake water quality.

1. Introduction

Excess internal loading of phosphorus (P) in lakes, a result of historical sediment P accumulation from external sources, is often the most important driver of in-lake P cycling and thus eutrophication (e.g. Pilgrim et al., 2007, Sondergaard et al., 2003). External P sources, e.g., leaching from agricultural soils and municipal/industrial wastewater are the primary source of excess nutrients in lakes (Conley et al., 2009). Even when external nutrient sources are controlled, recovery can be delayed by decades or longer due to the release of legacy (or mobile) P from lake sediments (Sas 1990). For more than 50 years, aluminum (Al)-salts have been used to permanently inactivate excess mobile P in lake sediments and restore lake water quality (Huser et al., 2016b; Welch and Cooke 1999). The longevity of Al-treatment, however, has been highly variable, with beneficial effects lasting from just a few months to more than 40 years (Egemose et al., 2011; Garrison and Knauer 1984; Huser et al., 2011; Huser et al., 2016b; James et al., 1991). Reported binding effectiveness (measured as Al:Al-P or Al:P_{Al} ratios) has varied by an order of magnitude, i.e., between 2.1 and 21.1 (Agstam-Norlin et al., 2020; 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).

Treatment longevity and effectiveness are influenced by multiple factors including external loading, lake morphology, mixing regime, bioturbation, Al dose, and application method. When external P loading remains elevated after Al-treatment, ongoing P inputs can overwhelm Al binding capacity, resulting in new mobile sediment P accumulation over the treated layer and elevated internal P loading (Huser et al., 2016c). The ratio of lake to watershed areas (WA:LA) is an important predictor of treatment longevity, as nutrient levels in lakes with large watersheds relative to lake area are more controlled by external sources than lakes with relatively small watersheds (Huser et al., 2016b; Sas 1990). The rate of water renewal (i.e. residence time) can strongly affect treatment longevity, as a long residence time can result in P being retained in the lake and sediment instead of moving to downstream water bodies (Sas 1990).

Morphology can decrease overall binding efficiency in lakes with steep bed slopes through translocation and focusing of the added Al-mineral ($Al(OH)_3$) in deep areas. This is because freshly

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formed, amorphous Al-minerals have a similar density to the surrounding, organic-rich sediment and a large fraction can rapidly (within 6 months) move down-slope to deeper areas (Huser 2017). This can result in excess accumulation of Al (Egemose et al., 2012; Huser 2012), and in the absence of available P, the Al-mineral starts to crystalize resulting in a lower surface area and a loss of P binding sites (Berkowitz et al., 2006; deVicente et al., 2008; Huser 2012; Huser 2017).

The Al dose used is another critical factor influencing longevity and effectiveness. In the past, Al doses were often inadequate to bind all potentially releasable sediment P. This was usually a result of old dosing calculation methods where dose was based on lake water alkalinity or hypolimnetic P instead of targeting the total pool of available mobile P in lake sediment (Cooke et al., 2005). Greater Al doses tend to bind more P in the sediment, which can increase longevity (Huser et al., 2016b; Sas 1990). However, adding too much Al, or using excessive amounts of Al in one application, will generally decrease binding efficiency due to crystallization of the Al-mineral before P binding occurs (deVicente et al., 2008), with potentially negative effects on longevity (Agstam-Norlin et al., 2020; Huser 2012).

Mixing regime is also important. Shallow, polymictic lakes tend to have shorter treatment longevity (Huser et al., 2016b; Welch and Cooke 1999), but the underlying mechanisms behind this are not entirely understood. Shallow lakes generally have lower water volume per area of sediment, and thus alkalinity needed to support higher doses is often lower and as a consequence, lower Al-doses have generally been added which per se decreases longevity (Huser et al., 2016b). Dense populations of macrophytes often found in shallow polymictic lakes may increase internal loading by translocation of sediment P to the water column (through plant decomposition) or by stabilizing the water column and limiting oxygenation, thus increasing the potential for internal loading (Welch and Kelly 1990). In addition, benthic feeding fish often have much greater negative impacts on nutrients and water quality in small shallow lakes relative to deeper, stratified systems (Bajer and Sorensen 2014).

Bioturbation caused by benthic feeding fish, e.g., carp (*Cyprinus carpio)* can deepen the active sediment layer and mass of P available for release to the water column (Huser et al., 2016a), especially in shallow polymictic lakes (Parkos et al., 2003; Weber and Brown 2009). On the other hand, enhanced sediment mixing by benthic feeding fish may result in higher Al:P_{Al} binding efficiency by increasing the chance of Al to encounter P before crystallization of the mineral occurs (Huser et al., 2016a).

Different Al-application procedures have been used historically, with the most commonly used method being application of Al in solution to the water column and allowing the newly formed mineral to settle to the sediment surface (Welch and Cooke 1999). However, there is a newly developed technique where Al is injected into surficial sediment (10–15 cm deep, (Schütz et al., 2017)). The injection method minimizes Al transport and focusing because the Al-floc is trapped in the vertical sediment profile, which can lead to improved binding efficiency (Agstam-Norlin et al., 2020). Solid forms of Al (pellets) have also been used historically (Cooke et al., 2005), but a shift to liquid application occurred after the 1970s. However, binding effectiveness using pellets may be greater relative to liquid application in some cases (Agstam-Norlin et al., 2020). Treatment using Al pellets has been tested recently in countries lacking equipment needed for liquid application (Kuster et al., 2020).

Here, we determined the longevity of Al treatment and assessed the factors influencing effectiveness and longevity of Al-treatment using available monitoring data for six Swedish lakes of varying size, morphology, Al dose applied, and application technique (Table 1). Nutrient-related water quality variables including historical trends for surface water chemistry/quality were analyzed. Internal P release rates were calculated pre- and post-treatment when adequate data were available.

2. Methods

2.1. Study sites

Additional information about all study sites, including locations, is presented in Agstam-Norlin et al. (2020).

2.1.1. Dimictic lakes

Six lakes situated within a 30 km radius of Stockholm city were included in the study. Flaten is a 63 ha lake with a 403 ha catchment mostly covered by forest and recreational areas (70%). Al-application was performed in 2000 with combined sediment injection and hypolimnetic water application using a total of 24 tons of Al (as pre-hydrolyzed aluminum chloride (PAC, PAX XL100). Areas of the lake where water column depth was between 6 and 9 m were treated with 30 g/m^2 Al injected into the sediment and additionally 10 g/m^2 dispersed in the water near the sediment water interface. Deeper areas (9–10 m) were dosed with 40 g/m^2 via sediment injection and 14 g/m^2 to the water. At the deepest point of the lake (10–14 m) 53 g/m^2 was injected and 17 g/m^2 added to the water (Table 1). Partial water application was conducted to precipitate P already released from sediment.

Trekanten is 13.5 ha lake with a catchment of 60 ha dominated by urban park areas. Al-treatment was performed in 2011 using

Table 1
Background information including morphology, sediment characteristics and aluminum treatment details. Al-treatment method includes sediment treatment (S) and water treatment (W). Sediment data reworked from Agstam-Norlin et al. (2020), with permission.

Lake	Lejondalssjön	Flaten	Trekanten	Långsjön	Bagarsjön	Malmsjön
Max depth (m)	14.0	13.1	6.6	3.3	5.6	6.8
Mean depth (m)	7.5	8.7	3.6	2.2	2.3	4.7
Lake area (ha)	272	63	14	29	6	89
Osgood index	4.6	11.0	9.5	3.7	8.8	5.0
Watershed (ha)	1660	403	60	243	135	1175
Watershed:Lake area (WA:LA)	6.1	6.4	4.3	8.4	22.5	13.2
Volume (Mm^3)	20.5	4.6	0.6	0.6	0.2	4.2
Residence time (years)	7.0	4.0	3.0	0.8	0.8	1.3
Mean Al dose (g/m^2)	25	61	60	75	50	60
Treatment year(s)	1991–1993	2000	2011	2006	1997	2007
Al-treatment method	W	S	S	S	W	S
Treatment chemical	PAX XL60	PAX XL 100	PAX XL 100	PAX XL100	PAX XL 60	PAX XL 100
Mean Al:P_{Al}	11.4	9.0	10.7	12.9	16.0	14.6
Mean Mob-P (g/m^2)	7.3	4.9	8.6	2.8	5.3	3.5
Al dose:Mob-P	3.4	12.4	7.0	21.4	9.4	16.9

sediment injection of PAC (PAX XL 100). 60 g Al/m^2 was applied to all lake areas where water depth was > 4 m, with a total Al dose of 5 tons (Table 1).

