Potential toxicity and chemical processes of aluminium addition for sediment phosphorus control in Östhammarsfjärden

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Förord

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Innehåll

Sammanfattning

Målsättningen med den här studien var att utreda möjliga biologiska effekter av aluminiumtillsats till Östhammarsfjärden (Östhammars kommun) för att minska fosforläckaget från bottensediment. Risk för påverkan på biota i vatten och sediment bedömdes med hjälp av rapporter, vetenskapliga publikationer samt modellering baserad på data från inneslutningsförsök med och utan aluminiumtillsats i Löparöfjärden (Norrtälje kommun) sommaren 2011.

I sjöar har man i över fyrtio år använt aluminiumsaltlösning för att minska fosforhalten i vatten och sediment. Toxiciteten hos aluminium i sjöar bedöms vara försumbar under neutrala förhållanden, huvudsakligen på grund av att reaktiviteten och biotillgängligheten av aluminium vid ph 6-9 är väldigt låg. Den toxikologiska litteraturen stöder dock att det finns vissa möjliga biologiska effekter vid aluminiumtillsättning till sött eller bräckt vatten vid circum-neutralt pH och att kontinuerlig exponering av aluminium har större negativa effekter på biota jämfört med en enstaka behandling. De potentiella negativa effekterna av enstaka aluminiumbehandlingar sammanhänger med mängden aluminiumhydroxidflock, en amorf mineralisk massa som påverkar bottenfaunans livsmiljö. Några andra möjliga negativa effekter inkluderar minskade bottenfaunatäthet och förhöjd fysiologiskt stress på fisk. Tidigare studier har dock visat att dessa effekter är kortvariga (veckor för bottenfauna) till medellånga (1-2 år för fisk) och att de akvatiska samhällena återhämtar sig och uppnår ett bättre miljötillstånd jämfört med innan behandlingen på grund av förbättrad vattenkemi och livsmiljökvalitet. Direkt inblandning av aluminium till sedimentet gör att behandlingseffekterna på plankton och fisk i vattnet minskar eller uteblir helt. Det är svårt att utifrån studier i sötvatten dra säkra slutsatser för brackvattensystem, eftersom experimentella data från aluminiumbehandling i bräckt eller salt vatten i princip saknas. En del studier rekommenderar mindre restriktiva begränsningar för aluminium i saltvatten på grund av att vattenkemin skiljer sig åt från sötvatten, andra förslår mer restriktiva begränsningar på grund av risken för negativa effekter med högre biologisk mångfald och ett större antal känsliga arter. Bottenfaunan i Östhammarsfjärden är sparsam och domineras av ett stort antal okänsliga arter typiska för påverkade system med låg kvalitet. Resultat från ett inneslutningsförsök i bräckt vatten (Löparöfjärden 2011) där aluminium tillsattes i sedimentet visades inga negativa effekter på biota under de fyra månader som försöket pågick efter behandlingen. Eventuella negativa effekter på bottenfaunan vid aluminiumtillsättning bedöms därför blir obetydlig och kvalitén på bottenfauna samhället förväntas istället att öka på några års sikt.

De aluminiumhalter som uppmättes i ett inneslutningsförsök i Löparöfjärden var högre än modellerade halter. Det kan inte uteslutas att dessa förhöjda halter, efter tillsats av aluminium i sedimentet, kan påverka vattenorganismer. Aluminiumlösligheten kan öka något under det pH och den jonstyrka (salthalt) som råder i bräckt vatten men med de data som finns tillgängliga är det svårt att förklara varför detta har hänt. Den kemiska modelleringen baserades enbart på pH och uppmätta halter av aluminium, osäkerheterna för denna analys ökar utan en full kemisk analys och därför bör resultaten av modelleringen tolkas med försiktighet. Eftersom aluminiumhalterna var högre än vad som förväntades baserat på jämvikts beräkning med kristallin gibbsit är det nödvändigt att följa de kemiska processerna i framtida experiment för att fullt ut förstå de kemiska processer som sker.

Aluminiumbehandling är troligtvis en bra metod för att minska fosforläckaget från sediment i Östhammarsfjärden. Eventuellt kan kortsiktiga effekter på biota uppstå om aluminiumhalterna i vattnet når upp i de koncentrationer som uppmättes i Löparöfjärdens inneslutningsförsök efter behandlingen där. Men de effekterna blir obetydliga jämfört med ökningen av det akvatiska samhällets ekologiska

status efter behandling. Eftersom inneslutningsförsöken i Löparöfjärden inte visade på negativa effekter på biota efter aluminiumbehandlingen, bedöms risken för negativa konsekvenser på biota som låg med en fullskalig aluminiumbehandling i Östhammarsfjärden. Men eftersom det inte finns någon fullskalestudie av aluminiumbehandlingar i bräckt vatten är vår bedömning att det under och efter en fullskalig aluminiumbehandling behövs kompletta kemiska analyser av pH, alkalinitet, totalt organiskt kol, och katjoner och anjoner. Sedimentens halter av aluminium och olika fosforformer borde också undersökas för att utöka kunskapsbasen samt förståelsen för de kemiska processer som sker när man tillsätter aluminium till sediment i bräckt vatten.

Toxicity Review

An extensive literature review (peer reviewed journal articles and reports by governmental agencies) was conducted to define the potential effects of aluminum salt treatments on aquatic life (i.e. benthic invertebrates, plankton, and fish). The literature and agency reports cover both acute and chronic toxicological effects of alum as well as the physical effect of aluminium-floc accumulation on the alteration of benthic invertebrate habitat and the subsequent effect on invertebrate survival. The studies were conducted in laboratories, lakes receiving whole lake alum treatments, and water bodies downstream of continuous in-line treatment systems. It should be noted, however, that data on the use of aluminium salts in marine or brackish systems is very limited (Murgotroyd et al. 1996).

Aluminium salts have been used for over four decades in lakes as a management tool to reduce phosphorus levels (Landner 1970, Kennedy et al. 1987, Rydin et al. 2000, Cooke et al. 2005) and they are an attractive option because Al, unlike iron, is not redox sensitive. In general, when aluminium salts are applied to circumneutral waters, the aluminium ion undergoes a series of hydrolysis reactions forming a highly flocculent aluminium hydroxide ($Al(OH)_3$) that sinks to the sediment, binding phosphorus from both the water column and the sediment. Aluminium salts can also be applied directly to the sediment (either just above or below the surface), limiting direct impacts on the water column.

The toxicology of aluminium has been studied extensively but studies on the effects of aluminium salt application to natural, non-acidic waters are generally limited. Most of the work on aluminium toxicity has centered on the effect of acid rain, low pH, and the subsequent increase in aluminium toxicity due to acidification. A broad summary of the toxicity literature by Pilgrim and Brezonik (2005) suggests that the potential for aluminium toxicity to invertebrates, zooplankton, and fish is negligible if pH is above 6.0 but not significantly above 9.0. This is largely due to the fact that within this pH range aluminum is in a particulate, hydroxyl phase as $Al(OH)_3$ or bound to organic matter and the reactivity and bioavailability of aluminium is reduced.

Chemistry and reaction of aluminium in surface waters

Typical aluminium concentrations in fresh water lakes range from 0.01 to 0.1 mg/L (Wetzel 2001) under non-impacted conditions. Porewater concentrations from near shore sediments in marine/estuarine systems range from 0.001 to 0.2 mg/L (Caschetto and Wollast 1979, Stoffyn-Egli 1982, Beck et al. 2010). Aluminium concentrations increase from coastal seawater background values of around 0.005 mg/L downwards in the water column profile.

The bioavailability of aluminium in water depends upon the chemical speciation. Between pH levels of 5.5 and 9, organically bound aluminum and non-soluble forms of aluminium dominate (e.g. $Al(OH)_3(s)$). Positively charged, monomeric inorganic species ($Al^{3+,}$ $Al(OH)^{2+,}$ and $Al(OH)^{2+)}$ dominate at pH levels below 5.5 while the negatively charged inorganic $Al(OH)^{4-}$ dominates in alkaline waters at a pH above 7 to 8. The positively charged inorganic species of aluminium are considered the most toxic forms under acidic conditions (Driscoll et al. 1980, Gensemer and Playle 1999) and, while toxic, the inorganic anion of aluminium has lower toxicity towards fish (Exley et al. 1996). 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 ($Al(OH_4)^-$) tends to dominate the soluble fraction of aluminum due generally to higher pH levels (Figure 1).

