

Phosphorus binding by aluminium in sediment: A tool for restoring water quality in the Baltic Sea and other brackish surface waters

Effectiveness of phosphorus binding by aluminum under varying pH and salinity

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Summary

Lake and sea sediments act as stores for historical inputs of pollutants from both direct and diffuse sources including urbanization, agriculture, municipal and industrial waste waters, among others. Historical accumulation in sediments can provide a continual source of phosphorus to the water column for decades or longer after external sources have been controlled. Addition of metal salts, e.g. aluminium salts, can permanently bind this excess phosphorus in the sediment, thereby reducing internal phosphorus loading and improving water quality. Whereas this restoration method has been well studied in freshwater systems (over four decades of use), information on effectiveness in brackish and saltwater systems is limited.

For this study, five sediment cores were collected from Torsbyfjärden near Lid-
ingö. Sediment samples were initially analyzed for sediment phosphorus fractions and then aluminium was added to the sediment to convert mobile phosphorus to aluminum bound phosphorus. Mobile phosphorus is the pool of phosphorus that contributes directly to internal loading of phosphorus in surface waters and aluminium is used to convert this pool into an inert form that will remain in the sediment. Results from the initial analysis indicated that the potential for internal phosphorus loading in Torsbyfjärden is extremely high. Potential internal phosphorus loading rates ranged from 0.83 to nearly 40 mg/m²/d, with higher values generally being found in areas of greater water column depth (sediment accumulation areas).

Based on the mobile phosphorus content of the sediment, aluminium was added under varying salinity (0-8) and pH (7-9) to elucidate the effects of these two variables on phosphorus binding by aluminium in Baltic Sea sediment. Compared to pH, salinity had a relatively minor effect on phosphorus binding by aluminium, decreasing the effectiveness of binding by approximately 5% when comparing the 0 salinity level to a salinity of 8. pH, on the other hand, had a substantial effect on P binding by Al. The amount of mobile P inactivated by the added aluminium decreased by approximately 22% in areas with very high mobile sediment phosphorus and 33% in areas of moderate mobile phosphorus content in the sediment. The more important result, however, was that it may take more than twice the amount of aluminium to inactivate an equivalent amount of mobile sediment phosphorus (using pH 7 as a reference point) if pH in the treatment area is at 9 or higher. When

comparing pH 7 to pH 8 there was little change (approximately 5% difference) in conversion of mobile phosphorus to aluminium bound phosphorus. As part of this study, empirical models were developed to predict the effectiveness of phosphorus binding by aluminium under the above salinity and pH ranges.

The overall results of this study show that the use of aluminum salts in brackish waters has good potential to limit internal phosphorus loading by inactivating the pool of mobile phosphorus via conversion to aluminium bound phosphorus. Care must be taken, however, when pH levels approach 9 or greater due to the limitation of phosphorous binding by aluminium under these conditions.

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Introduction

Lake and sea sediments act as stores for historical inputs of pollutants from both direct and diffuse sources including urbanization, agriculture, municipal and industrial waste waters, among others. Management of pollutant inputs has reduced pollutant loading to surface waters in recent decades but water quality does not always show a corresponding improvement, especially with regard to nutrients and more specifically phosphorus. Historical accumulation in sediments can provide a continual source of phosphorus to the water column for decades or longer after external sources have been controlled (Sas, 1990). Release of phosphorus from the sediment to the water column, or internal loading, is a natural process but excess accumulation of phosphorus overwhelms the natural sediment binding capacity, leading to increased internal loading and poor water quality (Nürnberg, 2009). In many cases, sediment becomes the main source of phosphorus to the water body, instead of acting as a store or sink. Internal loading then causes severe algal blooms and limits food quality and habitat for fish and other aquatic biota (Welch and Cooke, 1995). Until the cycle of phosphorus transfer between the sediment and water is broken, it is extremely difficult to restore water quality to natural conditions.

Due to the substantial declines in water quality in the Baltic Sea, there is increasing interest in reducing internal phosphorus loading due to historical nutrient pollution. This is especially true in coastal areas where eutrophication effects are more pronounced (Schulz et al., 1992). Many areas in the Baltic have excess sediment phosphorus due to elevated inputs (Rydin and Westerlund, 2003; Virtasalo et al., 2005; Vahtera et al., 2007), which has led to decreased oxygen availability, negative effects on biota (Bonsdorff et al., 1997), and increased release of reductant soluble (mainly iron-bound) phosphorus (Jensen et al., 1995). These internal system feedback mechanisms can counteract external nutrient load reductions (Vahtera et al., 2007) and limit recovery in the Baltic (Munkes, 2005).

One of the most effective ways to reduce internal phosphorus loading is to increase the phosphorus binding capacity of the sediment. Aluminum, iron, and calcium are the main metallic elements that bind phosphorus in sediment and are naturally present to varying degrees based mainly on the characteristics of the surrounding

watershed soils. Aluminum, however, is the most stable element within the pH range found in most surface waters (Stumm and Morgan, 1996). Iron is redox sensitive and will release phosphorus under low oxygen conditions whereas calcium is less efficient at binding phosphorus at pH levels lower than 8.5. Thus, even though all three elements have been used to control internal phosphorus loading, the use of aluminum (in the form of aluminum salts) has resulted in much greater success and longevity compared with iron and calcium (Cooke et al., 2005). Aluminum salts have been used safely to control internal phosphorus loading in freshwater lakes for over four decades and in water treatment for hundreds of years (Kennedy et al., 1987; Rydin et al., 2000; Cooke et al., 2005). Once added to the sediment, aluminum forms a mineral compound (aluminum hydroxide), permanently binds phosphorus, and is buried by new sediment over time. Toxicity is negligible to invertebrates, plankton and fish when pH is between 6 and 9 in fresh (Pilgrim and Brezonik, 2005) and brackish (Huser and Köhler, 2012) waters. Abundance and diversity of aquatic communities increase after treatment due to improved water quality and oxygen conditions (Jeppsen et al., 2005).

Dosing of aluminum salts has progressed from the days when managers basically guessed how much to apply, to current methods in which specific binding relationships are used to determine the precise amount of aluminum needed to inactivate a known amount of sediment phosphorus (Rydin and Welch, 1999; Pilgrim et al., 2007). A dosing tool developed using these relationships (Pilgrim et al., 2007; Huser and Pilgrim, 2013) has been applied successfully in the restoration of dozens of freshwater lakes and reservoirs. This method, however, is designed for the chemistry of freshwater systems and does not take into account the elevated pH and salinity generally found in brackish waters. Aluminum is least soluble at a pH of 6.5, meaning greater phosphorus binding potential close to this pH. On the other hand, elevated salinity (or ionic strength) will interfere or limit phosphorus binding. Thus, better information is needed to maximize the effectiveness of aluminum salts for phosphorus inactivation in brackish waters.

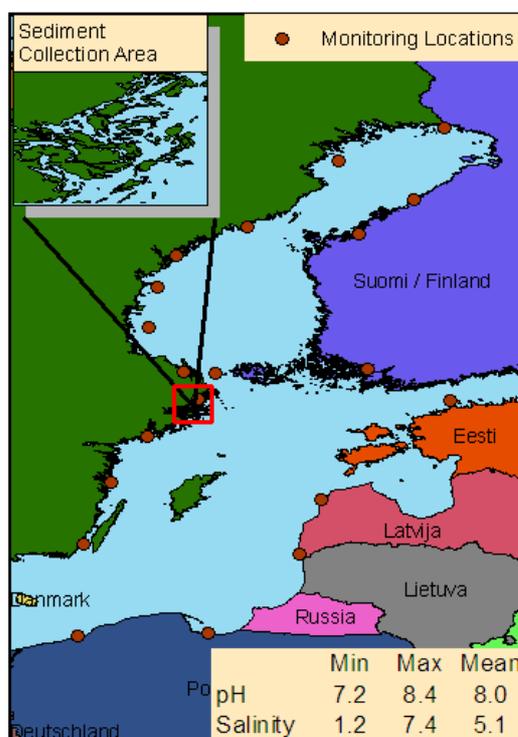
Methods

A Willner gravity sediment-coring device (Uppsala, Sweden) was used to collect sediment cores from Torsbyfjärden in October 2012 after lake water turnover in the (Figure 1). Cores were extruded on site, sliced into two cm sections, and stored in opaque containers at 4° C until analysis within one week of collection. Five sediment cores in total were collected with eight sediment intervals within each core (40 samples total) and these samples were initially analyzed for sediment phosphorus fractions. Aluminium was added to the sediment to convert mobile phosphorus to Al-P. Mobile phosphorus is the pool of phosphorus that contributes directly to internal loading of phosphorus in surface waters and aluminium is used to convert this pool into an inert form that will remain in the sediment.