Lejondalsjön has a surface area of 272 ha with a catchment of 1660 ha that is dominated by forest (58%), agriculture (crop- and pasture fields, 16%), and urban areas (2%). Al-treatment was performed during three consecutive years where a total of 28.6 tons of Al (as PAC, PAX XL 60) was applied to the hypolimnetic lake water. In 1991, a relatively low Al dose (10 g/m^2, total of 5 tons) was applied to the northern half of the lake where water depth was >10 m. In 1992, three small test areas of the northern part of the lake (total 12 ha) were treated with a total Al dose of 0.6 tons but with different areal doses (25, 50 and 75 g/m^2). The final PAC application in 1993 treated areas with water column depths exceeding 10 m (25 g/m^2, Table 1).

Bagarsjön is an urban, 6 ha lake with a catchment area of 135 ha that includes mainly residential (80%) and small park/forest areas. Al (as PAC, PAX XL 60) was applied in the hypolimnetic water at a total of 2 tons at a rate of 50 g/m^2 to areas with water depths greater than 2 m (Table 1).

2.1.2. Polymictic lakes

Långsjön is a 29 ha urban lake. The 243 ha catchment is mainly residential with some recreational areas. Al (PAC, PAX XL100) was applied by direct sediment injection with different doses for different depth zones of the lake. A dose of 25 g/m^2 was applied at water column depths between 1.5 and 2 m, 50 g/m^2 at water column depths between 2 and 2.5 m, and 75 g/m^2 from a water depth of 2.5 m to the maximum depth (3.3 m, Table 1).

Malmsjön is an 89 ha lake in an 1175 ha catchment dominated by forest (57%), farmland (23%), and urban areas (11%). In total, 53 ton of Al (PAC, PAX XL100) was applied using sediment Al injection. The area specific Al dose was 60 g/m^2 at all lake locations with a water column depth exceeding 1 m (Table 1).

2.2. Data handling

Average, annual growing season (May-Aug) TP, Chlorophyll a (Chl_a), and Secchi disk depth (SD) were used to describe differences in surface water quality between pre- and post-treatment periods. In stratified lakes, the increase in hypolimnetic TP during the growing season and corresponding hypolimnetic water volumes were used to calculate internal P loading rates (Li, $mg/m^2/day$) (Nürnberg 2009). A 4-year pre-treatment period of annual means for SD, Chl_a, surface TP, and Li were compared with following post treatment 4-year periods to compare whether the parameters had changed due to Al-treatment. Four-year periods were used in order to limit the effect of natural interannual variation.

Longevity was estimated using three different methods. For lakes where longevity had been reached (i.e. no improvement was detected compared to pre-treatment after a period of time), longevity was defined as the year when annual mean (or single August data point, when seasonal data was lacking) TP concentration exceeded one standard error of mean (SEM) below mean pre-treatment TP (4-year period). For lakes where water quality improvements were still ongoing throughout the monitoring period (e.g., Malmsjön, Långsjön and Bagarsjön), but TP showed a linear increase post Al-treatment, we estimated longevity using linear regression and extrapolation. Longevity was estimated as the time point where the linear regression exceeded one SEM below pre Al-treatment mean TP (4-year period). Finally, the longevity predicting equation (LPEq) of Huser et al. (2016b) was used to estimate treatment longevity in cases where there was no deterioration of post-treatment water quality through the end of the dataset (Eq. (1)). Three variables described 82% of the variation in Al-treatment longevity in Eq. (1), including Al dose, watershed area to lake area ratio (WA:LA) and Osgood index (Osgood 1988). It should be noted that this method for calculating longevity is almost certainly an underestimate as the regression developed weighted lakes highest where no external nutrient reduction occured. In addition, longevity predicted using LPEq has an arbitrary endpoint (i.e., longevity is considered to end when surface TP is 50% of the pre-treatment value), and thus is not a true representation of longevity of positive treatment effects.

$$\log(\mathit{Longevity}) = -0.5 + 1.3 \times \log(\mathit{Al\ dose}) - 0.79 \times \log(\mathit{WA} : \mathit{LA}) + 0.37 \times \log(\mathit{Osgood\ index}) \quad (1)$$

Graphical exploration for effect size was used to evaluate effect and longevity of Al-treatment and Principal component analysis (PCA) was used to evaluate driving factors for longevity. All statistical analyses was performed in JMP (SAS institute Inc., version 11.0.0).

3. Results

Nutrient-related water quality variables improved after Al-treatment in all lakes (Table 2). Flaten, Långsjön, Lejondalssjön, Bagarsjön and Malmsjön had changes in all measured water quality variables during the first 4 years after Al-treatment, whereas

Table 2
Mean, standard error and percent change for each post 4 year period compared to pre aluminum treatment conditions. Pre denotes parameter mean values of a 4-year period prior to treatment. Following columns shows similar information for 4-year periods post Al-treatment (e.g. 1–4 y). Column "Δ" denotes the percent change in each parameter. TP and Chl a in µg/L, SD in meters and Li in $mg/m^2/day$. N denotes mean annual observations (Li: mean number of TP observations below hypolimnion).

Lake	Parameter	Pre	1–4 y	Δ	5–8 y	Δ	9–12 y	Δ	13–16 y	Δ	17–20 y	Δ	N
Bagarsjön	SD	2.2 ± 0.4	3.5 ± 0.4	59%	3.1 ± 0.3	41%	2.5 ± 0.3	14%	2.7 ± 0.2	23%	3.0 ± 0.2	36%	1
	TP	60.3 ± 9.1	24.8 ± 4.4	−59%	37.3 ± 1.4	−38%	43.0 ± 2.5	−29%	23.8 ± 2.5	61%	20.8 ± 2.4	−66%	1
Flaten	SD	2.9 ± 0.4	6.4 ± 0.4	121%	6.3 ± 0.5	117%	4.8 ± 0.5	66%	5.5 ± 0.4	90%	*ND*	*ND*	4
	Chl a	12.7 ± 2.8	2.8 ± 0.3	−78%	3.2 ± 0.6	−75%	5.4 ± 1.0	−57%	4.7 ± 1.0	63%	*ND*	*ND*	4
	TP	33.3 ± 5.6	9.2 ± 0.4	−72%	8.9 ± 0.6	−73%	9.5 ± 0.6	−71%	11.0 ± 1.6	67%	*ND*	*ND*	4
	Li	3.4 ± 0.4	0.2 ± 0.1	−94%	0.2 ± 0.1	−94%	0.3 ± 0.1	−91%	0.3 ± 0.1	91%	*ND*	*ND*	19
Lejondalssjön	SD	2.9 ± 0.3	4.4 ± 0.2	52%	4.3 ± 0.2	48%	4.1 ± 0.2	41%	*ND*	ND	*ND*	*ND*	4
	TP	35.3 ± 2.6	25.0 ± 1.4	−29%	27.2 ± 2.7	−23%	24.0 ± 1.4	−32%	*ND*	ND	*ND*	*ND*	4
	Li	5.0 ± 0.5	1.6 ± 0.4	−68%	2.9 ± 1.0	−42%	3.7 ± 0.2	−26%	*ND*	ND	*ND*	*ND*	11
Långsjön	SD	0.9 ± 0.1	1.5 ± 0.1	67%	1.6 ± 0.1	78%	1.7 ± 0.1	89%	ND	ND	*ND*	*ND*	7
	Chl a	53.6 ± 7.5	22.7 ± 2.4	−58%	17.0 ± 4.9	−68%	16.4 ± 2.6	−69%	ND	ND	*ND*	*ND*	4
	TP	97.5 ± 5.7	33.3 ± 1.6	−66%	38.2 ± 3.1	−61%	46.5 ± 2.6	−52%	ND	ND	*ND*	*ND*	4
Malmsjön	TP	96.5 ± 25.6	19.3 ± 3.3	−80%	28.8 ± 4.5	−70%	43.8 ± 8.7	−55%	ND	ND	ND	*ND*	1
Trekanten	SD	3.0 ± 0.2	2.8 ± 0.2	−7%	3.6 ± 0.2	20%	*ND*	ND	*ND*	ND	*ND*	*ND*	4
	Chl a	14.4 ± 2.6	7.2 ± 0.8	−50%	5.9 ± 0.8	−59%	*ND*	ND	*ND*	ND	*ND*	*ND*	5
	TP	53.1 ± 7.0	24.3 ± 2.5	−54%	23.4 ± 1.4	−56%	*ND*	ND	*ND*	ND	*ND*	*ND*	5
	Li	3.3 ± 0.9	0.2 ± 0.	−94%	0.1 ± 0.1	−97%	*ND*	ND	*ND*	ND	*ND*	*ND*	12