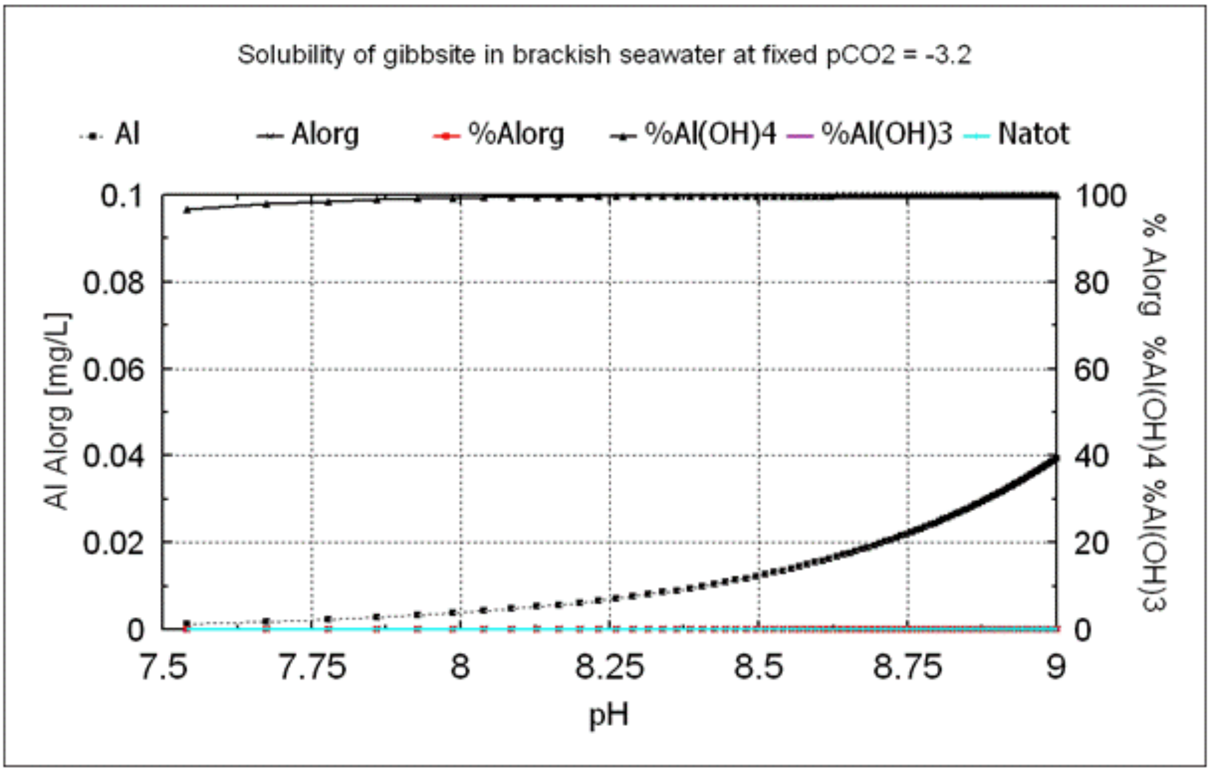

Figure 1. Calculated solubility (this study) of Al (■) in presence of gibbsite ($Al(OH)_3$) and relative importance of Al species as a function of pH. Inorganic $Al(OH)_4^-$ (▲) dominates the soluble fraction in alkaline waters at a pH above 6.5.

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). Thus, it appears that mainly desorption of phosphorus occurred (instead of aluminium dissolution), as high Si levels may have promoted the formation silicate phases at this pH.

Dissolved and total aluminium decreased after treatment of Long Lake (Washington, US) with alum (Welch 1996). The author suggested this was due to a decrease in humic binding of natural aluminium in this brown water lake. Two deep, clear water lakes in Minnesota (US) were treated with alum in 2001 and also showed aluminium levels (as total Al) lower than pre-treatment conditions a few months after treatment. It was again suggested that a lower level of living organic matter in the lake (algae) was the reason for lower aluminium concentrations in the water column (Huser 2011).

Aluminum toxicity and concentration limits

Toxicity of aluminium in water can be limited or completely negated when by dissolved constituents present in natural waters. Water containing dissolved silica (Si) can reduce or eliminate aluminium toxicity to fish (Cooke et al. 1993), even at low pH (Birchall et al. 1989). Complexation of aluminium by dissolved organic matter (DOM) will also reduce or eliminate aluminium toxicity (Birchall et al. 1989, Dobbs et al. 1989, Driscoll et al. 1980).

A review of toxicity literature is provided by Pilgrim and Brezonik (2005) and no observed effect concentrations (NOEC), or the concentration where no effect is seen on the organism, are summarized for aluminium (usually as total Al) in this study. Some of these studies were preformed in tap, distilled, or groundwater that can be expected to be low in constituents that will limit aluminium toxicity (e.g. DOM and Si). NOECs (as total Al) were >400 µg Al/L for fathead minnow (4-week juvenile), >1000 µg Al/L for largemouth bass (larvae), and from 830 to 1050 µg Al/L for rainbow trout (juvenile) during 4-day exposures. 16-day exposures gave a NOEC range of 1180 to 2640 µg Al/L for rainbow trout (Pilgrim and Brezonik 2005).

Environmental limits in surface waters have been developed by a number of authorities. Niva (Norsk institut for vannforskning) developed criteria or conditional limits for a number of common water chemistry parameters including aluminium (dissolved inorganic or labile) in surface waters (Niva 2008). These limits were based on water chemistry that can be found in different types (classes) of surface waters in Norway and limits for lakes, based on 780 lakes in Norway, are shown in Table 1.

Table 1. Level classification for dissolved, inorganic Al (in µg/L) for lakes in Norway (Niva 2008).

Region	Lake Type	Ref. Value	Excellent	**Good**	Poor	Very Poor
Lavland	Ca poor, TOC<2	<5	5	**30**	65	95
	Ca poor, TOC 2-5	<5	5	**30**	65	95
	Ca poor, humic	<5	5	**30**	65	95
Skog	Ca very poor, TOC<2	<5	5	**10**	20	40
	Ca very poor, TOC 2-5	<5	5	**15**	25	60
	Ca very poor, humic	<5	5	**20**	30	60
	Ca poor, TOC<2	<5	5	**30**	65	95
	Ca poor, TOC 2-5	<5	5	**30**	65	95
	Ca poor, humic	<5	5	**30**	65	95
Fjell	Ca very poor, TOC<2	<5	5	**10**	20	40
	Ca very poor, TOC 2-5	<5	5	**15**	25	60
	Ca poor, TOC<2	<5	5	**30**	65	95
	Ca poor, TOC 2-5	<5	5	**30**	65	95

The methodology used to determine reference values and the different class boundaries was based upon an intercalibration of class boundaries, dose response curves, and regression models describing relationships between the most sensitive aquatic species and gradients of eutrophication and acidification (Niva 2008). Thus, the values presented in the table above can be considered conservative in that they tend to refer to “worst case” scenarios for the protection of aquatic life. The values in the “Good” class are considered the environmental objectives and the classification takes into account the toxicity limiting effects from both Ca and TOC in the water bodies. However, the classification system notes that these values should be used for systems that are of high quality or good ecological status. Aluminium limits in other water bodies with moderate to poor ecological status should be decided on a case by case basis based on the aquatic life present in the system. Recently Köhler and Erlandsson (2011) published values on the natural presence of aluminum in non-acidified surface waters. In their study they conclude that concentrations of monomeric Al_i (labile aluminium measured spectrophotometrically) should be below 30 µg/L if pH is above 5.6.

Murgotroyd et al. (1996) provides a review of aluminium containing polyelectrolyte compound toxicity to marine organisms. Although data were limited, suggested EC50/LC50 ranges for both anionic (>1000 mg/L) and cationic (1000-2370 mg/L) compounds were one to two orders of magnitude higher than for the same compound in fresh waters. Note that the concentrations are for the compounds and the concentrations of aluminium would be lower. The main reasons for the large differences in EC50/LC50 values between the two types of systems was the propensity for toxicity to be lessened by particulate and dissolved organic matter and pH levels generally found in marine areas. Thus, any potential toxicity would be more easily neutralized or inactivated.

Crane et al. (2007) suggest predicted no effect concentrations (PNECs) of monomeric aluminium of 0.005 µg/L (long-term) and 0.025 µg/L (short term) in salt waters. Because aluminium and toxicity data in salt or brackish waters were limited, PNECs were based on freshwater counterparts and using a safety factor of 10. The authors argued that the higher species richness in marine systems requires lower limits to protect species potentially more susceptible to Al. This information is, however, difficult to reconcile with some of the measured concentrations of aluminium in both seawater and porewaters mentioned earlier. In addition, the freshwater PNECs used to extrapolate salt water PNECs were based on the lowest, short term effect concentration on Atlantic salmon at pH 4.4 (short terms PNEC) and the lowest, long term effect concentration on the alga (*Chlorella pyrenoidosa*) at pH 6. Factors of 30 and 150 were then used (to account for uncertainty) to develop the short and long term freshwater PNECs. Thus, PNECs developed for salt water monomeric aluminium exposure had overall safety factors of 300 and 1500 for short and long term criteria, respectively, leading to extremely low values below the detection limit of current analytical systems. It should be noted again that these values are not based on actual toxicity tests but rather toxicity data from freshwaters with very large factors of safety applied.

Background aluminium concentrations were determined in areas around an enclosure experiment to test the effect of polyaluminium chloride (PAX21) addition to the sediment in Löparöfjärden (a brackish bay similar to Östhammarsfjärden, BalticSea2020) on phosphorus and biota. Both filtered and total aluminium concentrations were near (12 µg/L) or below the detection limit of 10 µg/L. A number of biota were added to the treatments during the length of the experiment including:

- Blåstång (*Fucus vesiculosus*)
- Musslor (*Mytilus edulis*)
- Storspigg (*Gasterosteus aculeatus*)
- Rödalg (*Ceramium* sp.)

Treatment effects on these organisms and other species naturally present in the bay are discussed in detail in the following sections.

Aluminum effects on plankton

The main mode of disturbance to plankton communities is through settling of phyto- and zooplankton with the Al-floc formed after application of Al-salts to surface waters. Although short term changes in water chemistry are detected after aluminium salt application, these are generally short lived and are on the order of hours to days and recovery of plankton communities is quite rapid. For example, zooplankton abundance and diversity declined immediately after treatment with alum in Newman Lake in Washington (Shumaker et al. 1993) but the community recovered after two months. Additionally, no lasting adverse effects on zooplankton were reported after alum was added to Liberty Lake, Washington (Gibbons et al. 1984).