Water chemistry and sediment collection area

The sediment collection area (Torsbyfjärden, Figure 1) was chosen because sediment phosphorus content has recently been studied (Baltic Sea 2020, 2011). The matrix of salinity and pH values chosen for this study (see below) covers the general pH and salinity ranges detected in coastal areas of the Baltic Sea (see Figure 1). The aluminum addition ratios were chosen to cover a range from no phosphorus binding (the control) to complete binding and inactivation and are based on previous work by Rydin and Welch (1999) and Huser and Pilgrim (2013).

Figure 1. Water chemistry monitoring and sediment collection location. Range of mean salinity and pH values for all sites shown.



Sediment Analysis

Sediment phosphorus fractions (including mobile phosphorus and aluminium bound phosphorus (Al-P)) were determined for all cores using a modified sequential extraction technique for wet sediment described by Psenner et al. (1998) and modified by Hupfer et al. (2005). Although all fractions were determined for most sediment cores, only data from the mobile phosphorus and Al-P fractions are shown. All extracts were centrifuged at 3000 rpm for 10 minutes before analysis as soluble reactive phosphorus¹². Total solids content was determined by freeze-drying sediment after storage at -70°C for 24 h, and sediment density was calculated according to Håkanson and Jansson (1983) after loss on ignition (LOI) at 550°C for 2 h.

To convert mobile phosphorus to the inert Al-P form, aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18(\text{H}_2\text{O})$) was dissolved in deionized water, buffered and adjusted to pH 7, 8, and 9 using 2 N NaOH, resulting in a final concentration of approximately 300 mg Al/L. Salinity of stock solutions was then adjusted by adding NaCl to achieve salinities ranging from 0 to 8 (grams of salt per liter water). The adjusted stock solutions were then added to slurries (~15 mg dry weight) of fresh sediment to achieve ratios of aluminium to Al-P formed (or mobile phosphorus lost) of 25, 50, 75, 100:1 (by weight). The samples were shaken continuously for 48 h to allow for surface adsorption of phosphorus by aluminium. Mobile phosphorus and Al-P were then determined according to the above fractionation procedure. Potential internal phosphorus release rates following mobile phosphorus conversion were calculated using the relationship between net internal phosphorus loading rate and mobile sediment phosphorus content developed by Pilgrim et al (2007). Statistical analyses were conducted using Sigmaplot software (version 11, build 11.1.0.102).

Results

Results from the initial analysis indicated that the potential for internal phosphorus loading in Torsbyfjärden is extremely high. Mobile phosphorus was very high in some areas of Torbyfjärden, ranging from 0.18 to over 3 mg/g (Table 1). Using the relationship developed by Pilgrim et al. (2007), potential internal phosphorus loading rates (based on mobile phosphorus content) ranged from 0.83 to nearly 40 mg/m²/d (Table 1), with higher values generally being found in areas of greater water column depth (sediment accumulation areas).

Table 1. Sediment characteristics, phosphorus fractions, and potential internal phosphorus loading rates for sediment collected from Torsbyfjärden.

Core	Interval (cm)	Water content (%)	Density (g/cm ³)	Mobile P	Aluminium-P	Calcium-P (mg/g)	Organic-P	Total P	Mobile P (g/m ² /cm)	Internal loading rate (mg/m ² /d)
AF5	0-2	94,6	1,02	0,18	0,01	0,48	0,33	1,00	0,10	0,83
	2-4	90,8	1,04	0,22	0,06	0,26	0,35	0,89	0,21	2,47
	4-6	88,8	1,05	0,21	0,09	0,20	0,31	0,81	0,25	3,06
	6-8	86,6	1,07	0,17	0,05	0,21	0,30	0,74	0,25	3,04
	8-10	85,6	1,07	0,17	0,08	0,23	0,29	0,76	0,27	3,35
	12-14	84,4	1,08	0,23	0,07	0,24	0,27	0,82	0,40	5,29
	18-20	86,7	1,07	0,24	0,06	0,21	0,34	0,85	0,34	4,45
	28-30	85,4	1,08	0,21	0,04	0,22	0,33	0,80	0,33	4,30
AF4	0-2	94,4	1,02	3,04	0,45	0,30	0,51	4,30	1,73	25,37
	2-4	90,0	1,04	0,35	0,12	0,26	0,40	1,13	0,37	4,88
	4-6	85,3	1,08	0,18	0,08	0,26	0,36	0,88	0,29	3,71
	6-8	82,3	1,10	0,20	0,06	0,27	0,32	0,84	0,39	5,22
	8-10	82,0	1,10	0,23	0,06	0,25	0,31	0,84	0,45	6,03
	12-14	82,6	1,10	0,22	0,07	0,25	0,32	0,86	0,42	5,63
	18-20	87,2	1,06	0,21	0,09	0,21	0,41	0,92	0,28	3,54
	28-30	83,5	1,09	0,15	0,06	0,27	0,28	0,76	0,27	3,45
AF3	0-2	97,0	1,00	0,10	-0,02	0,23	0,38	0,69	0,03	-0,23
	2-4	93,4	1,02	0,16	0,02	0,21	0,30	0,70	0,11	0,96
	4-6	89,4	1,05	0,15	0,03	0,23	0,27	0,68	0,17	1,83
	6-8	89,0	1,05	0,16	0,03	0,21	0,28	0,68	0,19	2,11
	8-10	89,5	1,05	0,14	0,03	0,24	0,29	0,70	0,16	1,67
	12-14	89,4	1,05	0,13	0,04	0,26	0,32	0,75	0,14	1,44
	18-20	85,6	1,07	0,16	0,05	0,26	0,27	0,75	0,25	3,15
	26-28	85,1	1,08	0,13	0,05	0,30	0,32	0,80	0,21	2,49
AF2	0-2	83,8	1,09	0,66	0,09	0,41	0,27	1,43	1,16	16,85
	2-4	78,7	1,12	0,27	0,07	0,34	0,23	0,92	0,65	9,19
	4-6	75,9	1,15	0,12	0,05	0,31	0,24	0,71	0,33	4,30
	6-8	76,4	1,14	0,09	0,07	0,27	0,26	0,70	0,24	2,89
	8-10	77,2	1,14	0,13	0,08	0,27	0,29	0,77	0,33	4,21
	12-14	75,6	1,15	0,00	0,03	0,35	0,26	0,65	0,01	-0,55
	18-20	82,7	1,09	0,20	0,06	0,25	0,40	0,92	0,38	5,03
	20-22	84,1	1,08	0,10	0,09	0,14	0,39	0,71	0,16	1,78
AF1	0-2	85,8	1,07	1,72	0,20	0,33	0,36	2,61	2,62	38,82
	2-4	81,2	1,11	0,16	0,21	0,41	0,29	1,07	0,33	4,34
	4-6	79,9	1,12	0,19	0,11	0,25	0,31	0,85	0,42	5,72
	6-8	80,3	1,11	0,15	0,17	0,29	0,19	0,81	0,33	4,36
	8-10	81,1	1,11	0,18	0,20	0,24	0,17	0,79	0,39	5,13
	10-12	83,1	1,09	0,21	0,11	0,21	0,33	0,86	0,39	5,23
	12-14	82,9	1,09	0,16	0,14	0,26	0,32	0,89	0,30	3,82

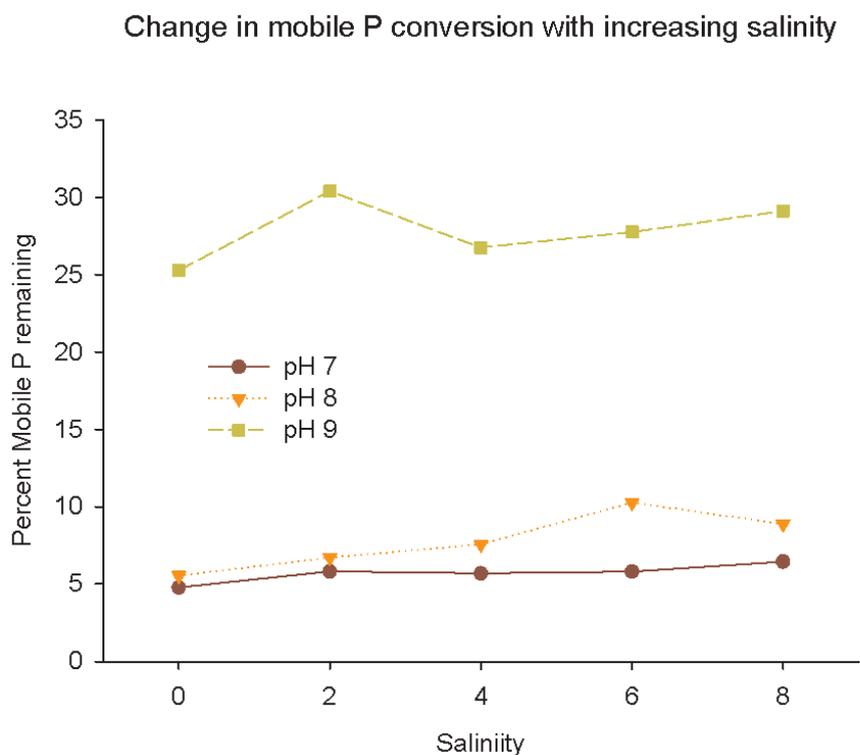
To elucidate the effect of varying salinity and pH on the binding of sediment phosphorus by Al, five sediment samples (AF 5 4-6, AF4 0-2, AF 2 0-2, AF 2 2-4, AF 1 0-1) were used in the aluminium addition experiments. These samples provided a large range of mobile sediment phosphorus contents (0.25 to 2.62 g/m²/cm) insuring the results and models developed will cover a broad range of sediment types (Table 2).