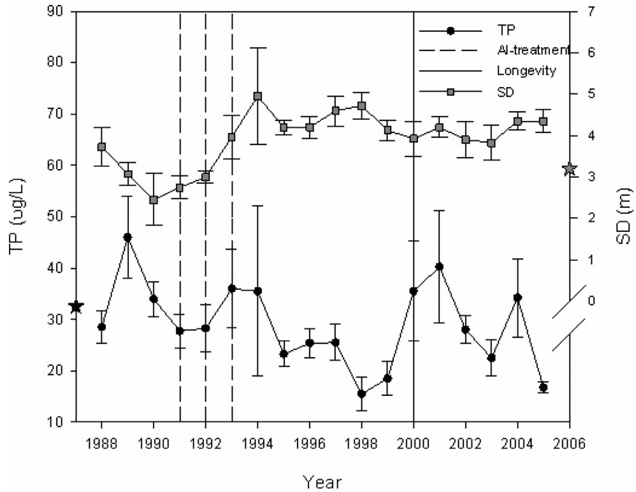

Fig. 1. Annual growing season surface water TP and SD mean and SEM (May-Aug) in Lejondalssjön. Longevity was estimated as the year when one SEM below mean pre-treatment (4-year period) was exceeded by annual post-treatment mean TP. Stars with corresponding color to time series at each Y-axis indicate one SEM below (or above for SD) mean for years before Al-treatment. Observations: SD=70, TP=74.

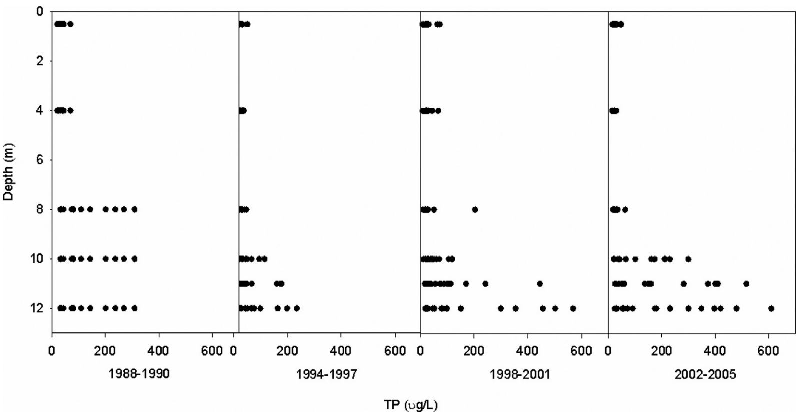

Fig. 2. Water column depth profiles showing concentrations of TP at different depth intervals in Lejondalssjön. 1988–1990 represents pre Al-treatment and following consecutive 4-year period represents post-treatment observations of TP. Pre-treatment data was collected as mixed water samples collected between 0 and 4 m, and 8–12 m. Post-treatment observations was collected at stated depths according to the graph. Observations: 1988–1990=62, 1994–1997=90, 1998–2001=95, 2002–2005=96.

Trekanten showed no initial increases in SD, but TP declined substantially (Table 2). Flaten, Långsjön, Malmsjön and Trekanten had changes in all measured water quality variables at the end of each available data series (16, 12, 12 and 12 years post treatment, respectively). Lejondalssjön had improved TP until 7 years post treatment and showed deeper SD throughout the monitoring period (Table 2).

3.1. Dimictic lakes

3.1.1. Lejondalssjön

TP decreased by 29% from 35.3 to 25.0 µg/L (mean values) during the first 4 year post-treatment. During the second post-treatment 4-year period the annual TP mean exceeded the pre-treatment breaking point (one SEM below annual TP mean) and longevity of the TP decline was 7 years (Table 2, Fig. 1). Li decreased as well, from a mean of 5.0 to 1.6 mg/m^2/day (68%) over the first 4-year period post Al-treatment, but during subsequent 4-year periods the Li rate started to return to pre-treatment conditions (2.9 mg/m^2/day) (Table 2, Fig. 2). A SD increase of >40% was sustained throughout the available data series, from an average of 2.9 m before treatment to an average of 4.1 m at the end of the data series (12 years post treatment).

3.1.2. Flaten

Surface TP averaged 33.5 µg/L before treatment and decreased to 9.2, 8.9, 9.5 and 11.0 µg/L during subsequent consecutive 4-year periods (4, 8, 12 and 16 years post-treatment), meaning the longevity of treatment with respect to surface water TP exceeded the end of this study. There was a decrease Chl_a, with con-

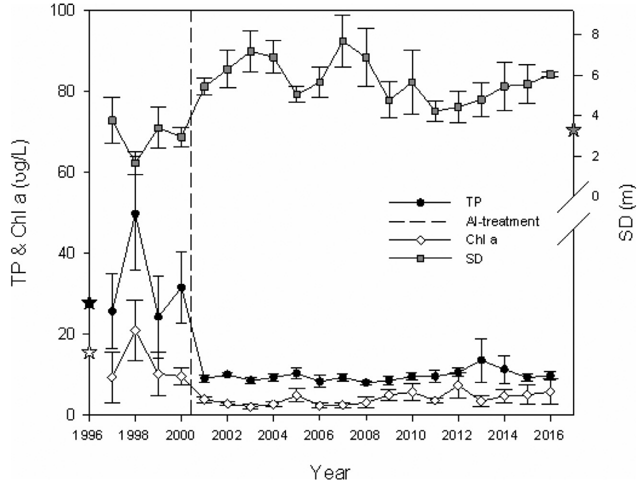

Fig. 3. Annual growing season surface water TP, Chl a and SD mean and SEM (May-Aug) in Flaten. Longevity was estimated using LPEq. Stars with corresponding color to time series at each Y-axis indicate one SEM below (or above for SD) mean for years before Al-treatment. Observations in total time series: Chl a = 85, SD=88, TP=77.