Phytoplankton are affected similarly to zooplankton by aluminium application to surface waters (Gibbons et al. 1984) in that physical settling, promoted by the Al-floc, clears the water column of most plankton. Direct toxicity in circum-neutral waters is low because the amount of aluminium in solution is low and bioaccumulation does not generally occur. Unfortunately most studies discussing aluminium effects on phytoplankton deal with acidic systems which do not represent the conditions in Östhammarsfjärden. Sacan and Balcioglu (2000) showed that aluminium accumulation and toxicity to a green algae (*Dunaliella tertiolecta*) decreased at pH 8.2 compared to pH 6.2 in conditions resembling natural sea water (psu = 24.7). In addition, the accumulation of other measured metals (Pb and Cu) was greater than that for Al. A review of 35 cases with internal phosphorus loading control using Al-salts showed that overall phytoplankton biomass declined and the number of sensitive, “high quality” taxa increased in most cases (Jeppesen et al. 2005). This was likely due to reduced phosphorus availability (decreased productivity and overall biomass) and improved water quality which led to better habitat conditions for more sensitive, high quality taxa.

In a recent experiment, polyaluminum chloride (PAX 21) was added to sediment in enclosures in Löparöfjärden outside of Bergshamnraviken, Sweden (BalticSea 2020). There were three sets of enclosures and one area outside of the experimental setup that were sampled over a period of approximately four months before and after treatment.

- One set of enclosures with PAX 21 added to the sediment
- One set of enclosures with PAX 21 added to the sediment where water from the bay was allowed to flush the enclosure shortly after addition of aluminium to simulate water exchange in the bay
- One set of enclosures used as a control with no added aluminium
- A sampling outside the enclosure setup used as a comparison for both the control and aluminium treated enclosures

Although aluminum levels increased in the treated enclosures, there was no effect on plankton respiration or primary production or growth (*Ceramium* sp., a red algae) when comparing enclosures treated with aluminum (47 g Al/m^2) and the control with no aluminum or in the waters around the enclosure experiment. There was also no clear effect on epifauna attached to blåstång (*Fucus vesiculosus,* a seaweed) or *Fucus vesiculosus* itself between treated and non-treated enclosures. There was lower growth of epiphytic algae on the walls of the aluminium treated enclosures, possible due to phosphorus limitation of growth. Aluminum content in the epiphytic algae was significantly lower in the aluminum treated enclosures versus the control and the area outside of the enclosures.

Phosphorus content in epifauna was also tested and while there was no significant difference among the four treatments, when the aluminium and non-aluminium treatments were grouped, phosphorus was lower in the aluminum treated enclosures.

Aluminium effects on benthic invertebrates

The literature indicates that aluminium is generally not toxic to benthic invertebrates when pH is above 6.0, while notable toxicity is had near pH 5.0 (Gensemer and Playle, 1999; Pilgrim and Brezonik, 2005). Lamb and Bailey (1981) studied the effect of alum floc on benthic invertebrates in a laboratory setting to determine if proposed whole lake alum treatments would have adverse effects on benthic invertebrates. They reported significant mortality of a chironomid (*Tanytarsus dissimilis*) was seen in chronic laboratory tests only with very high aluminium doses of 80 to 480 mg Al/L. The authors suggested that observed mortality was potentially due to aluminum toxicity but they also noted that there was significant alum floc accumulation and the chironomids were using the floc as habitat by burrowing within the floc. It was noted that heavy alum floc was likely causing stress and mortality for tests with higher alum doses. This study also demonstrated that there were minimal chronic effects with an aluminium dose of 10 mg Al/L and that there were no acute effects even at doses as high as 960 mg Al/L. The authors noted that Al-salt treatments generally occur when invertebrates are dormant rather than during developmental stages. They further concluded that the floc layer would likely settle before the dormant period ended and the animals again became active. A study of a chaoborid species (*Chaoborus punctipennis*) and a chironomid species (*Chironomus anthrocinus*) found both to be tolerant of aluminium (Havas and Lichens 1984).

Potentially more relevant to Östhammarsfjärden are studies conducted on lakes that have received one-time, whole lake treatments of alum (although not directly injected into the sediment). Studies by Narf (1990) and Doke et al. (1995) evaluated changes in benthic populations in alum-treated lakes. Narf found that benthic populations either increased in diversity and abundance or there was no change with alum treatment. The alum doses for these lakes ranged from 7 to 13 mg Al/L whereas the estimated dose for Östahmmarsfjärden is 12.5 mg Al/L. Doke et al. (1995) found a similar outcome with a doubling of chaoborids (an aquatic insect) following alum treatment. One of the potential explanations for the increased benthic community abundance with these aluminium salt treatments was the subsequent improvement in lake water quality. Smeltzer et al. (1999) initially detected a 90% decline in macroinvertebrate density in the hypolimnion after treatment with alum in 1986 but the benthic community recovered by 1988 and continued to improve in the following years with higher levels of diversity and abundance compared to pre-treatment levels (again likely due to improved water quality). Alum was added to a lake (80 g Al/m^2, approximately 10 mg Al/L) in Michigan (US) in the fall of 2005 (Steinman and Ogdahl 2008). Total macroinvertebrate density declined substantially after treatment (2006 compared to 2004), with Oligochaetes and Chaoborids showing the greatest reductions and Chironomidae showed no reduction. However, there were a number of confounding factors. Even though internal loading decreased substantially, water quality did not improve substantially due to a relatively high level of external phosphorus loading. Thus, secchi depth and dissolved oxygen levels were actually worse during benthic invertebrate sampling after treatment. Water depths were also higher in 2006, potentially contributing to the lower oxygen levels detected in the hypolimnion (lower diffusion and light penetration). And, as the authors state, single point sampling of benthic invertebrates are highly variable so caution must be taken when interpreting results.

A number of recent studies examined the effect on in-line and seasonally continuous alum treatment systems on benthic invertebrates. As part of a district-wide evaluation of wetland health, the Ramsey Washington Watershed District (Minnesota, U.S.) performed benthic invertebrate monitoring as well as water quality monitoring of a wetland (T-31) that is downstream of an in-line alum treatment facility (Ramsey Washington Watershed District 2005). The alum treatment facility has been operating from spring though the fall of each year since 1998. During that time the concentration of aluminum entering the wetland has averaged from 1 to 6 mg Al/L. Aluminium was enriched in the wetland sediment, indicating that aluminium entered the wetland and was deposited as Al-floc or organically complexed aluminium in the wetland. Benthic invertebrate monitoring results and IBI (index of biotic integrity) analysis for the T-31 wetland revealed that the wetland had similar quality to the high quality reference (unimpacted) wetlands in the study. The conclusion of this study was that the deposition of alum floc in this wetland had not adversely affected the biota of the wetland.

A study similar to the Ramsey Washington Watershed District (US) study was conducted for a wetland and a lake downstream of an in-line treatment system in Eagan, Minnesota. This study found no effects on the benthic invertebrate community downstream of the alum treatment system with the accumulation of 10 cm of alum floc (Pilgrim and Brezonik 2005). However, the benthic invertebrate community was nearly eliminated with over 1 foot (approximately 35 cm) of alum floc accumulation. The alum floc had an aluminum content of 200 mg/g of dry sediment. The authors suggested that the loss of the invertebrate community was largely due to the physical disruption of suitable habitat and the creation of severe anaerobic conditions below the floc layer. The potential for significant alum floc accumulation to disrupt benthic invertebrate communities also has been documented for an experimental treatment system on the Cuyahoga River (Barbiero et al. 1988).

Some data exist for benthic invertebrate species in Östhammarsfjärden (Ridderstople 1991, Uppsala Länstyrelsen 2001); seven species were detected between 1990 and 1999 (Table 2). Only three species were detected in 1990, probably due to low oxygen levels detected during the November sampling. Similar oxygen depletion was detected during the 1999 (August) sampling and by November, half of the benthic invertebrate population had died (Ridderstolpe, 1991). Although some sensitive species are present in Östhammarsfjärden (*Ostracoda, Prostorna obscurum, Potamogyrgus*), the most abundant benthic species during both 1990 and 1999, *Chironomidae*, can tolerate a wide range of conditions, including low oxygen in the hypolimnion. *Chironomidae* presence can be a symptom of degraded habitat and low biodiversity due to eutrophication because of their tolerance and dominance in degraded systems.

It appears that the benthic community in Östhammarsfjärden is low in diversity and dominated by species that can tolerate conditions found in nutrient rich, eutrophic systems (low oxygen, elevated turbidity) but there are a number of higher value species present as well. Based on the studies presented previously in this section, some short-term impacts to the benthic community are to be expected with aluminium addition to the sediment. Over the long term, however, diversity is likely increase due to improved habitat conditions from nutrient reductions in Östhammarsfjärden. While there are a number of benthic species that are active in the sediment and will contribute to bioturbation (see section 1.6), the impact would likely be limited to the area above the sediment water interface and there is no evidence from previous studies that this type of action would limit the overall effectiveness of aluminium addition to the sediment.

In the Löparöfjärden experiment (BalticSea 2020) there were no significant effects on community structure detected in the enclosures treated with aluminium between the start of the experiment (June 2011) and the end (September 2011). There was a difference between the abundance (mainly *Chironomidae*) between the aluminium treated enclosures (higher) and the areas with no aluminium added (lower). This difference was consistent at both the beginning and end of the experiment. There was one additional fauna detected in the aluminum treated enclosures (*Gammarus* spp.) that was not detected in the control or in the bay outside of the experimental setup. Benthic fauna mortality and aluminium content also were unaffected by aluminium treatment.

Mytilus edulis respiration showed no effect between treated and non-treated areas. *Gasterosteus aculeatus*, however, did show elevated respiration during sampling in August in enclosures treated with aluminium (with water replacement after treatment) but there were no significant effects detected during the July sampling.

Phosphorus content was also measured after the experimental period in *Fucus vesiculosus* and *Gammarus spp*. While no significant difference was detected among the four treatements for *Fucus vesiculosus*, when treated and untreated tests were grouped, phosphorus content was lower in the aluminium treatments. No treatment effects were seen for phosphorus in *Gammarus spp*. No significant differences in phosphorus content of *Mytilus edulis* or *Gasterosteus aculeatus* were detected.