Table 2. Analysis matrix for testing effects of aluminium addition to Baltic Sea sediment.

Salinity	pH			Mobile P
(ppt)	7,0	8,0	9,0	(g/m ² /cm)
0,0				0,25
2,0				0,65
4,0				1,2
6,0				1,7
8,0				2,6
0	25	50	75	100
Aluminum dosing ratios				

As salinity increased from 0 to 8, little change occurred in binding of phosphorus by aluminium (Figure 2). There did, however, appear to be a combined effect of pH and salinity. At pH 7, the amount of mobile P remaining (not converted to Al-P) in sample AF 1 (0-2 cm) increased from 4.8% to 6.4% as salinity increased from 0 to 8. At pH 8, the remaining mobile phosphorus increased from 5.6 to between 10.2 and 8.9 at salinities of 6 and 8, respectively. At pH 9, the amount of remaining mobile phosphorus increased from 25% to 29%, although this relationship appeared to be somewhat more variable (see discussion below) and is likely due to the lower stability of aluminium at higher pH values.

Figure 2. Change in percent of mobile phosphorus inactivated (converted to Al-P) with changing salinity.



When pH of the solution was increased, more variation was seen in the amount of mobile phosphorus inactivated by the added aluminium. Only small changes in the amount of mobile phosphorus inactivation occurred between pH 7 and 8, whereas much larger changes were detected at pH 9 (Figures 3 and 4). In sediment with both low and high mobile phosphorus content, the amount of mobile phosphorus remaining in the sediment after aluminium addition increased from between 5 and 13% to between 41 and 25% in sediment with low and high mobile phosphorus content, respectively.

Figure 3. Change in mobile P inactivation as pH increases from 7 to 9 in sediment with low mobile phosphorus mass (0.25 g/m²/cm).

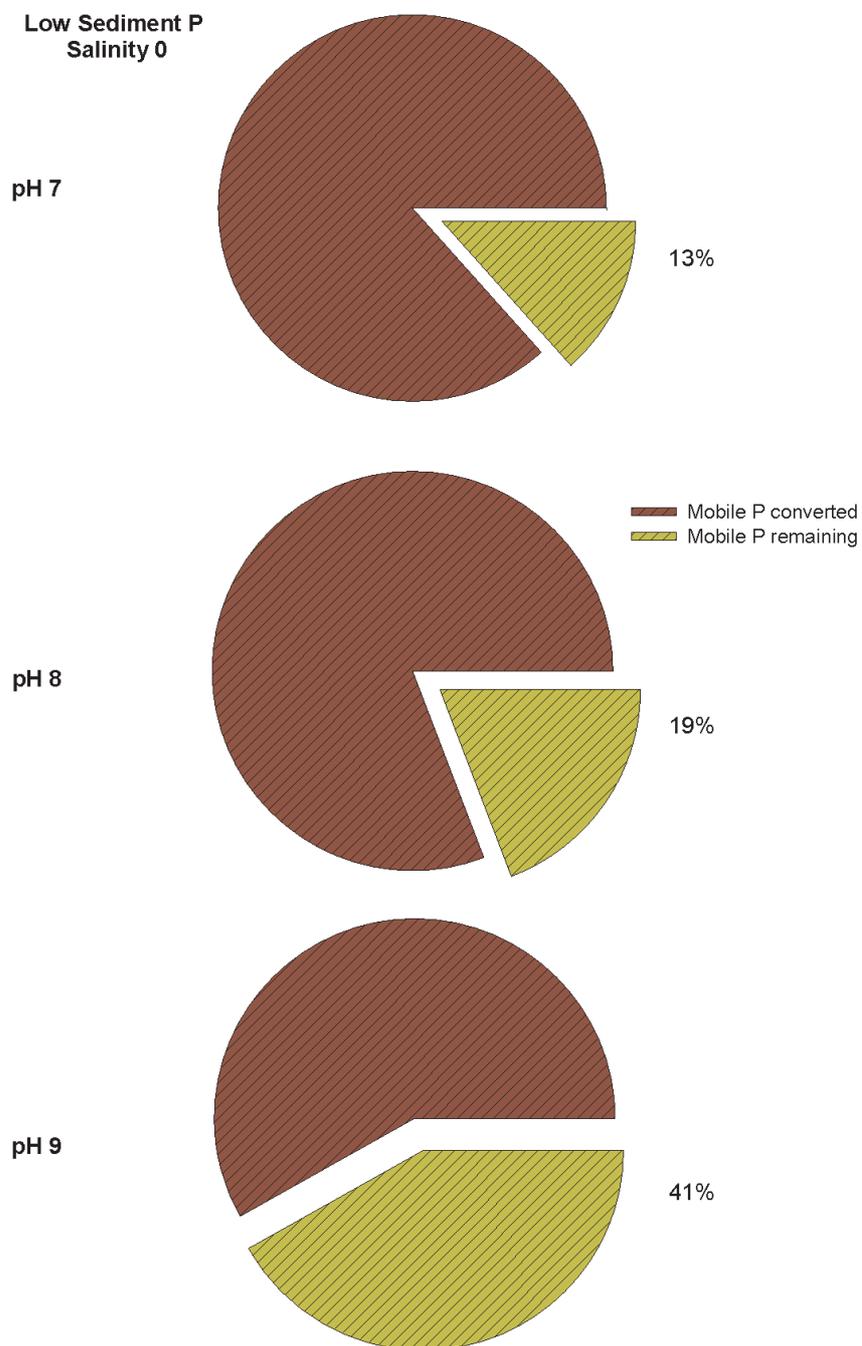
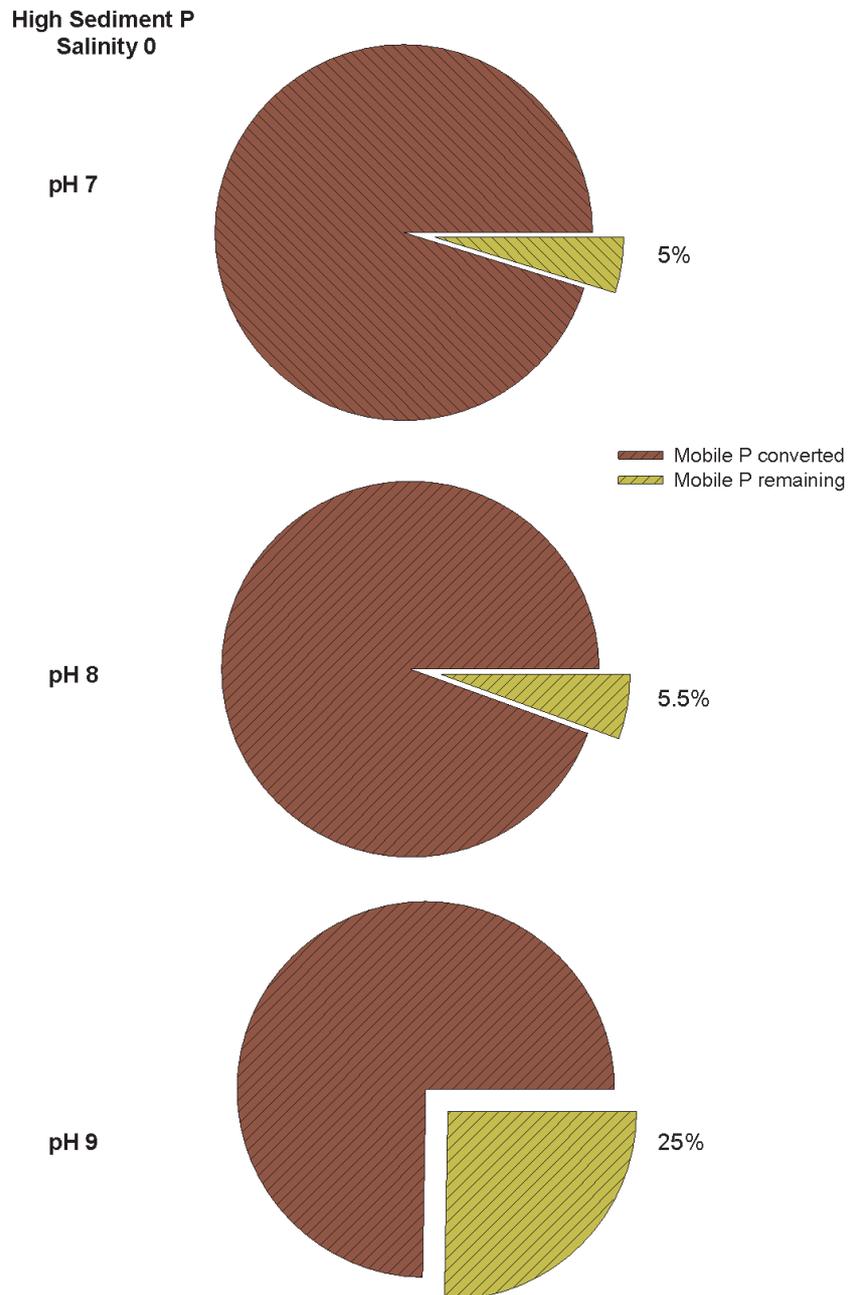