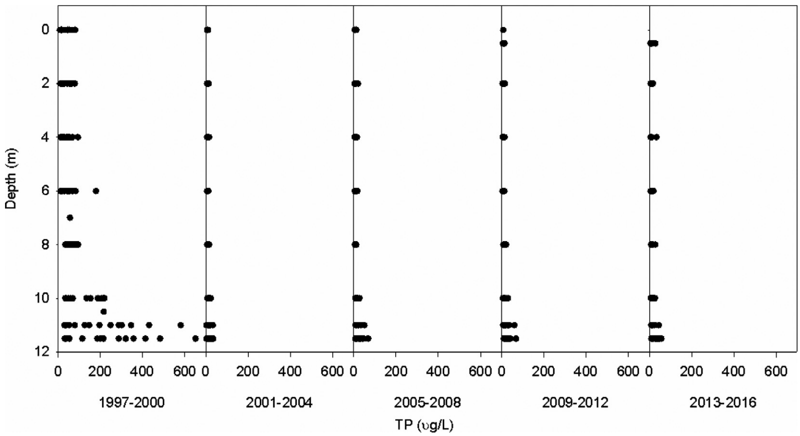

Fig. 4. Water column depth profiles showing concentrations of TP at different depth intervals in Flaten. 1997–2000 represents pre Al-treatment and following consecutive 4-year periods represents post-treatment observations of TP. Observations: 1997–2000=150, 2001–2004=125, 2005–2008=129, 2009–2012=129, 2013–2016=120.

centrations declining from a pre-treatment mean of 12.7 µg/L to 2.8, 3.2, 5.4, and 4.7 µg/L respectively for 4, 8, 12 and 16 years post-treatment. SD significantly improved as well, increasing from a pre-treatment mean of 2.9 m to 6.3, 6.4 4.8, and 5.5 m during 4, 8, 12 and 16 years post-treatment. Due to continued improvement of all nutrient related water quality variables (Fig. 3) throughout the duration of monitoring, treatment longevity could not be calculated but was instead estimated using LPEq to 37 years (Huser et al., 2016b). Li decreased (90%) for all available post-treatment data, with a pre-treatment mean of 3.4 mg/m^2/day and post-treatment averages were all below 0.3 mg/m^2/day (Table 2, Fig. 3 and 4).

3.1.3. Trekanten

Pre-treatment TP averaged 53.1 µg/L and decreased to a mean of 24.3 µg/L during the first 4-years post treatment period and decreased further to 23.4 µg/L through the end of the data set (5–8 years post treatment) (Table 2, Fig. 5). Chl_a decreased from a 14.4 µg/L pre-treatment mean to 7.2 µg/L and 5.9 µg/L, 4 and 8 years post treatment, respectively. SD, however, did not improve until the three last years of the study record (Table 2 and Fig. 5). Li decreased by over 90% throughout the available data series, initially at 3.3 mg/m^2/day before treatment and decreasing to 0.2 and 0.1 mg/m^2/day at 4 and 8 years post Al-treatment, respectively (Fig. 6, Table 2). Longevity was estimated to 47 years, using LPEq.

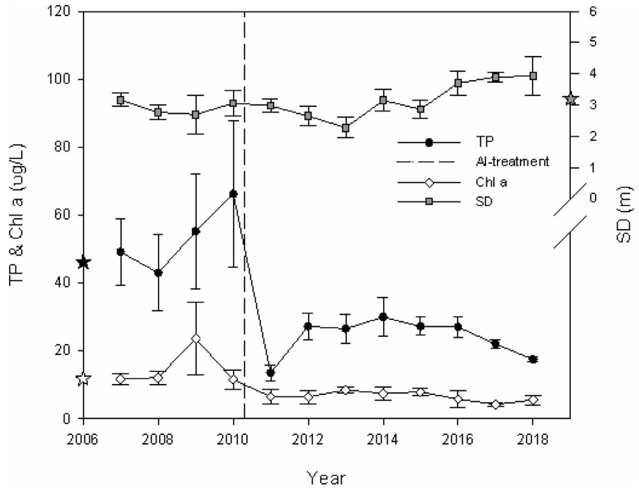

Fig. 5. Annual growing season surface water TP, SD and Chl a mean and SEM (May-Aug) in Trekanten. Longevity was estimated using LPEq. Stars with corresponding color to time series at each Y-axis indicate one SEM below (or above for SD) mean for years before Al-treatment. Observations in total time series: Chl a = 54, SD=53, TP=55.

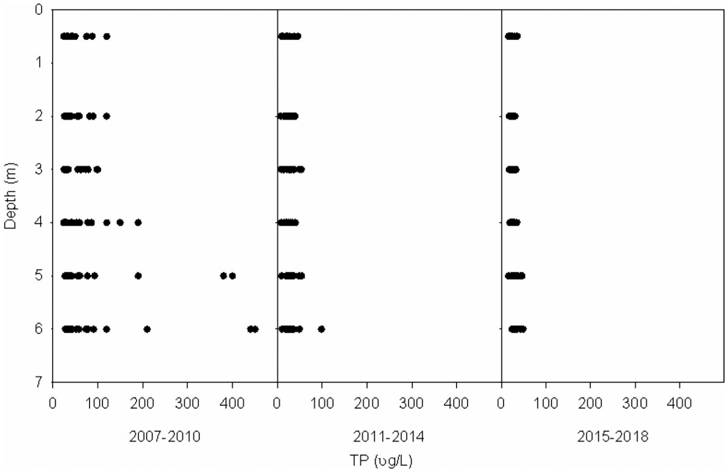

Fig. 6. Water column depth profiles showing concentrations of TP at different depth intervals in Trekanten. 1997–2000 represents pre Al-treatment and following consecutive 4-year period represents post-treatment observations of TP. Observations: 2007–2010=96, 2011–2014=96, 2015–2018=96.

3.1.4. Bagarsjön

During the first two 4-year post-treatment periods (e.g. eight years), TP was substantially lower compared to pre-treatment, decreasing from a mean of 60.3 μg/L to 24.8 and increasing to 37.3 μg/L respectively. During the following 4-year period (9–12 years post treatment) an increasing trend of TP was observed (mean=43.0 μg/L) (Table 2, Fig. 6). However, due to other management efforts such as freshwater dilution and hypolimnetic aeration during the 16, and 20 years post treatment periods, TP decreased again and was lower than pre-treatment conditions. SD did increased with 59% and 41% at the first and second 4-year period post Al-treatment, respectively. At years 9–12 post-treatment SD had decreased to 14% improvement. (Table 2, Fig. 7). Li was not analyzed due to lack of available data. Treatment longevity was determined to 14 years (Fig. 7).

3.2. Polymictic lakes

3.2.1. Långsjön

All variables (TP, SD, and Chl_a) improved by over 50% through the end of the study data series (12 years post Al-treatment). SD increased from a mean of 0.9 m to 1.7 m during the final post-treatment period. Chl_a decreased from a pre-treatment mean of 53.6 μg/L to 16.4 μg/L and TP decreased from a mean 97.5 μg/L to 46.5 μg/L 4, 8, and 12 years post-treatment. (Table 2, Fig. 8). Longevity using the post-treatment,

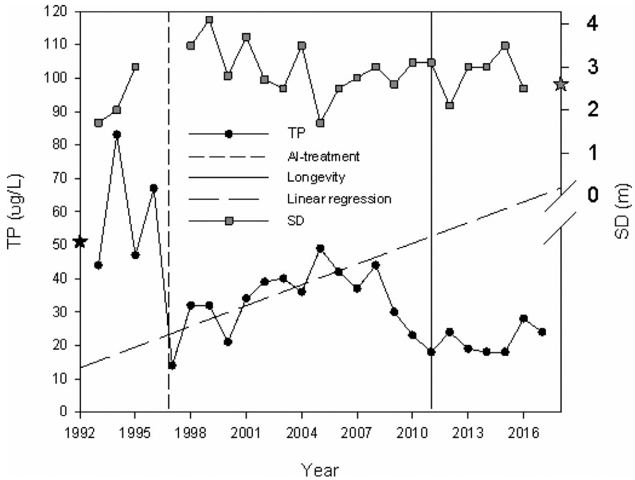

Fig. 7. Annual August surface water TP observation in Bagarsjön. Longevity was estimated as the time point where the linear regression exceeded one SEM below pre Al-treatment mean TP (4-year period). Star at each Y-axis indicate one SEM below (above for SD) mean pre-treatment TP and SD (4-years period). Observations in total time series: SD=22, TP=25. The decrease in TP after 2008 was likely due to installed hypolimnetic oxygenating system and not Al treatment.