Table 2. Benthic invertebrate species in Östhammarsfjärden, 1990 and 1999. Sensitivity represented by the benthic quality index (BQI, 1 is the lowest quality)

Reported Taxonomic Name	Swedish Name	Group	Year(s) Detected	BQI
Ostracoda	Musselkräftor	Crustacea	99	15
Chironomidae	Fjädermyggor	Chironomidae	90, 99	1
Prostoma obscurum	Brackvattensnemertin	Nemertea	99	10
Macoma baltica	Östersjömussla	Bivalvia	99	5
Marenzelleria viridis	Amerikansk havborstmask	Polychaeta	99	5
Oligochaeta		Oligochaeta	90, 99	1
Potamopyrgus antipodarum	Nyzeeländsk tusensnäcka	Gastropoda	90, 99	10

Aluminium effects on fish

Various studies have shown that aluminium can be toxic to fish under certain circumstances. Toxicity generally occurs when aluminium accumulates on fish gills, causing ion regulatory and/or respiratory difficulties. Positively charged, monomeric inorganic species (Al^{3+}, $Al(OH)_2^+$, and $Al(OH)^{2+}$) dominate at pH levels below 5.5 while the negatively charged inorganic $Al(OH)_4^-$ dominates in alkaline waters at a pH above 9 to 9.5. The positively charged inorganic species of aluminium are considered the most toxic forms under acidic conditions (Driscoll et al. 1980, Gensemer and Playle 1999) while the inorganic anion of aluminium is considered less toxic towards fish (Exley et al. 1996). However, Gundersen et al. (1994) found 65-100% mortality of rainbow trout exposed to 1 mg Al/L (dissolved) at pH 8.6 during 96-hour acute tests. No mortality was found at lower pH levels (8.0-8.2) and lower concentrations of dissolved aluminium (less than 0.2 mg/L). Polymerization may also occur under non-equilibrium situations during which polymeric species of aluminium are formed. Polymeric species can be highly toxic (Henry et al. 1999, Rosseland et al. 1992) but generally only in Al-rich, non-alkaline waters (Exley et al. 1996) and even if formed during treatment would diminish rapidly within hours after the treatment as floc particles continue to conglomerate, increase in size and settle to the sediment. These polymeric species might potentially form temporarily at interfaces with large pH differences, i.e. at the sediment water interface.

Buergel and Soltero (1983) showed aluminium salt treatment (120 g/m^2, 12 mg/L) did not lead to an increase in aluminium content of rainbow trout gills in a Washington (US) lake. In fact, aluminium content in the fish gill tissue was lower in the treated lake (compared to the reference lake) after treatment, possible due to less naturally available aluminium in the water column due to lower organic matter (from lower productivity) in the lake. No significant differences for aluminium were detected in other tissues except for the liver and kidney when comparing the control to the treated lake. These differences were between age classes, however, so the data are difficult to interpret.

A buffered aluminium salt ($NaAl(OH)_4$) was added over a period of 5 years (2001-2005) in lake Tiefwarensee (Waur and Teien 2010). The aluminium solution was added directly to the hypolimnion 2 to 3 times each summer with each application lasting two weeks followed by two weeks of aeration/mixing. Even though aluminium concentrations dropped substantially after each treatment phase, artificial mixing help keep aluminium levels above background concentrations previous to treatment. During the treatment, aluminium increased in the gills of perch (*Perca fluviatilis*) but other species including roach (*Rutilus rutilus*), bream (*Abramis brama*), and silver carp (*Hypophthalmichthys mo-*

trix) were unaffected. In the three years after treatment, aluminium concentrations in the hypolimnion and epilimnion were not significantly different from each other and had reached pre-treatment levels.

Smeltzer et al. (1999) some weight loss (11-20%) was detected in yellow perch (*Perca flavescens*) likely due to elevated dissolved aluminium during treatment in 1986 but the fish species had rebounded by 1991. It should be noted that there was a leak in the treatment apparatus during application which caused concentrations as high as 200 ug Al/L in the water column. Eight day exposure of yolk-sac fry of graylings(*Thymallus thymallus*) to levels of 0.4 to 0.8 mg Al/L in slightly acidic water (pH 6) showed between 40 and 100% mortality with no dissolved humic matter but mortality was reduced entirely with addition of 10 mg/L natural humic matter (Vuorinen et al. 1999).

Sediment resuspension

The $Al(OH)_3$ floc formed after Al-salt application (if applied near the water surface) will generally settle to the sediment surface within a matter of hours and become buried with new sediment over time. However, benthic organisms or bottom feeding fish and water mixing may resuspend the sediment and the $Al(OH)_3$ floc, potentially impacting treatment effectiveness and water chemistry. A laboratory resuspension experiment was conducted on intact sediment cores collected from Lake Möllen (Germany), which was treated with alum (33 g Al/m2, 16.5 mg Al/L)) in 2006 (Egemose et al. 2009). With increased water velocity over the sediment surface, freshly precipitated Al-floc was resuspended but aged floc (2 to 4 months) was much less prone to resuspension. When resuspended, the Al-floc partially redissolved when pH levels were greater than 10.5. Some dissolution of Al-floc was detected at pH levels as low as 9 when the floc was freshly precipitated (3 weeks after aluminium addition).

Steinman et al. (2004) showed sediment agitation (to a somewhat artificial degree) increased particulate phosphorus (and probably aluminium) in the water column but no release of phosphorus occurred from the Al-Floc, implying no dissolution of Al-hydroxide. This was a laboratory experiment where alum was added (in concentrations from 0 to 25 mg Al/L) to sediment cores with lake water overlying the sediment and agitation occurred 24 days after aluminium treatment.

Bioturbation effects from benthic invertebrates were also assessed by Steinman et al. (2004). Overall the data from the study suggests that, at the invertebrate densities studied (approximately 1000 individuals/m^2), bioturbation did not affect sediment phosphorus release during the experiment (24 days), again implying the Al-floc remained stable.

Aluminum application to surface water versus sediment injection

Al-salts are generally added to lakes either just below the water surface or in the hypolimnion. aluminium can be added directly to the sediment however, potentially avoiding impacts to organisms in the water column. Zooplankton and phytoplankton would not be directly affected during sediment injection and the resulting lower aluminium concentrations in the water column should also limit effects on non-benthic feeding fish. One of the reasons for applying Al-salts in the water column is that the less expensive forms are slightly acidic and the alkalinity in the water column acts as a buffer to limit decreases in pH. Direct injection of Al-salts to the sediment would localize the treatment area, potentially causing greater changes in pH. There are buffered aluminium compounds, however, that can limit changes in pH so that direct injection into the sediment would be possible without decreasing the pH substantially.

Another potential benefit with sediment injection of Al-salts is the mixing of the $Al(OH)_3$ floc formed after treatment with the sediment. This will limit the amount of floc resting on the surface (as would happen with a water column treatment) and may increase the phosphorus binding effectiveness of the added Al.

Modelling

The geochemical model PHREEQC was used to explain the chemical observations of the various water chemical data for filtered and total aluminum. This program uses known chemical equilibria to predict which phase (particulate or aqueous) metal ions will occur and in which form (free or bound to other ions or macromolecules) they are present in the aqueous phase depending on varying factors such as ionic strength, temperature, total metal content, total organic matter and pH. The modelling was conducted to explain changes in surface water concentrations of aluminium and their potential effects on biota.

The analytical data of two separate enclosure experiments in which dissolved aluminium (PAX) was mixed with the sediment were evaluated using the time series of available chemical data on pH and measured aluminium concentrations (report from Baltic Sea 2020, in prep). In one enclosure (No 3) the complete water column was exchanged shortly after the addition while in another enclosure (No 5) no exchange occurred. The variations in aluminium concentrations in these two enclosure experiments are interpreted to stem from three processes:

> (I) Formation of amorphous $Al(OH)_3$ phase in the water column shortly after the addition of dissolved aluminium chloride (PAX 21)
> (II) Recrystallization of this amorphous phase to a more crystalline form of $Al(OH)_3$
> (III) Mixing of cold and warmer water that have significantly different aluminium solubility.
> (IV) An unknown process that lead to increases in pH in the closure No 5.

Measured aluminium concentrations in enclosure No 5 almost exclusively lie above the solubility of crystalline gibbsite both when calculating at 5°C and at 20°C while those of enclosure No 3 lie in between gibbsite solubility at these two temperatures. During the initial six weeks (I) of the experiment, aluminium solubility in enclosure 5 might be controlled by a more soluble amorphous phase that is then transformed into a more crystalline phase (II). An alternative explanation of the decreasing aluminium concentration is the welling up of colder water with a lower solubility of Al. (III). Chemical modelling indicates that an amorphous phase with a solubility product (K_{sp}) = 10.3 at 5°C describes the temporal evolution of aluminium concentrations in enclosure No 5. If such a phase were to temporarily control the aluminium solubility then aluminium concentrations of around 300 ug/L, higher than many of the recommendations mentioned earlier in the text, are to be expected at a typical seawater pH of 8.3. After recrystallization these concentrations decrease to around 30 ug/L in equilibrium with crystalline gibbsite at around 10°C and only slightly higher than what was measured in the reference systems.

Methods

Experimental setup

Aluminium (50 g Al/m^2 PAX) was added to enclosures in Löparöfjärden (Baltic Sea 2020, in prep). Here, results from two of the enclosures (3 and 5) are used to support chemical modeling. Water samples represent an average of the water column (3 m).

Chemical analysis

Both filtered (GFC) and unfiltered samples were taken at eight different places as described in the experimental setup. At two sites (enclosure 3 and 5) additional parameters (temperature, oxygen content, salinity and pH) were analysed). These data are displayed in table x in the appendix.