Figure 4. Change in mobile P inactivation as pH increases from 7 to 9 in sediment with moderate to high mobile phosphorus mass ($1.7 \text{ g/m}^2/\text{cm}$).

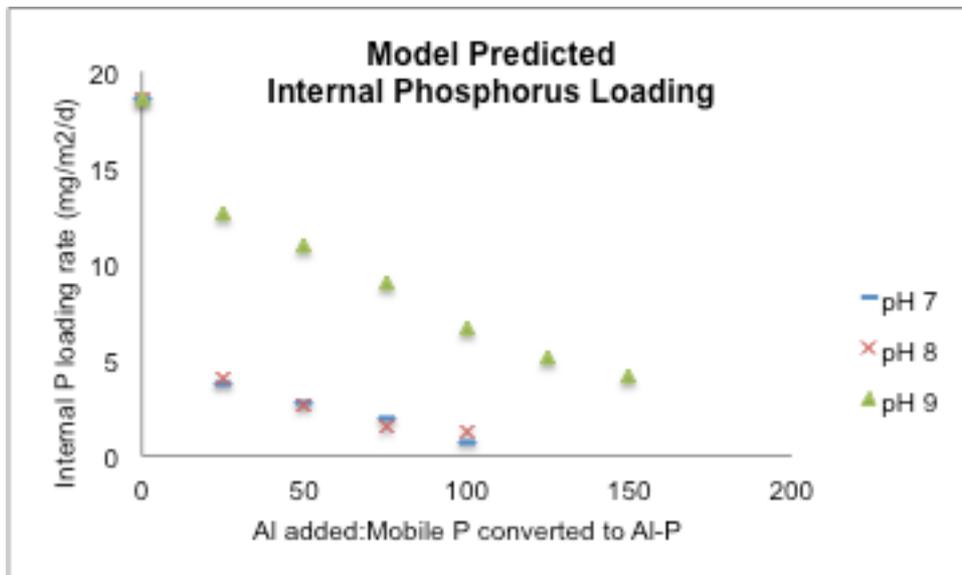


To put these numbers into perspective, the change in internal phosphorus loading (phosphorus released from the sediment to the water column) was quite low after aluminium addition at pH 7, decreasing from 3.5 (with no aluminium added) to 0 $\text{mg/m}^2/\text{d}$. At pH 9, however, the internal phosphorus loading rate decreased to 1

mg/m²/d. In the sample with higher mobile sediment phosphorus (AF 4, 0-2 cm), the internal phosphorus loading rate decreased from approximately 24 mg/m²/d to 6 mg/m²/d at pH 9, whereas it decreased to 0.34 mg/m²/d at pH 7. Thus, internal phosphorus loading was basically eliminated at pH 7 in both the low and high mobile phosphorus content samples whereas at pH 9, a substantial portion of mobile phosphorus was left unbound to Al, resulting in significantly higher levels of internal phosphorus loading after treatment at this pH level.

Based on the information gained during the experiments under varying salinity and pH, models were developed (see Appendix A) to predict the outcome of aluminium addition to sediment and the eventual conversion of mobile phosphorus to Al-P. These relationships can then be used to predict the resulting internal phosphorus loading rate after treatment, which is the information required for management and restoration of water bodies negatively affected by excess nutrients. To test the model output, the average mobile sediment phosphorus content of Torsbyfjärden was used in the analysis (1.28 g/m²/cm). The output from the model at salinity 6 is shown in Figure 5.

Figure 5. Model output for internal phosphorus loading rate under varying pH at salinity 6.



The initial internal loading rate is high before treatment at approximately 18 mg/m²/d. At both pH 7 and pH 8, the internal loading rate decreases to 0.7 and 1.3

mg/m²/d, respectively, when the ratio of added aluminium to mobile sediment phosphorus is approximately 100 (Figure 5). These are both reasonable endpoints for management of water bodies undergoing nutrient management. At pH 9, however, the internal phosphorus loading rate was still 4.2 mg/m²/d after the same amount of aluminium was added to the sediment. This is a substantial improvement from the initial 18 mg/m²/d, but remains high enough to limit water quality improvement. If we extrapolate the results at pH 9 to determine how much additional aluminium would be required to achieve the similar results to the pH 7 test, approximately 2.5 times the amount of aluminium would be required which would lead to an obvious and substantial cost increase.

Discussion

The results of this study indicate limited effect of salinity on binding between aluminium and phosphorus, whereas elevated pH had a substantial, negative impact. This is somewhat surprising, because a number of studies have previously indicated limited release of phosphorus from aluminium at up to pH 9.5 (e.g. Rydin and Welch 1998). The results detailed herein have implications not only for restoration activities aimed at reducing phosphorus in water bodies such as the Baltic Sea, but also potential toxicity. Aluminium is generally in an insoluble form from pH 6 to 9, and thus presents limited toxicity potential to aquatic biota. Outside these bounds, however, aluminium can be toxic, although more so at low pH (<5.5).

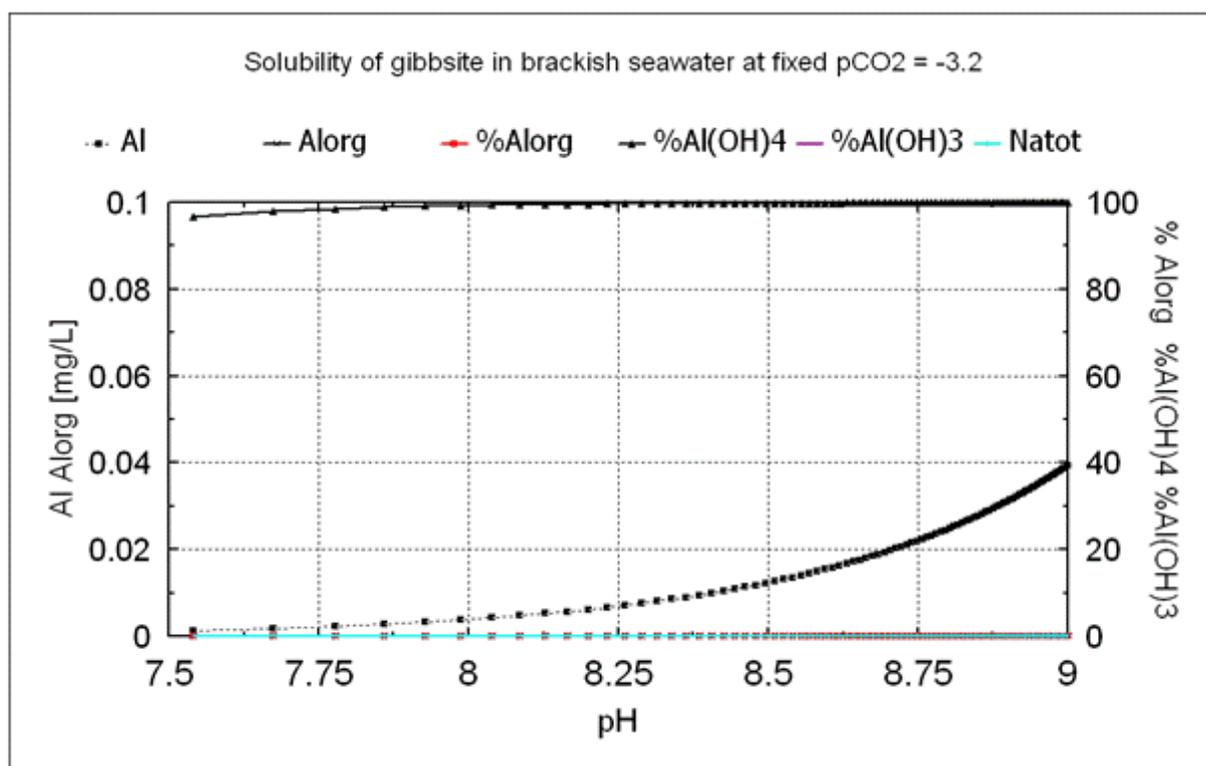
Aluminium chemistry and phosphorus binding