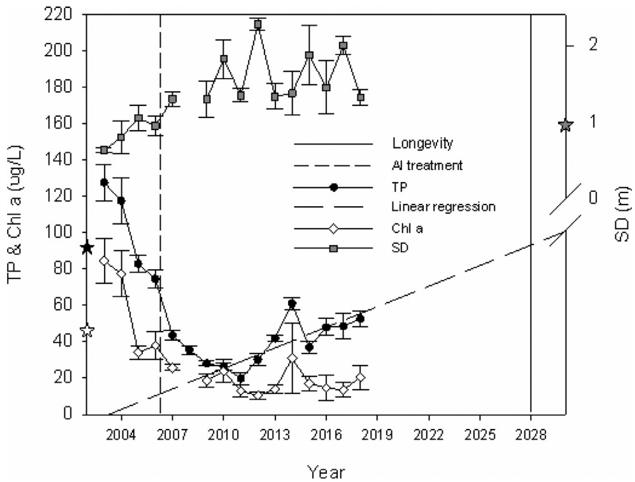

Fig. 8. Annual growing season surface water TP, SD and Chl a mean and SEM (May-Aug) in Långsjön. Longevity was estimated as the time point where the linear regression exceeded one SEM below pre Al-treatment mean TP (4-year period). Stars with corresponding color to time series at each Y-axis indicate one SEM below (or above for SD) mean for years before Al-treatment. Observations in total time series: Chl a = 57, SD=56, TP=114.

linear increase in surface water TP was estimated to be 21 years (Fig. 8).

3.2.2. Malmsjön

Surface water TP concentrations decreased by over 50% in the three post Al-treatment periods (4, 8 and 12 years post treatment, the entire dataset). Pre-treatment TP averaged 96.5 µg/L and was 43.8 µg/L at 12 years post treatment. (Table 2, Fig. 9). Longevity, using the linear increase in surface TP after treatment, was estimated to be 20 years. No other water quality data were available for Malmsjön.

3.3. Factors influencing longevity of Al-treatment

Principal Components Analysis (PCA) including factors in Table 1 was used to determine factors driving longevity and explained 79% of the variation in the data set with two components. Longevity was positively correlated to Osgood index suggesting that deeper lakes (dimictic) have higher longevity than small polymictic lakes. The analysis also showed that larger Al-doses were correlated with greater longevity. Al:P_{Al} was negatively correlated to longevity, meaning that poor binding efficiency (i.e. high Al:P_{Al}) results in lower longevity. Finally, WA:LA also

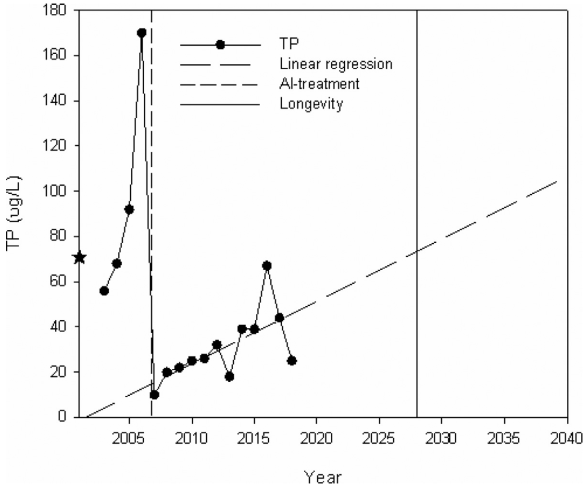

Fig. 9. Annual August surface water TP observation in Malmsjön. Longevity was estimated as the time point where the linear regression exceeded one SEM below pre Al-treatment mean TP (4-year period). Star at Y-axis indicate one SEM below mean pre-treatment TP (4-years period). Observations in total time series: TP=25.

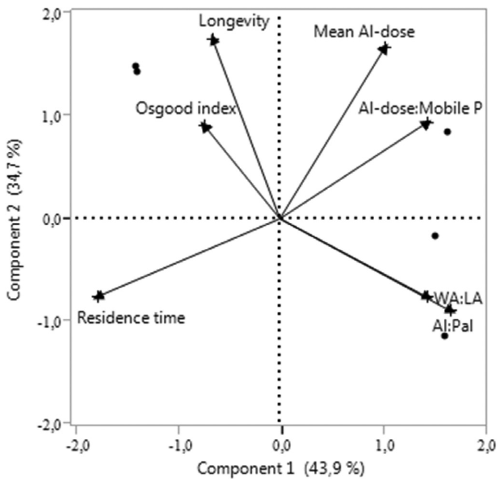

Fig. 10. Biplot from principal component analysis on variables from Table 1, explaining 79% of the total variation.

had a negative correlation to longevity, suggesting that lakes with greater watershed area relative to lake area have shorter longevities (Fig. 10).

4. Discussion

4.1. Water quality response to Al-treatment

4.1.1. Dimictic lakes

Three dimictic lakes (Lejondalssjön, Trekanten and Flaten) were historically monitored at a level required determining the effect of Al-treatment on surface water quality. The data series from these lakes included monthly (May-September) measurements of Chl_a, SD and TP for both surface water and depth intervals covering the vertical water profile (except for Lejondalssjön, which lacked pre-treatment Chl_a data). This provided the possibility to include within-year (May to August) variation when studying historical trends in surface water quality. Vertical profiles with samples taken from different water depths enabled calculation of historical internal loading rates, which are generally a better indicator of the effects of Al-treatment. However, this direct quantification of internal loading is only applicable to dimictic lakes, where the lake remains stratified and hypolimnion remains stable throughout the growing season.

4.1.1.1. Lejondalssjön. Internal loading rates decreased 68% during the first 4-year period post Al-treatment. During the following 4-year post-treatment periods, however, internal loading gradually returned to levels not different to pre-treatment conditions (Table 2, Fig. 1& 2). This is likely due to a combination of factors. The high amount of legacy (mobile) sediment P remaining after Al-treatment (Agstam-Norlin et al., 2020) (Table 1) likely overwhelmed the Al-treatment, as was the case for numerous historical treatments where Al doses were added that were inadequate to bind the entire excess mobile P pool (Huser et al., 2016b; Welch and Cooke 1999). Even though Li improved substantially after treatment (at least initially), surface water TP only decreased by 29% during the first 4-year period. This can likely be explained by ongoing, excess external P inputs.

Limited treatment longevity has been seen elsewhere when external loading was not reduced adequately or inadequate Al doses were used (Egemose et al., 2011; Garrison and Knauer 1984; Huser et al., 2011; Huser et al., 2016b; James et al., 1991; Mehner et al., 2008). Thus the limited treatment longevity in Lejondalssjön is likely explained by a combination of continued excess external loading and the low Al dose (25 g/m^2) added. Dose calculation methods based on other variables besides sediment P were common before 2000. For Lejondalssjön, Al dose was calculated based on the internal P loading rate (Kennedy et al., 1987). One problem with this approach is that it only accounts for sediment P release during one year, even though the sediment often contains enough mobile P to support many years of internal loading. Without looking at sediment P content, it is impossible to determine how much mobile P exists in the sediment, and thus underdosing of Al is a likely result (Kuster et al., 2020).