The chemical analysis of aluminium was done spectrophotometrically at the Erken laboratory according to SS 02 82 10 (not accredited). All filtered samples (Al_{diss}) were corrected with filter blinds while unfiltered samples (Al_{tot}) were corrected with laboratory analysis blanks. Values below <10 µg/l are given as <10 µg/l according to the standard. The aluminium analysis was used to calculate the distribution between dissolved (Al_{diss}) and particulate aluminium (Al_{part}) by subtraction ($Al_{part} = Al_{tot} - Al_{diss}$) . Particulate aluminium was set to zero if the total aluminium values was below 10 µg/l.

Chemical model

Modelling of equilibrium conditions was done using the freeware PHREEQC (Parkhurst and Appelo 1999) using the PHREEQC database. Some additional chemical species for dissolved aluminium complexes including those with organic matter were added as described in the appendix. As an example all inorganic complexes of aluminium (Al*i) may be calculated including the following species:

$Al^*_i = [Al^{3+}] + [Al(OH)^{2+}] + [Al(OH)_2^{+}] + [AlF^{2+}] + [Al(F)_2^{+}] + [AlSO_4^{+}] + [Al_2(OH)_2^{4+}] + [Al_2(OH)_2CO_3^{2+}] + [Al_3(OH)_4^{5+}] + [AlCl^{2+}] + [AlH_3SiO_4^{2+}]$

Given an average seawater composition (as described in the appendix) of around 5% salinity (ca. 0.07 M NaCl) in equilibrium with carbon dioxide ($pCO_2 = -3.2$) and $Al(OH)_3$ (SI = 0.0) the program may be used to calculate the solubility of aluminium in equilibrium with a hypothetical $Al(OH)_3$ solid phase for example gibbsite at 25°C:

$$Al(OH)_3 + 3H^+ \Leftrightarrow Al^{3+} + 3H_2O \quad ; \log Ksp = 8.3 \quad at 25^o C$$

Results

Results of aluminium additions in two enclosures are shown below. In enclosure 3, unaffected water was allowed to flush into the enclosure shortly after the addition of aluminium and then it was closed again while enclosure 5 was closed during the length of the experiment.

Time series of aluminium concentrations

The first two graphs display the temporal evolution of aluminium concentrations in the two enclosures.

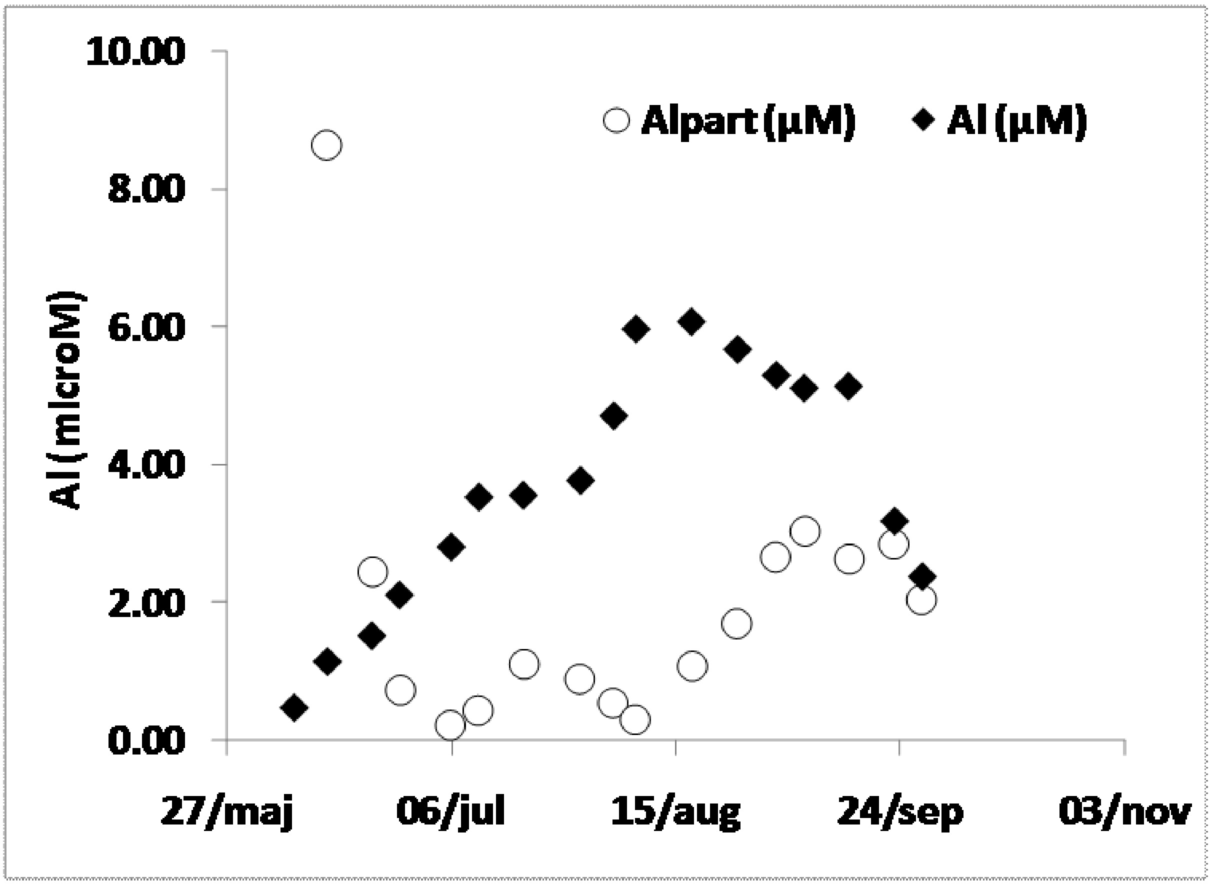

Figure 2. Concentration of dissolved (Al,◆) and particulate Al (Alpart,○) as a function of time in enclosure 5.

After the aluminium addition, high concentrations of particulate aluminium are measured in enclosure 5 in early June (Figure 2). Over time the particles dissolve leading to an increase of dissolved aluminium concentration until around mid august. From then new particles seem to form that decrease the overall aluminium concentrations. This may be indicative of a crystallization process and one may anticipate that this process will probably continue during autumn.

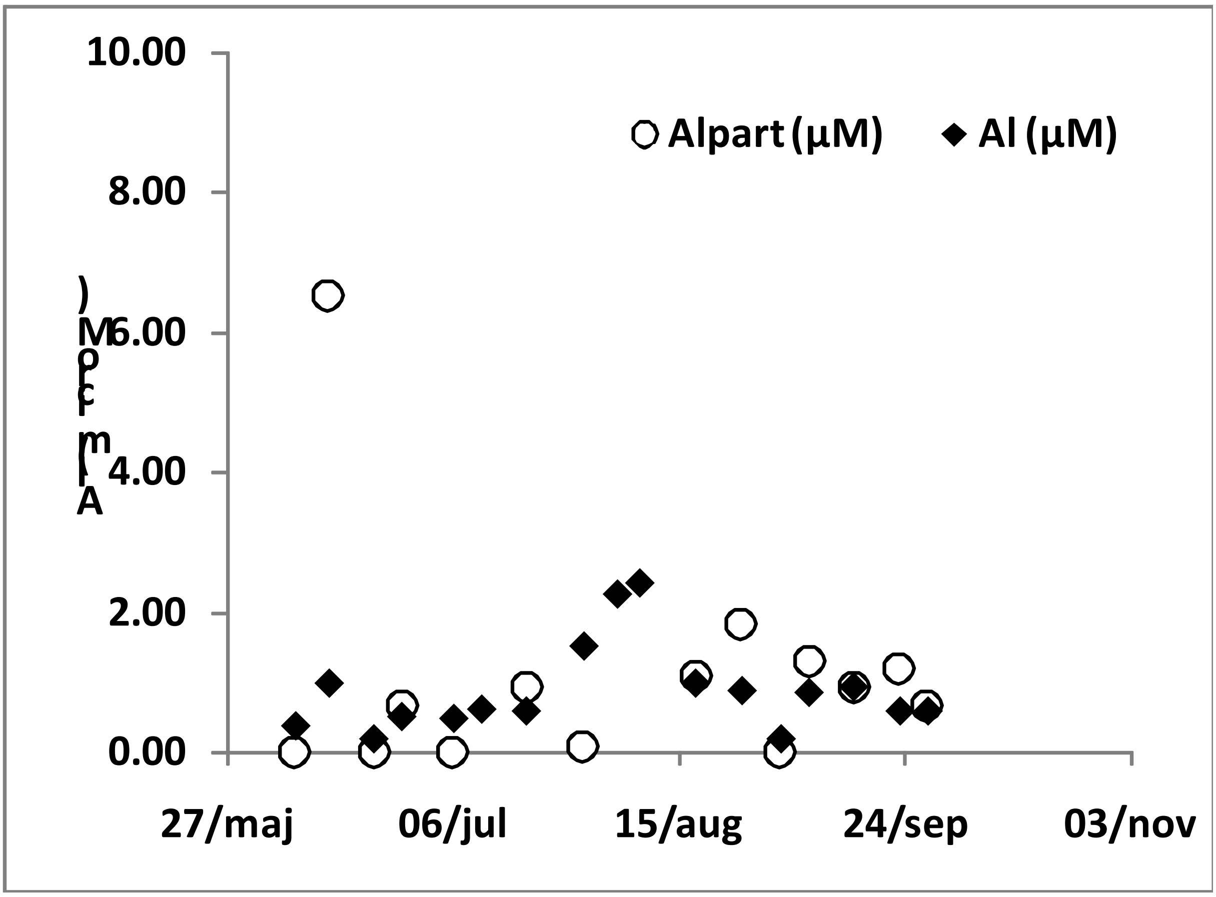

Figure 3. Concentration of dissolved (Al,◆) and particulate Al (Alpart,○) as a function of time in enclosure 3.