The effectiveness of aluminium binding of phosphorus in water and sediment depends upon the chemical speciation. Between pH levels of 5.5 and 9, organically bound aluminium and non-soluble forms of aluminium dominate (e.g. $\text{Al}(\text{OH})_3(\text{s})$). Positively charged, monomeric inorganic species (Al^{3+} , $\text{Al}(\text{OH})^{2+}$, and $\text{Al}(\text{OH})_2^+$) dominate at pH levels below 5.5 whereas the negatively charged inorganic $\text{Al}(\text{OH})_4^-$ dominates in alkaline waters at a pH above 7 to 8. In an extremely hard water, alkaline lake, Anderson (2004) found that aluminium concentrations rose after aluminium addition (approximate 50 mg Al/L dose), increasing to 0.2 mg/L at pH 7.0 and to over 1 mg/L when pH was greater than 7.9. Aluminium levels decreased again within 10 to 14 days after treatment. In brackish waters, the anionic form of aluminium ($\text{Al}(\text{OH})_4^-$) tends to dominate the soluble fraction of aluminium due generally to higher pH levels (Figure 6).

Al-floc formed previously to treat upstream agricultural runoff was exposed to Salton Sea water with high salinity (46 g/L) and pH (8.6). Between 2.3 and 46% of the aluminium bound phosphorus was released (at original aluminium doses of 30 and 3 mg/L, respectively) however, only 0.3% and 2.9% of the aluminium was released, respectively (Rodriguez et al. 2008). This is similar to the results of this study where salinity had only a minor effect (approximately 5% total difference) at pH levels of 7 and 8.

A previous study by Rydin and Welch (1999) showed that at a Al added:mobile phosphorus ratio of approximately 100, more than 90% of the mobile sediment phosphorus would be converted to Al-P. Even though we show similar results at pH 7 and pH 8 (Figure 5), this is clearly not the case at pH 9. The reason for this, as stated above, is that the fraction of Al in soluble form starts to increase slightly above pH 8 and then continues to increase at a steeper, almost exponential slope after pH 8.5 (Figure 6). Thus, an increasingly smaller amount of aluminium is in solid form ($\text{Al}(\text{OH})_3$) and less effective binding of phosphorus occurs.

Figure 6. Calculated solubility (this study) of Al (■) in presence of gibbsite ($\text{Al}(\text{OH})_3$) and relative importance of Al species as a function of pH. Inorganic $\text{Al}(\text{OH})_4^-$ (▲) dominates the soluble fraction in alkaline waters at a pH above 6.5.



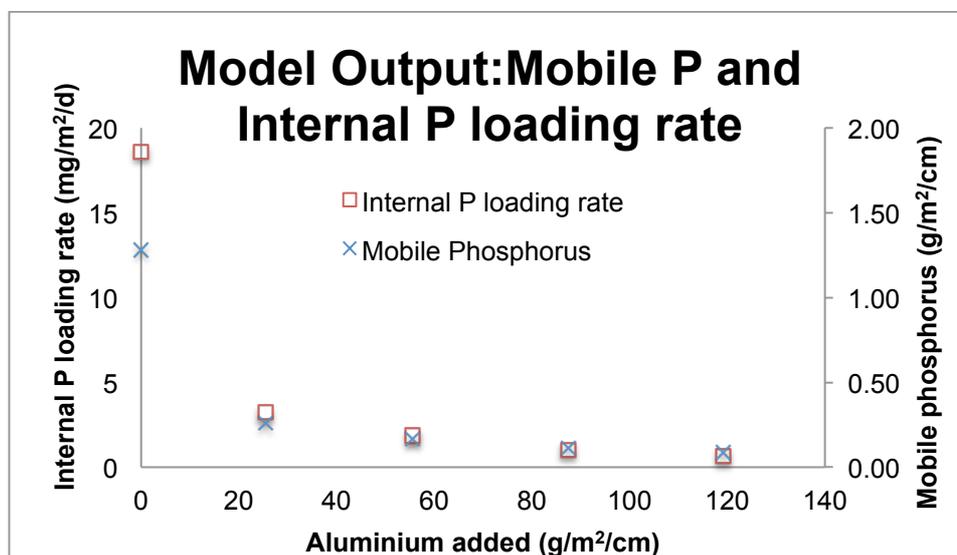
The study by Rydin and Welch (1998) that showed insignificant dissolution of phosphorus bound by aluminum at pH 9.5 may have had different results from this study for a number of reasons. First, the study was conducted for 12 hours instead of 48, a factor of four difference. Second, other elements in the sediment may have limited binding of phosphorus by aluminium. The study by Rydin and Welch was conducted on sediment collected from a freshwater lake (Wisconsin, USA), where-

as this study used sediment from the Baltic Sea. Brackish and saltwater systems contain different types and amounts of ions that may interfere with binding between aluminium and phosphorus (Stumma and Morgan 1996). Unfortunately the types of analysis needed to determine if this led to any changes in binding effectiveness were outside the scope of this study. Given the low salinity of brackish waters, and the fact that similar results were seen when no salt was added to the aluminium solutions used in this study, it seems likely that the difference in exposure time led to the differences in aluminium binding effectiveness.

Modelling of phosphorus binding and internal phosphorus loading

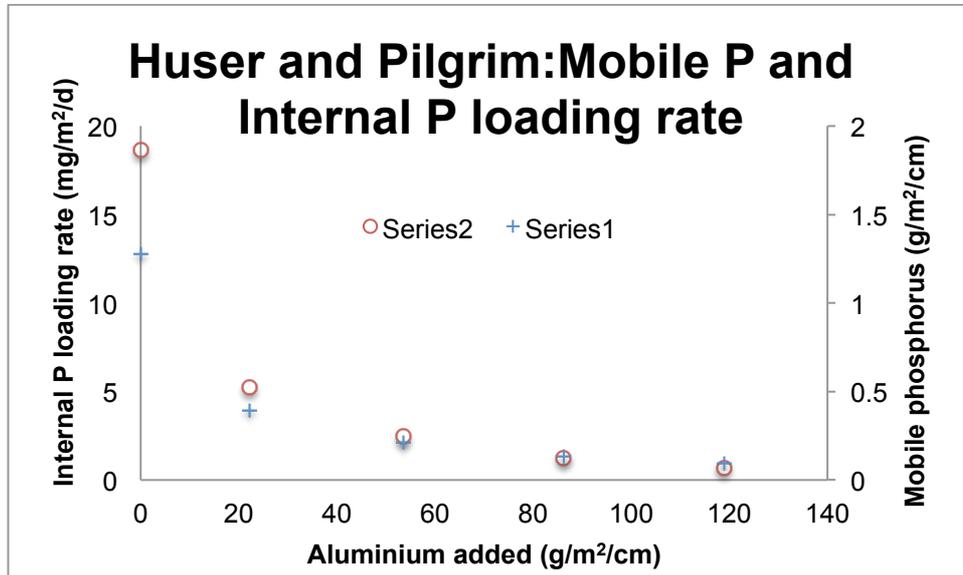
The empirical models developed as part of this study (graphical representations found in Appendix A) will be useful to those looking to predict the reduction of internal phosphorus loading from brackish water sediment after aluminium addition. One of the strong points of these models is that they cover a broad range of sediment phosphorus content, salinity, and pH. This information was only previously available for freshwater systems and at a pH of 6.5 to 7. Using the empirical models and the average concentration of mobile sediment phosphorus found in Torsbyfjärden as an example of model application, we can see the decrease in mobile sediment phosphorus as it is converted to Al-P (Figure 7). The decrease in internal phosphorus loading can also be predicted using the relationship developed by Pilgrim et al. (2007).