4.1.1.2. Flaten. When this lake was treated in 2000, the understanding of Al dosing had improved substantially and was based on the available pool of mobile P (labile organic P, P bound to Fe, and loosely sorbed/porewater P) in the lake sediment (Rydin 2000). The mean dose of Al across the lake was 61 g/m^2 (Schütz et al., 2017), however dose was adjusted higher or lower depending on the amount of mobile sediment P in different locations. The application technique employed was also different compared to most Al-treatments. A combination of sediment injection and hypolimnetic water application was used, where approximately a fourth of the Al dose was applied to the water and the rest injected into the sediment. Surface water TP concentrations decreased by over 60% due to Al-treatment and this decrease was sustained through the end of the data series (Table 2, Fig. 3 & 4). Chl_a had a similar response and remain reduced throughout the study period. SD increased more than two fold, which also was sustained through the end of the data series.

4.1.1.3. Trekanten. The most recent treatment presented in this study was performed in 2011 in Trekanten, where a similar dose to that used in Flaten was applied (60 g/m^2). However, the application technique differed slightly and only sediment injection was used (i.e., no water application). As with Flaten, the Al dose was determined from the amount of mobile P in the sediment. The water quality data covered only two 4-year periods post treatment (i.e. 8 years) and showed a twofold decrease of TP and Chl_a throughout the measurement period (Table 2, Fig. 5). Because internal loading rates decreased by nearly 100%, but the lake water still has a TP concentration of nearly 25 µg/L, it seems likely that external sources of P are still elevated. This may, to some extent, be due to sewage water pipes that had been incorrectly connected to storm water runoff pipes between 2006 and 2013, unfortunately contributing excess external P load during these years. The excess external loading does not seem to have had an effect on internal loading (Fig. 6), but if not controlled, it is likely internal loading will return (Huser et al., 2011).

While SD did not initially improve post treatment, there was an increasing trend from 7% during the first 4-year period to 20% increase at the end of the data set (5–8 years). Similar, delayed effects have been seen after Al-treatment in a number of US lakes (Huser et al., 2011). The lack of immediate response in SD does not seem to be controlled by algal presence, because Chl_a decreased by 50%. This suggests a number of alternatives, e.g., sediment resuspension due to winds or benthic feeding fish causing sediment mixing (bioturbation), turbid storm water inflows, or increasing water color (total/dissolved organic carbon) that has been shown to be occurring in boreal regions across Sweden and elsewhere (de Wit et al. 2016; Huser et al., 2012; Monteith et al., 2007). Unfortunately, the lack of data did not allow us to explore any of these possible effects.

4.1.1.4. Bagarsjön. Whereas the previously described dimictic lakes were monitored in enough detail to calculate historical trends for Li, data for Bagarsjön only included surface water TP and SD at one occasion per year (August). Thus, it was not possible to calculate Li and within year variation (seasonal mean) could not be included in the analysis. However, the effect of Al-treatment on surface water TP was clear for the initial 4-year period (Fig. 7). Surface water TP began to increase after treatment but decreased again during the last two 4-year periods post treatment (from 2009). This decrease is likely a result of another separate management action starting in 2009, when an aeration pump was installed in order to keep hypolimnetic water oxygenated. There was no clear change in SD after 6 years post Al-treatment (including after aeration started).

4.1.2. Polymictic lakes

Because polymictic lakes are generally shallow and well or partially mixed, the lack of a well-defined hypolimnion makes it is difficult to calculate internal loading rates. Dynamic modeling would be needed in such cases but monitoring of inflows and outflows was not conducted or data available were too sparse to use dynamic or even simple mass balance models. Surface water quality trends, however, could be analyzed and used to estimate treatment effect, as has been done in previous studies (Huser et al., 2016b; Welch and Cooke 1999).

4.1.2.1. Långsjön. Historical water chemical data for TP, SD and Chl_a, together with water profile measurements of TP were available. Because the lake is polymictic, often no accumulation of TP occurs in the bottom water, which limits the possibility to estimate Li. However, there was a positive effect for all measured parameters for all 12 years of post-treatment data, with all variables improving by >50% (Table 2, Fig. 8). It should be noted that other management actions including freshwater dilution were performed simultaneously to Al-treatment. These actions will, of course, improve water quality due to dilution of nutrients in the lake. External loading remains elevated, however (Table 2), and will likely overwhelm the effects of Al-treatment in the future (see Longevity section below).

4.1.2.2. Malmsjön. Available water chemical data included surface water TP concentrations from single samples taken in August each year. The lack of water column profile measurements of TP precluded calculation of internal loading, making quantification of the direct effect of Al-treatment impossible. Despite the limited data available, the effect of Al-treatment on surface water TP was clear for the complete data record. Surface water TP started to increase after treatment (Table 2, Fig. 9), and TP was estimated to return to pre-treatment levels after 20 years.

4.2. Al-treatment longevity in polymictic and dimictic lakes

If external P sources are reduced sufficiently and Al is added at a dose necessary to inactivate the entire legacy sediment P pool, treatment longevity would theoretically be infinite. Once P is bound to Al, it is considered permanently inactivated (Welch and Cooke 1999) and the sediment layer with elevated aluminum bound P will, over time, be buried by new sediment. For most lakes discussed herein, however, external loading remains elevated, in some cases substantially (i.e., Malmsjön and Långsjön (Table 2)). In these cases, estimates of longevity are mainly a factor of how much external loading has been reduced, with Al dosing and treatment methods that affect how much Al was added relative to legacy sediment P (Kuster et al., 2020) and binding efficiency between Al and P (Agstam-Norlin et al., 2020; Huser 2012) having a smaller effect.

4.2.1. Dimictic lakes

Nutrient cycling in Flaten is mainly controlled by in-lake processes rather than external sources due to the low WA:LA ratio (6.4) and low intensity of land use in the watershed. Further, the Al dose was relatively high (mean 61 g/m^2) and mostly applied directly into the sediment rather than to the water column, which likely increased binding efficiency (mean 9.0, Table 1) (Agstam-Norlin et al., 2020). Given that no increase has been detected for Li or surface water TP after Al-treatment, longevity in this case may be infinite. The LPEq-estimated treatment longevity in Flaten was

37 years (i.e. surface water TP increases to 50% of pre-treatment), which is above the mean treatment longevity (21 years) for dimictic lakes (Huser et al., 2016b). However, treatment longevity will likely be substantially longer than predicted using LPEq given no significant increase in Li or surface water TP has been detected to date.

The treatment of Trekanten was in many ways similar to the situation in Flaten, with an even lower WA:LA (4.3), similar sediment binding efficiency (mean $Al:P_{Al} = 10.7$) (Agstam-Norlin et al., 2020), and a relatively high Al dose (mean = 60 g/m^2) injected exclusively into the sediment. Because water quality was still improved with no decline throughout the measurement period, a determination of total longevity was not possible. With an LPEq-estimated treatment longevity of 47 years, it is possible that total longevity (e.g., the time it takes for surface water TP to reach pre-treatment levels) may be a century or longer.

The treatment of Bagarsjön differed from the previous two cases (Al was applied exclusively to the water column), resulting in a lower binding efficiency (mean $Al:P_{Al}=16.0$, (Agstam-Norlin et al., 2020)). Additionally, nutrient cycling and availability is likely controlled mostly by external sources because the lake has a relatively small area compared to the watershed (WA:LA = 22.5). These two factors likely decreased longevity (14 years), which is lower than what would be predicted for an average dimictic lake (Huser et al., 2016b). Similarly, Lejondalssjön also had a shorter than expected longevity (7 years), which can be explained by other factors, namely a low dose (25 g Al/m^2, calculated using outdated methods) applied to the water column together with moderately high binding efficiency (mean $Al:P_{Al} = 11.4$).

4.2.2. Polymictic lakes

The longevity of the Långsjön treatment was estimated to be 20 years using linear increase and extrapolation (Fig. 8) of TP. This is above the previously reported Al-treatment longevity of polymictic lakes (mean 5.7 years) according to Huser et al. (2016b). The much longer predicted longevity can partly be explained by the relatively low WA:LA (8.4), meaning that in lake processes are likely more important than external sources for nutrient cycling. Långsjön was treated with a relatively high Al dose (mean = 60 g/m^2) directly applied to the sediment, which led to a moderately high binding efficiency (mean $Al:P_{Al} = 12.9$). Further, another restoration effort was simultaneously performed using freshwater dilution (30 l/s, since 2002), likely increasing longevity.