In enclosure 3, similar elevated total aluminium concentrations were measured (surface water). Due to the exchange with fresh sea water during stage 2 of the experiment, the concentrations decreased much faster in enclosure 3 (Figure 3). Even in enclosure 3, however, increasing aluminium concentrations were observed until mid august. As in enclosure 5, total and particulate aluminium concentrations decrease over time from this point.

Modelling aluminium concentrations

The solubility of aluminium is affected by a number of factors such as temperature, ionic strength and presence of a number of solutes that increase solubility such as sulphate, fluoride or organic matter. As no analytical data was available for any of these three solutes some assumptions about the chemical composition of the seawater were necessary (see appendix for exact concentrations). Salinity was set at 5%, which is higher than what would normally be found in Östhammarsfjärden but at this level, the modeling (Figures 4 and 5) can be considered a worst case scenario because aluminium solubility increases as ionic strength (salinity) of the solution or water body increases. In addition, salinity tends to increase in bottom waters as oxygen is depleted due to increased solutes in the deeper water near the sediment surface.

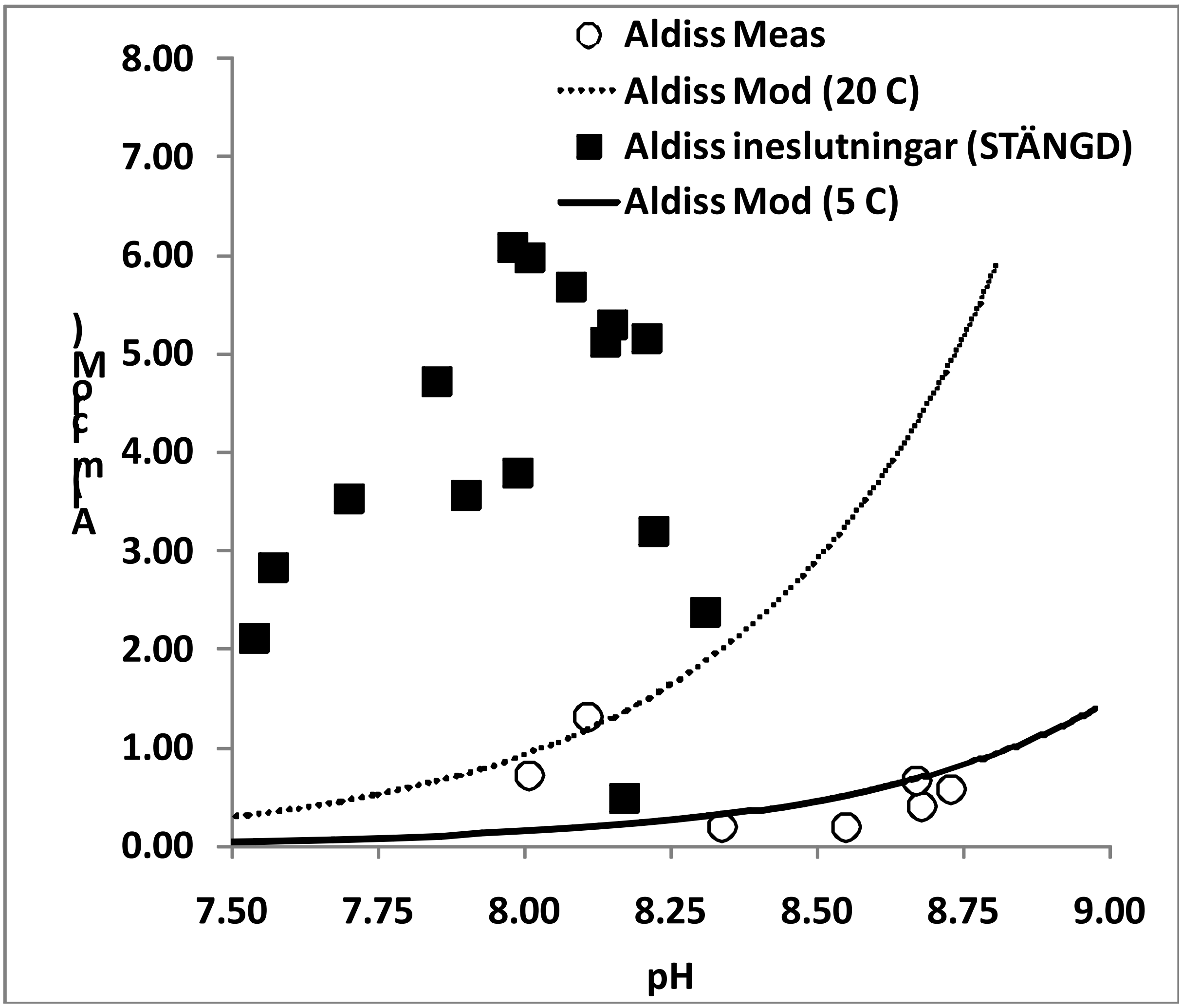

Figure 4. Measured concentration of filtered Al (Aldiss) in closure 5 (■), open reference Al (O) and modelled concentration of Al (Aldiss Mod) in brackish water in equilibrium with crystalline gibbsite (Ksp = 8.77) as a function of pH and temperature..

Temperature in itself has a large impact on the apparent solubility of aluminium in seawater. While the analytical data in enclosure 3 (Figure 5) and in the reference sampling site are in between the calculated equilibrium concentrations at 5° and 20°C some other factor would need to be invoked to explain the observed concentrations at enclosure 5 (Figure 4).

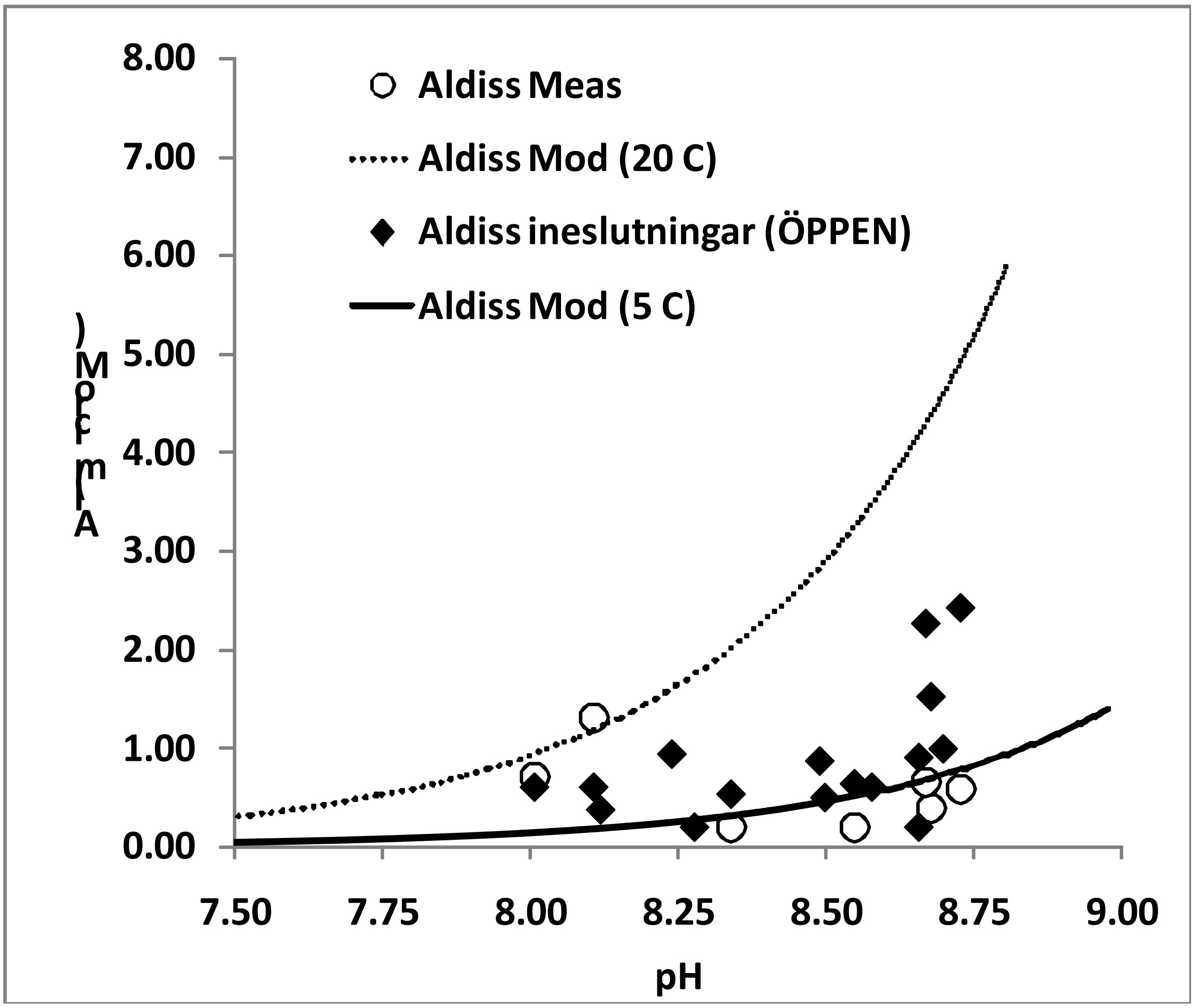

Figure 5. Measured concentration of filtered Al (Aldiss) in closure 3 (◆), open reference Al (○), and modelled concentration of Al (Aldiss Mod) in brackish water in equilibrium with crystalline gibbsite (Ksp = 8.77) as a function of pH and temperature.