Figure 7. Model output using one of the empirical models (pH 7, salinity 0) developed herein and an average mobile sediment phosphorus (P) content of 1.28 g/m²/d.



The models for mobile phosphorus reduction and decreased internal phosphorus loading after aluminium addition at pH 7 (and to a lesser extent pH 8) and salinity 0 are similar to the model developed by Huser and Pilgrim (2013) using sediment collected from 20 freshwater lakes in the USA (Figure 8). This is not unexpected given that the Huser and Pilgrim model was developed for freshwater systems with a study pH of approximately 6 to 7. Clearly the major difference comes into play when pH is at 9 or higher (presumably) and less mobile phosphorus is converted to Al-P, leading to a less effective reduction of internal phosphorus loading (Figure 5).

Figure 8. Model output using the model developed Huser and Pilgrim (2013) and an average mobile sediment phosphorus (P) content of 1.28 g/m²/d.



This is not entirely unexpected because the chemistry of aluminium in water dictates that an increasing portion of aluminium will be present in the soluble, anionic form ($\text{Al}(\text{OH})_4$), which is unable to bind phosphorus in the sediment. The results of this study show that a good portion of the mobile sediment phosphorus was inactivated, but not nearly as much as was detected at pH 7 or even pH 8 (Figures 3 and 4). With the models developed herein, however, we will now be able to predict the resulting effectiveness of treatment with aluminium in brackish systems with pH values ranging from approximately 7 to 9. This will allow for better management of surface waters such as the Baltic Sea, and will prevent costly failures in situations where aluminium is shown to be less effective than once thought.

References

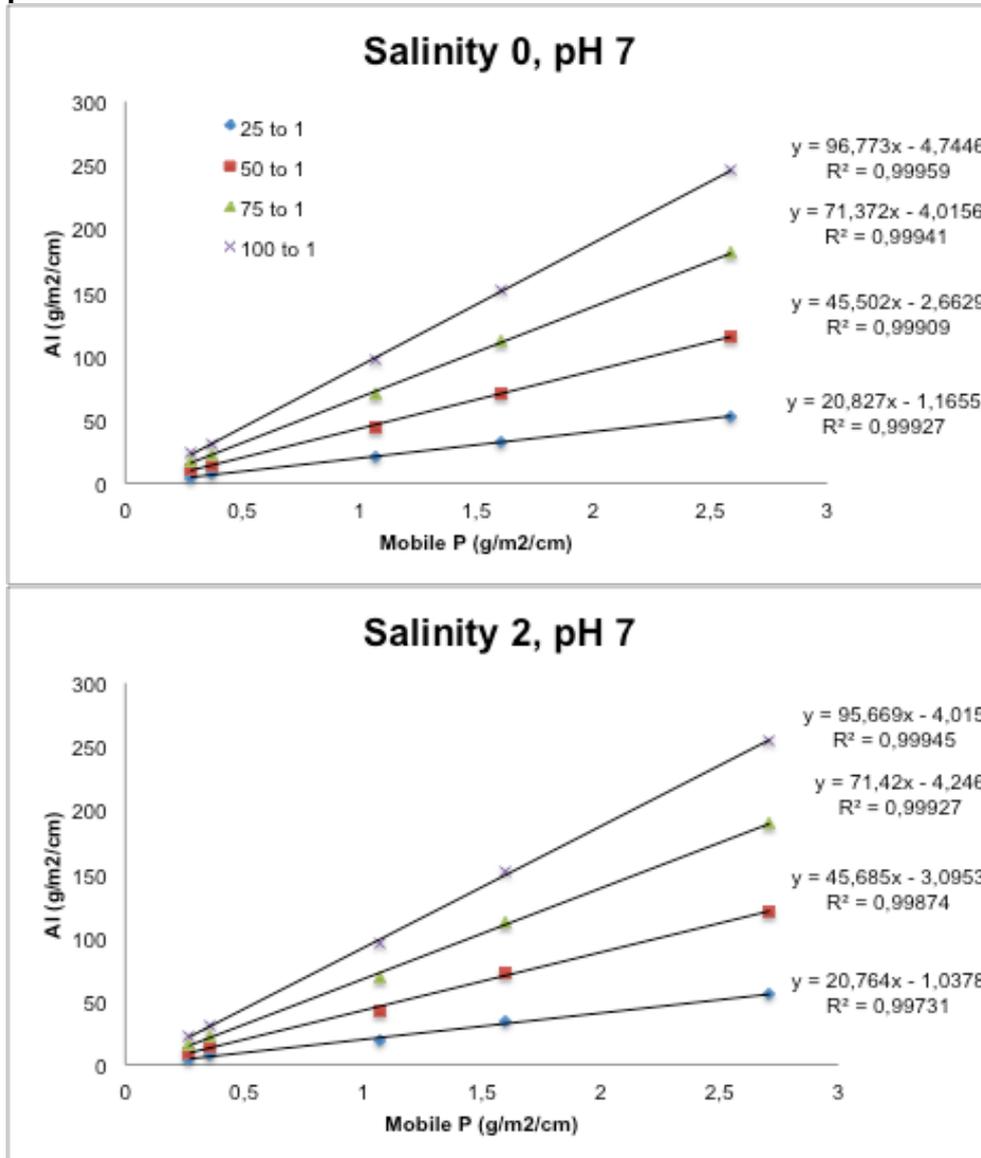
- BalticSea 2020. 2011. Fosforfällning för en förbättrad skärgårdsmiljö – ett meso-kosmförsök. www.balticsea2020.org. 38pp.
- Bonsdorff, E., Blomqvist, E. M., Mattila, J., and Norkko, A. 1997. Estuarine, Coastal and Shelf Science 44 (A), 63-72.
- Cooke, G.D., Welch, E.B., Peterson, S.A. and Nichols, S.A. 2005. Restoration and management of lakes and reservoirs, CRC Press, Boca Raton.
- Hupfer, M., Gachter, R. and Giovanoli, R., 1995. Transformation of phosphorus species in settling seston and during early sediment diagenesis. Aquat Sci 57(4), 305-324.
- Huser, B., Brezonik, P. and Newman, R., 2011. Effects of alum treatment on water quality and sediment in the Minneapolis Chain of Lakes, Minnesota, USA. Lake and Reservoir Management 27(3), 220-228.
- Huser, B.J. and Köhler, S.J. 2012. Potential toxicity and chemical processes of aluminium addition for phosphorus control in Östhammarsfjärden. <http://publikationer.slu.se>. Report 2012:2. 37pp.
- Huser, B.J. and Pilgrim, K.M. 2012. A predictive model for phosphorus binding by aluminum in lake sediments. Manuscript in revision, Water Research. 15pp.
- Håkanson, L., Jansson, M.. 1983 *Principals of lake sedimentology*. Springer-Verlag: Berlin, p 316.
- Jensen, H.S., Mortensen, P.B., Andersen, F.O., Rasmussen, E. and Jensen, A. 1995. Phosphorus cycling in a coastal marine sediment, aarhus bay, denmark. Limnol Oceanogr 40(5), 908-917.
- Jeppesen, E. et al. 2005. Lake responses to reduced nutrient loading – an analysis of contemporary long-term data from 35 case studies, Freshwater Biol, 50, 1747-1771.
- Kennedy, R.H., Barko, J.W., James, W.F., Taylor, W.D. and Godshalk, G.L. 1987. Aluminum sulfate treatment of a eutrophic reservoir: Rationale, application methods, and preliminary results. Lake Reserv Manage 3(1), 85-90.
- Munkes, B. 2005. Eutrophication, phase shift, the delay and the potential return in the greifswalder bodden, baltic sea. Aquatic Sciences - Research Across Boundaries 67(3), 372-381.
- Nürnberg, G.K. 2009. Assessing internal phosphorus load – problems to be solved. Lake Reserv Manage 25(4), 419 - 432.
- Pilgrim, K.M. and Brezonik, P.L. 2005. Treatment of lake inflows with alum for phosphorus removal. Lake Reserv Manage 21(1), 1-9.