Treatment longevity for Malmsjön, which was estimated at 20 years using the linear increase in surface water TP after treatment (Fig. 9), was well over the typical range for polymictic lakes (Huser et al., 2016b). Similar to Långsjön, direct sediment Al application was done with a relatively high dose (60 g/m^2). Binding efficiency (mean $Al:P_{Al}= 14.6$) and the WA:LA (13.2) were moderate in comparison to the other study lakes. The generally shorter longevity in shallow, polymictic lakes is not solely due to lake characteristics, but because historically these types of lakes usually received lower Al doses, which per se results in short longevity. Because Långsjön and Malmsjön received relatively high Al doses (calculated using the mobile sediment P pool) applied directly into the sediment (increasing binding efficiency), longevity exceeded expectations compared to earlier treatments (Agstam-Norlin et al., 2020; Huser et al., 2016b).

4.2.2. Factors influencing Al-treatment longevity

In this study we showed that observed factors generally controlling longevity for the most part follow current understanding in the literature. Al-dose, WA:LA, and Osgood index (i.e. polymictic versus dimictic lakes) drove longevity for the study lake, similar to previous conclusions from Huser et al., al.(2016b) where 114 lakes were analyzed for factors controlling longevity, and 82% of the variation in longevity was explained by WA:LA, Al-dose and Osgood index. This is also supported by PCA analysis of the study lakes (Fig. 10), where a higher Osgood index (i.e. a greater chance for stratification) was positively related to longevity and WA:LA ratios were negatively correlated. Al-dose had a weak positive correlation to longevity, possibly explained by the similarity of dose across the study lakes (Table 1). A new factor, $Al:P_{Al}$ ratios, was also shown to control longevity, with greater ratios (i.e. lower binding efficiency) being negatively correlated to longevity of treatment. This is plausible, as a lower binding efficiency means that less sediment P will be bound per unit Al added.

4.3. Recommendations for assessing Li with water quality monitoring

The duration and intensity of lake water quality monitoring before and after Al-treatment constrains the evaluation of effectiveness and longevity. In many situations it may not be sufficient to only measure changes in surface water nutrient related parameters such as SD, Chl_a, and TP in the lake. This is because other restoration efforts may be used simultaneously and/or external loading may remain high, potentially masking the effect of Al (or other treatments) designed to reduce internal phosphorus loading. Three dimictic lakes in this study were monitored in a sufficient manner to determine changes to Li associated with Al-treatment (Lejondalssjön, Flaten and Trekanten). Monthly water profile measurements of TP, with multiple samples collected through the vertical water profile and temperature every meter, made it possible to calculate the volume of the hypolimnion and the mass of TP in hypolimnetic water and follow the increase throughout the growing season when lake was stratified (Nürnberg 2009). Higher resolution monitoring is likely needed in polymictic systems, as in Huser et al. (2011) where biweekly observations were used to assess Li. This is due to the fact that internal loading events are likely shorter (i.e. periodic stratification and/or high pH events). The polymictic Långsjön was monitored monthly with vertical water chemical profiles and temperature at least every meter, however assessing Li using the same methods as for dimictic lakes was not possible due to the lack of stabile stratification during the growing season. Thus, in polymictic/shallow lakes, monitoring of flow and nutrient concentrations is needed in the inlets as well so that external and internal loading can be differentiated. Further, to assess Li accurately, it will generally be necessary to use dynamic modeling approaches, including spatially representative information on sediment P forms and potential flux, with data series covering pre and post periods of Al-treatment.

5. Conclusions

An Al dose adequate to bind legacy sediment P and appropriate treatment methods, depending on lake morphological characteristics, are crucial for sustainable restoration of surface water quality using Al-treatment. Al dose needs to be large enough to inactivate the entire pool of excess mobile P in the lake sediment, which drives the long term potential for internal loading. External load reduction is also important, as continued excess P loading will eventually overwhelm any measure designed to reduce sediment P release, as we showed in this study. Based on available data, the positive effects from Al-treatment in two lakes (Flaten and Trekanten) are likely to last a century or longer. On the other hand, lakes with high levels of excess external loading had (or will have) shorter treatment longevity ranging from 7 to 21 years. In addition, elevated external loading will limit the positive effects of reduced internal loading. In Lejondalssjön, internal loading was reduced substantially after Al-treatment (before the treatment was overwhelmed by new P), but surface water TP decreased by a much smaller amount due to continued elevated external loading.

Assuming adequate reduction of external loads, Al dose becomes the most important factor for restoration success. Newer methods, based on sediment P, have been developed and have led to substantially greater treatment longevities primarily due to greater Al doses being added. However, care should be taken with Al doses added during one treatment as high, single treatment doses decrease the overall efficiency of Al-treatment, as was seen in Malmsjön, and can limit the amount of sediment P that is inactivated per unit Al added. Doses should be split into smaller subtreatments to improve binding efficiency and increase the amount of P inactivated per unit Al added.

Finally, Al-treatment success was based (in most cases) on surface water quality improvement in this study, however the main goal of Al-treatment is to reduce P release from sediment. We attempted to evaluate reduction in internal loading for all lakes, but too often adequate data to do this were lacking. In cases where variables such as TP, Chl_a, and SD have unexpected responses, it is important to be able to evaluate whether these responses are due to internal, external or both types of loading. Proper monitoring, both before and after treatment, is a necessary requirement to be able to evaluate and optimize methods to reduce P loading and eutrophication in surface waters in the future.

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

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Phosphorus
Internal loading

A B S T R A C T

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.

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 (km^2). 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 $AlCl_3$) 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

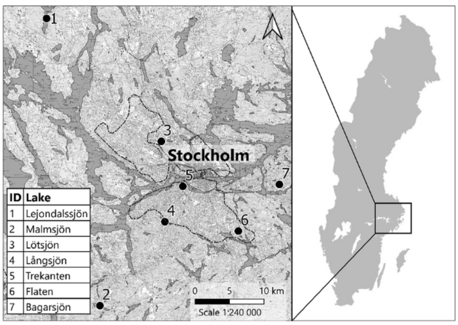

Fig. 1. Map showing position of the study lakes located within a 30 km radius of Stockholm city in Sweden.

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

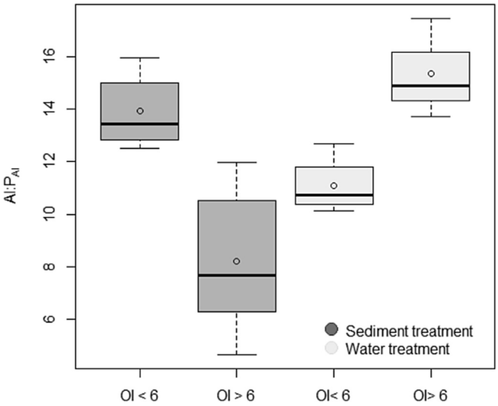

Fig. 2. Boxplot showing Al:P_{Al} ratios for individual cores grouped by Al treatment method (sediment vs. water) and lake morphology (Osgood index <6 or >6). Solid lines and circles within the boxplots represents median and mean values, respectively.

(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:$P_{Al} = 8.2 \pm 2.6$) than gradual bed slope lakes treated with the same Al application methods (mean Al:$P_{Al} = 13.9 \pm 1.4$; $p < 0.001$) (Statistical details in Tables S1–S10). The highest ratios were generally found in the steep bed slop Lake Bagarsjön where Al was applied to the water column (mean Al:$P_{Al} = 15.4 \pm 1.9$) 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)):

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

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:

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

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.