To study this further, an attempt was made to capture the measured aluminium concentrations during the early part of the experiment in enclosure 5 (Figure 6). The initially elevated concentrations of aluminium can be reproduced when using an apparent solubility constant (Ksp = 10.3 at 5°C). The good comparison between the measured and modelled data, however, does not prove that this solid actually existed as microcrystalline particles in suspension.

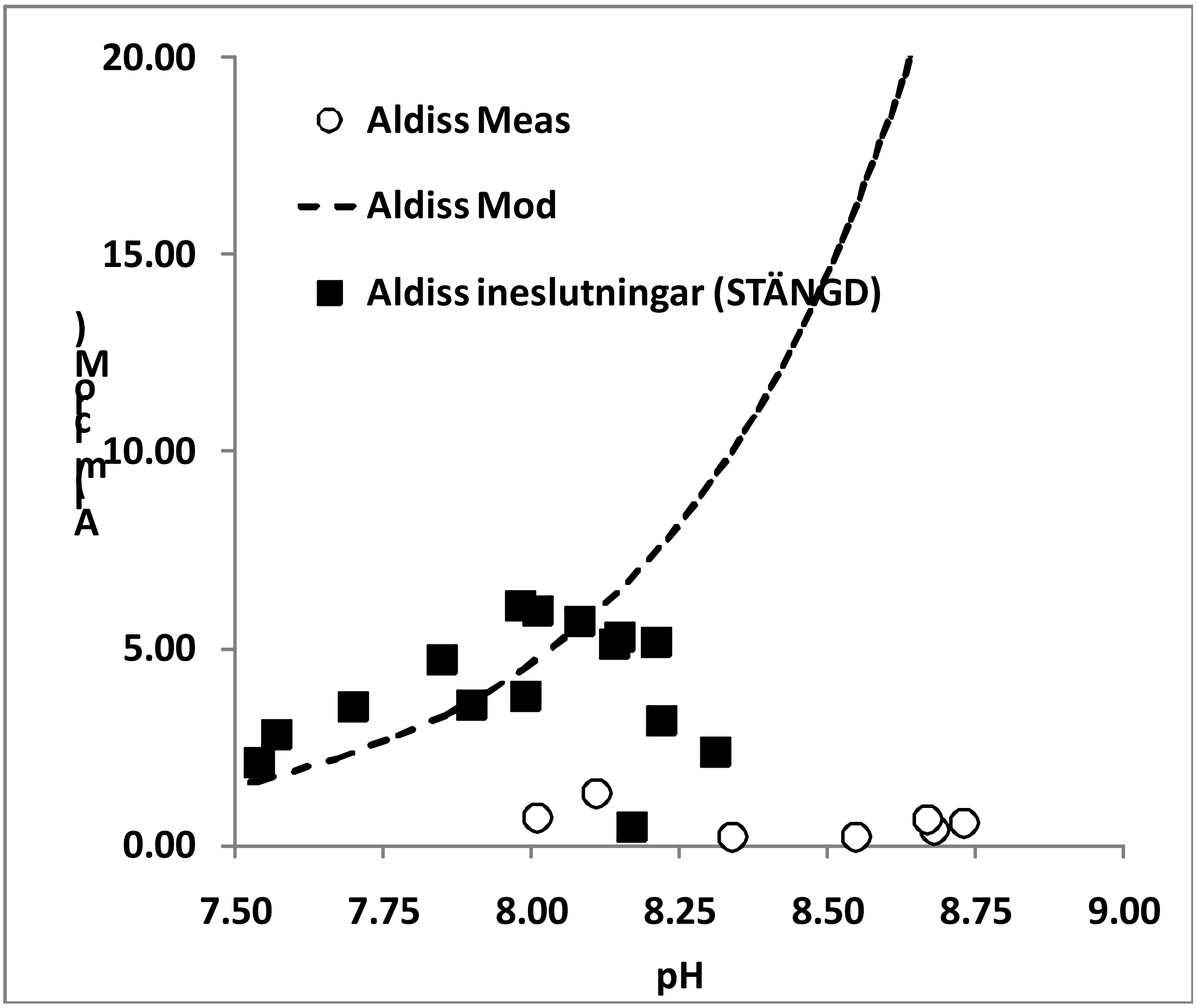

Figure 6. Measured concentration of Al in enclosure 5 (■), open reference (○), and modelled concentration of Al (Aldiss Mod) in brackish water in equilibrium with a hypothetical amorphous gibbsite phase (Ksp = 10.3) as a function of pH at 5°C.

The measured aluminium concentrations for samples with pH below approximately 8.1 can be modelled using the presence of an amorphous $Al(OH)_3$ solid phase. Amorphous phases form temporarily in waters that have been supersaturated with solid phases. In a later stage of the experiment these amorphous phases probably re-dissolve and other more crystalline compounds with lower solubility likely form. The reasonably good fit in the pH range 7.5 to 8.1 would suggest that at least 2 (ca. 55 ug/L) but up to 6 microM (ca. 160 ug/L) of total aluminium may have been temporarily buffered by suspended $Al(OH)_3$ particles forming during the experiment.

Modelling change in pCO_2 necessary to increase pH from 8.3 to 8.7

The observed change in pH in enclosure 5 is curious. Without further water chemical data the only potential process for increasing pH is a decrease in partial pressure in carbon dioxide. This could be due to an increased photosynthetic activity in the enclosure. The water chemical calculations indicate that partial pressure must decrease from -3.2 down to -3.6 to explain an increase of pH from 8.35 to 8.75 and is equivalent to a removal of 0.1 mM of carbonate from 3.4 mM to 3.3 mM (Figure 7). This may represent biological uptake of carbon dioxide (CO_2), such as photosynthetic activity by algae.

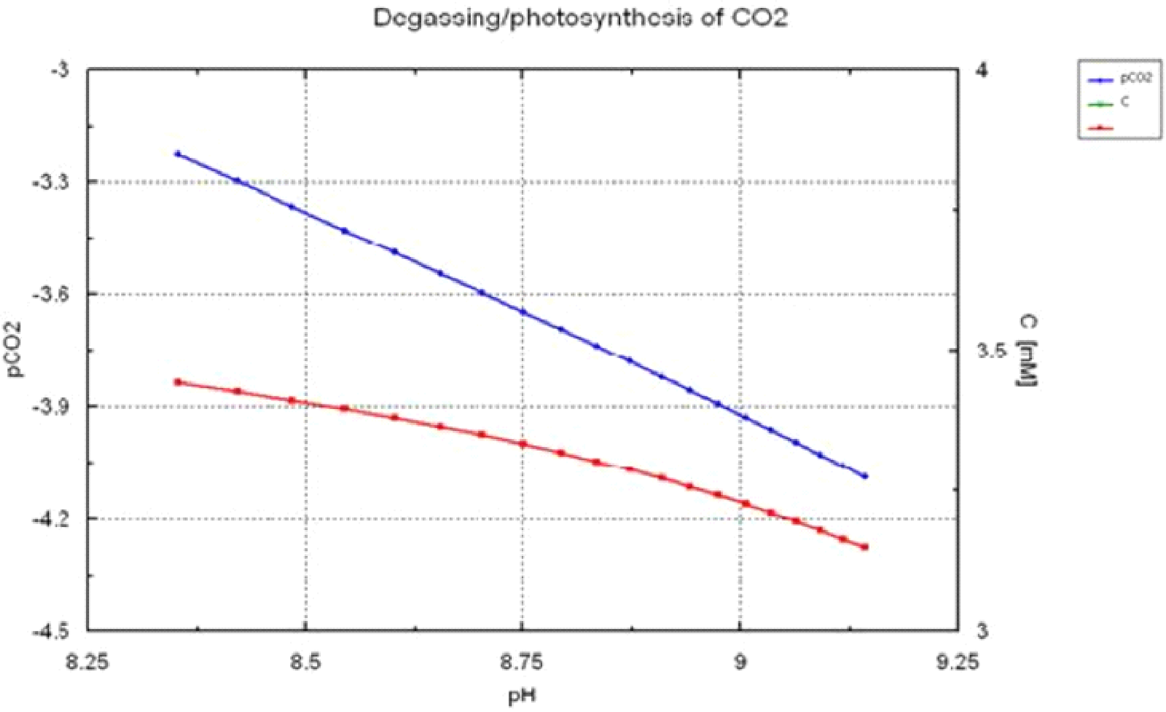

Figure 7. Change in pH, partial pressure (blue line) and content of inorganic carbon (red) during the degassing of seawater starting at pH 8.3

Modelling change in pH due to addition of PAX

The addition of PAX will lead to $Al(OH)_3$ being supersaturated. As $Al(OH)_3$ forms and precipitates it produces hydroxide ions according to:

$Al(OH)_4^- \rightarrow Al(OH)_3 + OH^-$

These hydroxide ions are buffered in the water phase due to the presence of a number of substances such as CO_3^{2-}, HCO_3^- or through the formation of mixed aluminium complexes.