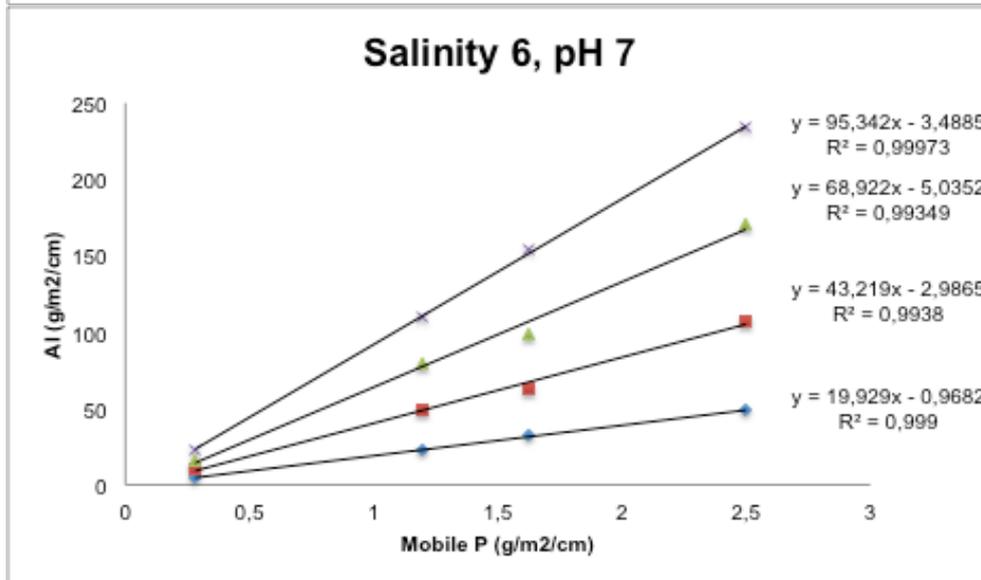
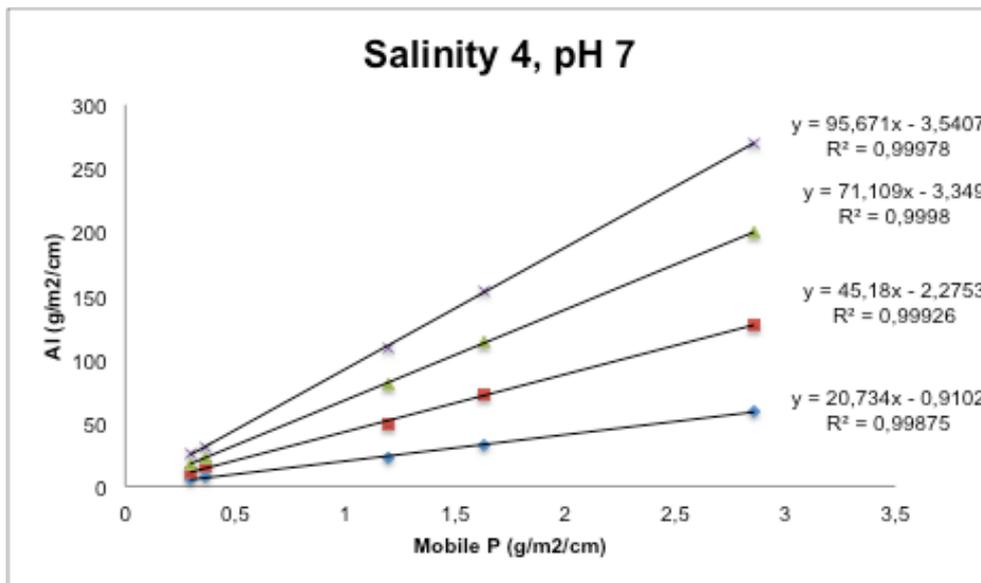
- Pilgrim, K.M., Huser, B.J. and Brezonik, P.L. 2007. A method for comparative evaluation of whole-lake and inflow alum treatment. *Water Res* 41(6), 1215-1224.
- Psenner, R., Boström, B., Dinka, M., Pettersson, K., Puckso, R., Sager, M. 1988. Fractionation of phosphorus in suspended matter and sediment. *Archiv Fur Hydrobiologie Supplement* (30), 98-103.
- Rodriguez, I.R., C. Amrhein and M.A. Anderson. 2008. Reducing dissolved phosphorus loading to the Salton Sea with aluminum sulfate. *Hydrobiologia*. 604:37-44.
- Rydin, E. and Westerlund, U. 2003. Effekten av reducerat fosforflöde från brackvattensediment– experiment i Östhammarsfjärden. www.svenskvatten.se. Rapport 1, Feb 2003. 24pp.
- Rydin E, Welch EB. 1998. Aluminum dose required to inactivate phosphate in lake sediments. *Wat Res*. 32(10):2969-2976.
- Rydin, E. and Welch, E.B. 1999. Dosing alum to wisconsin lake sediments based on in vitro formation of aluminum bound phosphate. *Lake Reserv Manage* 15(4), 324-331.
- Rydin, E., Huser, B. and Welch, E.B. 2000. Amount of phosphorus inactivated by alum treatments in washington lakes. *Limnol Oceanogr* 45(1), 226-230.
- Sas, H. 1990. Lake restoration by reduction of nutrient loading - expectations, experiences, extrapolations. *Int Ver Theor Angew* 24, 247-251.
- Schulz, S., Aertbjerg, G., Behrends, G. et al. 1992. The present state of the Baltic Sea pelagic ecosystem-an assessment. In *Proceedings of the 25th European Marine Biology Symposium*. pp. 35-44.
- Stumm, W. and Morgan, J.J. 1996. *Aquatic chemistry*, John Wiley and Sons, Inc, New York.
- Vahtera, E. et al. 2007. Internal ecosystem feedbacks enhance nitrogen-fixing cyanobacteria blooms and complicate management in the baltic sea. *Ambio* 36(2/3), 186-194.
- Virtasalo, J.J., Kohonen, T., Vuorinen, I. and Huttula, T. 2005. Sea bottom anoxia in the archipelago sea, northern baltic sea—implications for phosphorus remineralization at the sediment surface. *Mar Geol* 224(1–4), 103-122.
- Welch, E.B. 1996. Control of phosphorus by harvesting and alum- *Water Res. Series Tech. Rept.* 152. Univ. of Washington, Dept. of Civil and Environ. Eng.
- Welch, E.B. and Cooke, G.D. 1995. Internal phosphorus loading in shallow lakes: Importance and control. *Lake Reserv Manage* 11(3), 273-281.

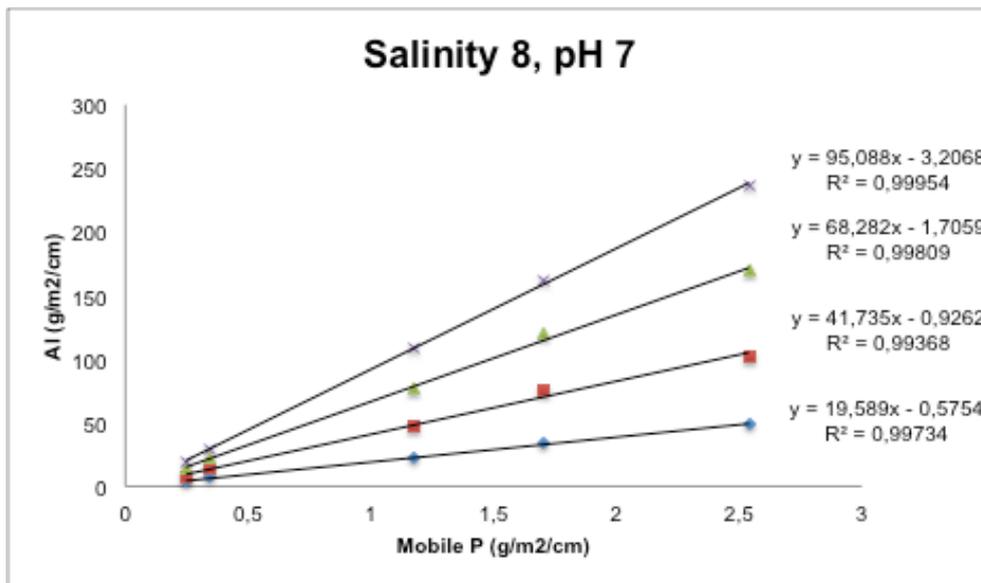
Appendix A

Empirical models developed for aluminium addition to sediment at varying salinity (0 to 8) and pH (7 to 9).