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

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;

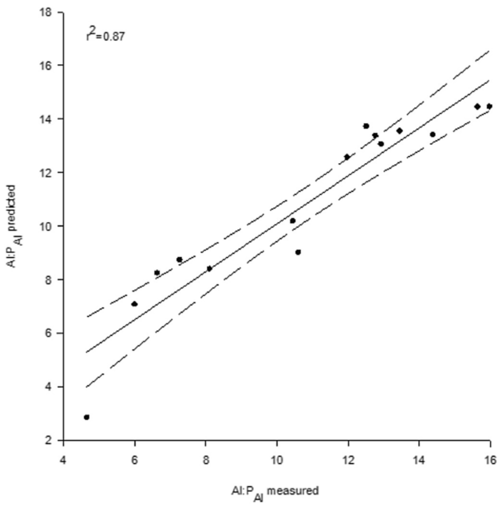

Fig. 3. Measured versus predicted values of Al:P$_{Al}$ for sediment treated lakes, described by the model Al:P$_{Al}$ = 15.93–0.82 × P$_{mob}$ + 0.11 × detected Al dose - 0.66 × Osgood index. Dashed lines represent 95% confidence intervals.

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 Sussersee (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.

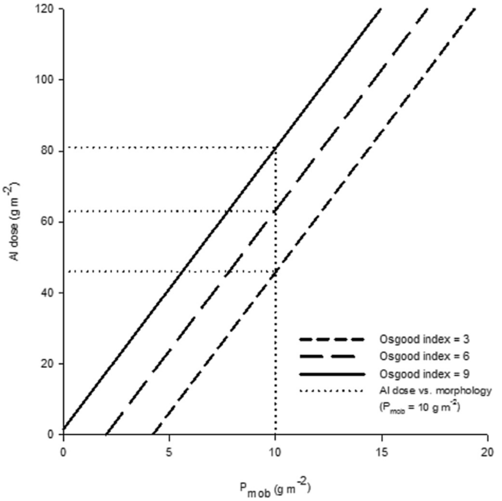

Fig. 4. Al dose allowed to achieve Al:P_{Al} = 10 using sediment Al application in three hypothetical lakes with Osgood index at 3, 6 and 9 and a range of sediment P_{mob} mass. Dotted line indicates doses for varying Osgood index with P_{mob} fixed at 10 g m^{-2}).

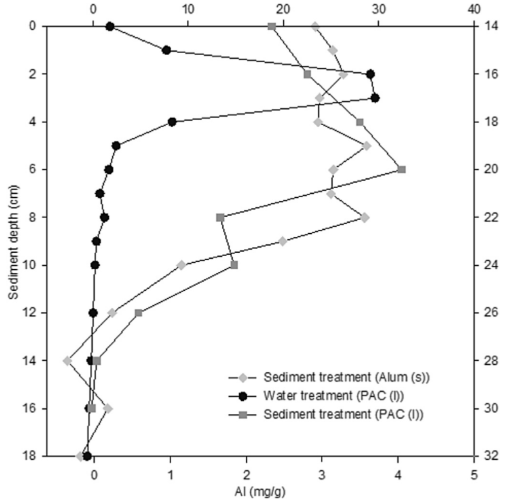

Fig. 5. Cores from two lakes where sediment treatment was used are shown. Lötsjön (Sediment treatment, Alum (s)) and Malmsjön (Sediment treatment. PAC (l)). Due to the differences in treatment age, the depth range of Lötsjön was adjusted to match the treatment date of Malmsjön (30 years difference in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

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-hydrolized polyaluminum chloride (PAC) was used in all lakes 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-hydrolized 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-hydrolized' 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.

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Supporting information

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

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Tables S1 to S10. Statistical details.

Table S1. Summary of fit for Oneway ANOVA. Lakes grouped by Osgood index > or < than 6, and water or sediment treatment.

RSquare	0.751245
RSquare Adj	0.709786
Root Mean Square Error	1.831745
Mean of Response	11.5286
Observations (or Sum Wgts)	22

Table S2. Analysis of variance. Lakes grouped by Osgood index > or < than 6, and water or sediment treatment.

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Osgood index	3	174.05657	58.0189	15.1941	<.0001
Error	18	68.73329	3.8185		
C. Total	21	242.78986			

Table S3. Statistical summary for Oneway ANOVA. "Steep" denotes Osgood index>6. "flat" denotes Osgood index <6. "wat" denotes water treatment. "sed" denotes sediment treatment.

Level	#Obs.	Mean	Std dev.	Std Error	Lower 95%	Upper 95%
flat sed	7	13.9433	1.40842	0.7386	12.392	15.495
flat wat	4	11.0768	1.12254	0.9771	9.024	13.13
steep sed	8	8.2048	2.55678	0.6909	6.753	9.656
steep wat	3	15.3602	1.90935	1.1282	12.99	17.73

Table S4. Ordered differences report for Tukey´s (HSD) post hoc test. "Steep" denotes Osgood index>6. "flat" denotes Osgood index <6. "wat" denotes water treatment. "sed" denotes sediment treatment.

Level	Level	Difference	Std Err Dif	Lower CL	Upper CL	p-Value
steep wat	steep sed	7.155402	1.322934	3.41641	10.8944	0.0002*
flat sed	steep sed	5.738505	1.011344	2.88015	8.59686	0.0001*
steep wat	flat wat	4.283345	1.49247	0.06519	8.5015	0.0458*
flat wat	steep sed	2.872057	1.196638	-0.50999	6.2541	0.1129
flat sed	flat wat	2.866448	1.224798	-0.59519	6.32808	0.1258
steep wat	flat sed	1.416898	1.348459	-2.39424	5.22803	0.7226

Table S5. Summary of fit, MLR for all lakes.

RSquare	0.751245
RSquare Adj	0.709786
Root Mean Square Error	1.831745
Mean of Response	11.5286
Observations (or Sum Wgts)	22

Table S6. Analysis of variance, MLR for all lakes.

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Model	3	182.39462	60.7982	18.1201	
Error	18	60.39524	3.3553		
C. Total	21	242.78986			<.0001

Table S7. Parameter estimates, MLR for all lakes.

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	15.706075	1.205103	13.03	<.0001
Osgood index	-0.550029	0.180386	-3.05	0.0069
P_{mob}	-0.787753	0.109304	-7.21	<.0001
Detected Al dose	0.1014427	0.018188	5.58	<.0001

Table S8. Summary of fit, MLR for sediment treated lakes.

RSquare	0.89621
RSquare Adj	0.867903
Root Mean Square Error	1.305401
Mean of Response	10.88275
Observations (or Sum Wgts)	15

Table S9. Analysis of variance, MLR for sediment treated lakes.

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Model	3	161.85731	53.9524	31.6609	
Error	11	18.74478	1.7041		
C. Total	14	180.60209			<.0001

Table S10. Parameter estimates, MLR for sediment treated lakes.

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	15.93434	1.013538	15.72	<.0001
Osgood index	-0.65854	0.141006	-4.67	0.0007
P_{mob}	-0.824116	0.095057	-8.67	<.0001
Detected Al dose	0.1074707	0.018275	5.88	0.0001

Acta Universitatis Agriculturae Sueciae

Doctoral Thesis No. 2022:2

Adequately designed restoration methods for managing eutrophication are vital in order to achieve good water quality in lakes. This thesis expands the knowledge base on how to assess the pools of phosphorus (P) to target when restoring lakes using aluminum (Al) for (P) inactivation in sediment. New fractions of P need to be considered to calculate and immobilize the correct amount of P, and novel practical application methods can increase the efficiency of Al-treatment.

Oskar Agstam-Norlin received his doctoral education at the Department of Aquatic Sciences and Assessment at the Swedish University of Agricultural Sciences. He holds a master's degree in limnology, and a bachelor´s degree in biology from Uppsala University, Department of Ecology and Genetics, Limnology.

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