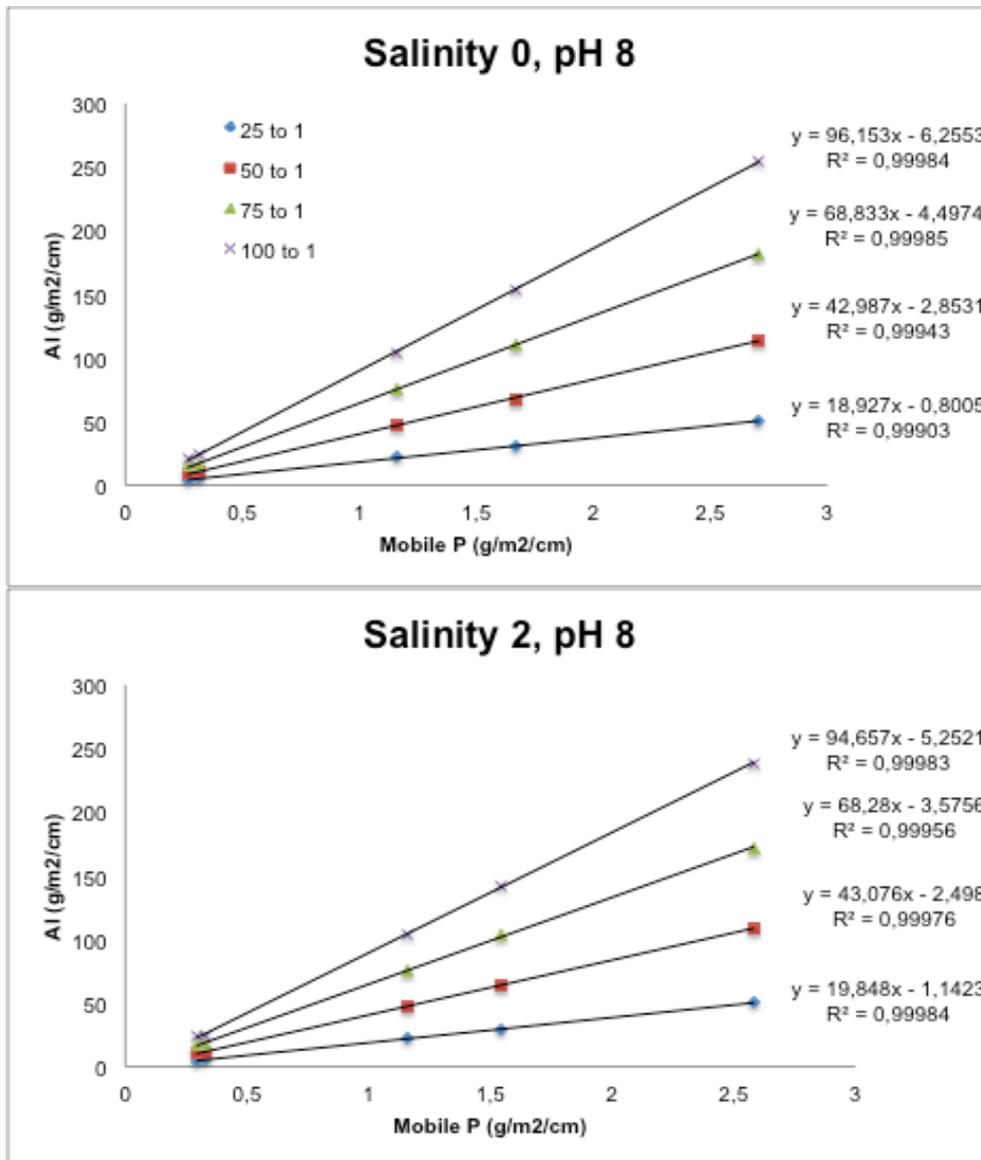
pH 7

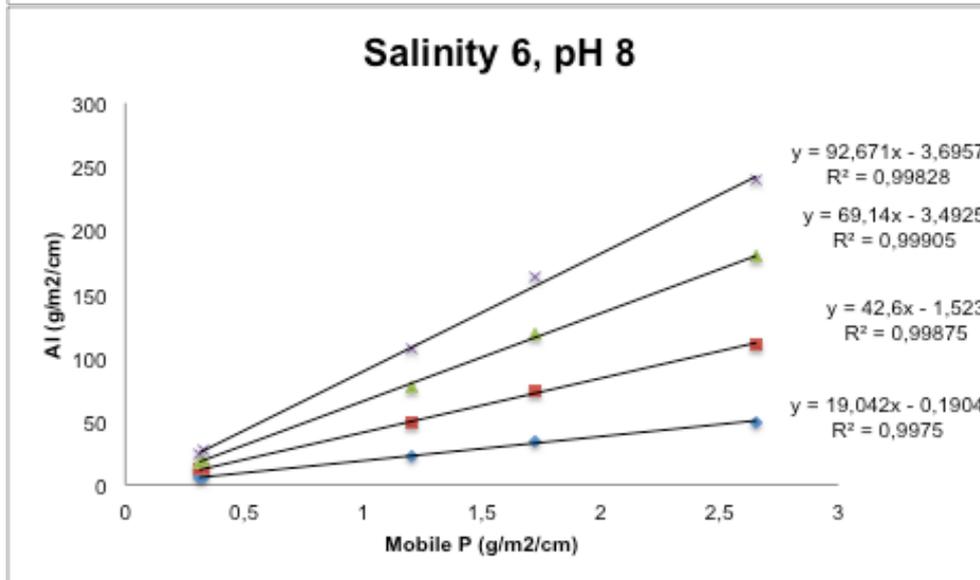
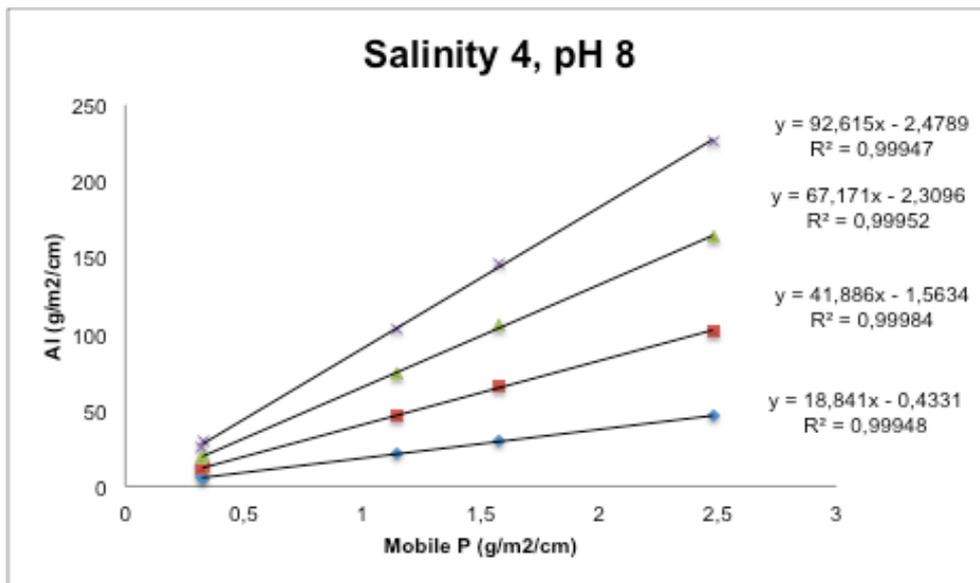


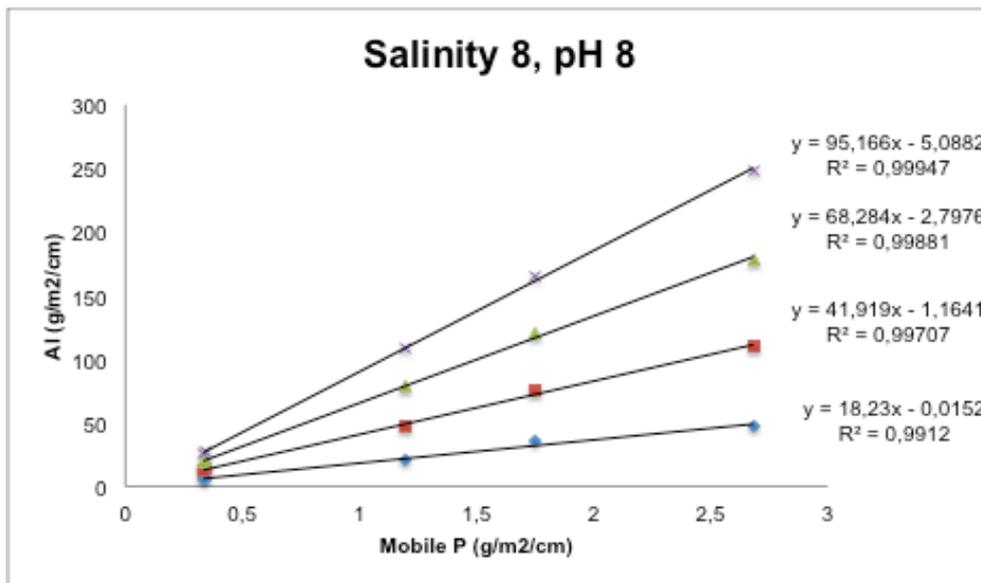




pH 8







pH 9