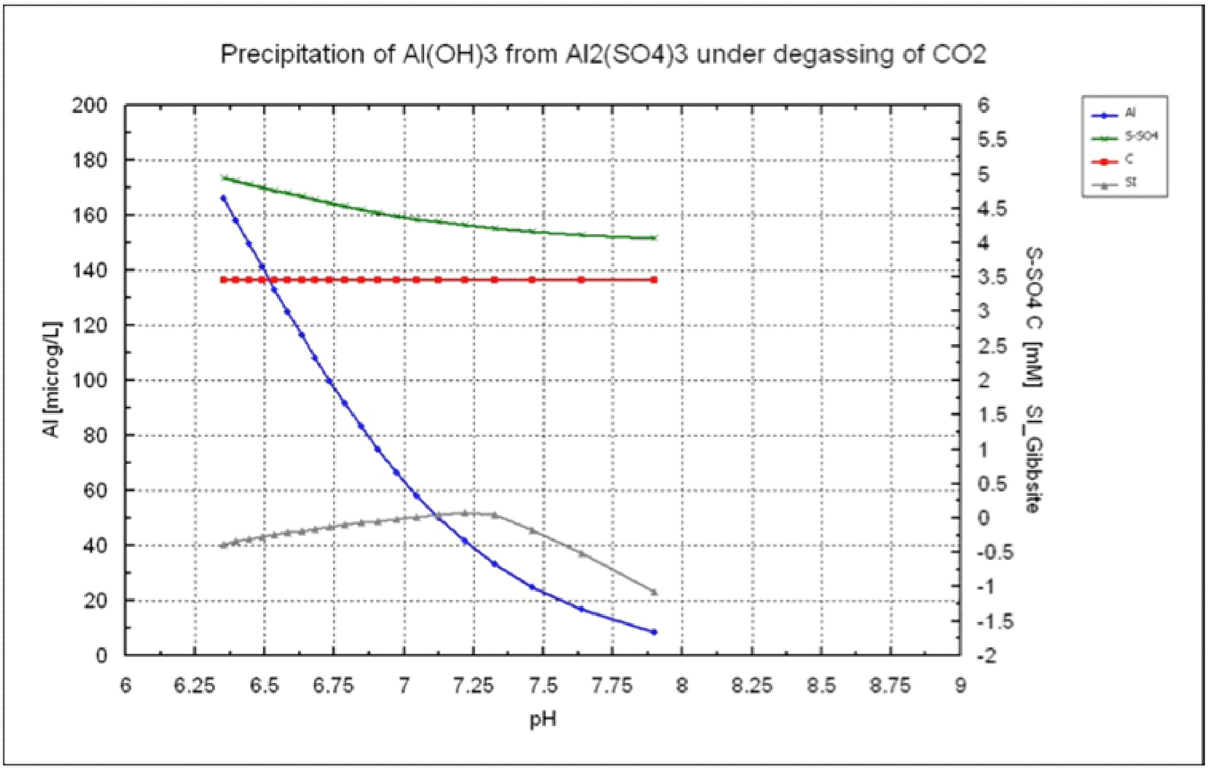

Figure 8. Chemical evolution of the addition/precipitation experiment. Change in Al (blue), sulphate (green) and carbonate (red) as well as calculated supersaturation index of $Al(OH)_3$ using a Ksp of 10.3 (grey)

Assuming that approximately 2% of the added aluminium stays in the water phase which is in accordance with mass balance calculations the predicted aluminium concentration in the water is around 165 µg/L close to the measured value of 176 µg/L in enclosure 3 and slightly lower than that in enclosure 5 (233 µg/L). Interestingly the solubility is close to saturation to a solid phase with a K_{sp} of 10.3 (Figure 8). The same value is needed to describe the observed values in Figure 6 for the early data in enclosure 5. The modelled pH is 6.4 as compared to the measured pH of 6.8. This difference is significant but without further measured chemical data we cannot explain these differences.

Modelling summary

Based on the observed experimental data and modeling, elevated aluminium concentrations are to be expected during the early phase of an aluminium treatment. This is expected due to the relatively high pH and ionic strength of the water in Östhammarsfjärden in comparison to most of the other, mostly fresh water systems previously studied. Almost all soluble aluminium in Löparöfjärden is in the form of $Al(OH)_4^-$. Because aluminium levels in the initial phase are higher than what is expected from theoretical solubility calculations and higher than in the studied reference systems, they should be quantified and documented when this kind of treatment is to be undertaken. Organisms that are present in the water column may be exposed to elevated aluminium concentration during a prolonged time period lasting from several days to weeks depending on the physical mixing of the water column after the addition. A study by Huser (2012) showed a similar result with elevated aluminium concentrations in the water column for approximately three months after treatment. However, within a year aluminium concentrations were lower than before treatment.

Summary

The main goal of this project was to determine the potential effects on biota from aluminum addition to Östhammarsfjärden (Östhammar county) for reduction of internal phosphorus loading. Potential risks to biota in the water and sediment were summarized from reports and scientific publications as well modeling based on data from an enclosure experiment where aluminum was added to the sediment in Löparöfjärden (Norrtälje county) during the summer 2011.

Aluminium salts have been used to reduce phosphorus in water and limit internal phosphorus loading in lakes for over forty years. Aluminium toxicity in lakes is considered negligible under neutral pH conditions because reactivity and bioavailability are generally low when pH is between 6 and 9. The toxicology literature, however, largely supports the conclusion that there is some potential for aluminium toxicity from treatment using aluminium salts when pH is maintained in the neutral range in fresh waters. Continuous exposures to aluminium are more likely to have adverse effects on aquatic life than single dose applications of Al-salts. Hence, the potential for adverse effects with one-time aluminium treatments lie primarily with significant aluminium floc accumulation and subsequent disruption of benthic invertebrate habitat. Other short-term effects are also possible, including reduced benthic invertebrate populations and stress to certain species of fish. Elevated concentrations of natural dissolved organic matter (DOM) capable of binding aluminium in the water of Östhammarsfjärden are likely to limit toxicity during and after application. Previous studies have shown that the effects are short (invertebrates) to medium term (fish), and aquatic communities affected by treatment with Al-salts generally rebound and improve from pre-treatment conditions due to increased water and habitat quality. A direct injection of aluminium to the sediment will likely limit much of the potential treatment impacts to plankton and fish in the water column. Given the lack of total and dissolved aluminium data in marine and brackish systems, it is difficult to compare the results from freshwater systems directly. Although some authors recommend less restrictive limits for aluminium in marine waters due to differing water chemistry, others propose more restrictive limits due to the potential for a greater diversity of aquatic species and potential toxicity to these species. Benthic species diversity appears to be somewhat poor in Östhammarsfjärden, potentially limiting any impact from treatment with Al. In addition, the experiment conducted in Löparöfjärden (which has similar water chemistry to Östhammarsfjärden) showed no significant effects on plankton, epifauna or benthic invertebrates after addition of aluminium to the sediment.

Enclosure experiments were conducted at Löparöfjärden in 2011 where aluminium was added directly to the sediment and chemical data were collected. Modelling shows that elevated concentrations can be expected during the early phase after aluminium addition and that aluminium levels (mostly in the form of $Al(OH)_3$ or soluble $Al(OH)_4^-$) may be higher than what is expected from theoretical solubility calculations and in studied reference systems. Without additional data, it is difficult to explain why this occurred but aluminium solubility may be slightly enhanced under the pH and ionic strength (salt content) conditions found in the brackish water of Östhammarsfjärden. Organisms that are present in the water column may be exposed to elevated aluminium concentrations during a prolonged time period lasting from several days to weeks depending on the physical mixing of the water column after the addition.

Based on the information in this report, use of aluminium salts is likely to be an effective method for reducing internal phosphorus loading in Östhammarsfjärden. Short term effects on aquatic biota should be expected, but long term improvements in the abundance and diversity of species should

increase due to the improvement in water quality. Given the results from the Löparöfjärden experiment, the risk for negative effects on plankton, epifauna and benthic fauna present in Östhammarsfjärden should be low. Because there are very few data on full scale brackish water aluminium treatments, however, we recommend a complete chemical analysis including pH, alkalinity, total organic carbon and major cations and anions during a full scale treatment for the sake of better understanding of the on-going chemical processes during aluminium addition to brackish water. The data may also be useful for describing the process or process behind the slightly elevated aluminium concentrations seen during the Löparöfjärden experiment. We also advise examination of sediment aluminium and phosphorus content as well monitoring of aquatic biota following treatment to assess the potential for long term impacts of treatment on sediment chemistry and the aquatic community.

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Appendix

Datum	Koral	Behandling	Temp (°C)	O_2 (mg/l)	Salinitet (promille)	pH	Filtered Al (µg/l)	Alpart (µg/l)	Total Al (µg/l)
2011-06-08	5	Al	21.8	10.44	5.1	8.17	13	-2	11
2011-06-14	5	Al	20.4	10.13	5.1	6.8	31	233	264
2011-06-22	5	Al	19.1	10.41	5.1	7.32	41	66	107
2011-06-27	5	Al	21	10.25	5.1	7.54	57	20	77
2011-07-06	5	Al	19.9	10.23	5.1	7.57	76	6	82
2011-07-11	5	Al	21.9	9.88	5.2	7.7	95	12	107
2011-07-19	5	Al	21.9	9.61	5.3	7.9	96	30	126
2011-07-29	5	Al	21.9	9.45	5.3	7.99	102	24	126
2011-08-04	5	Al	21.9	9.28	5.3	7.85	127	15	142
2011-08-08	5	Al	21.2	9.23	5.3	8.01	161	8	169
2011-08-18	5	Al	20.3	9.25	5.3	7.98	164	29	193
2011-08-26	5	Al	19.6	9.63	5.3	8.08	153	46	199
2011-09-02	5	Al	18.3	9.68	5.3	8.15	143	72	215
2011-09-07	5	Al	17.5	9.66	5.3	8.14	138	82	220
2011-09-15	5	Al	15.8	9.9	5.3	8.21	139	71	210
2011-09-23	5	Al	13.9	10.37	5.3	8.22	86	77	163
2011-09-28	5	Al	13.3	10.8	5.3	8.31	64	55	119

Datum	Koral	Behandling	Temp (°C)	O_2 (mg/l)	Salinitet (promille)	pH	Al (µg/l)	Alpart (µg/l)	Total Al (µg/l)
2011-06-08	3	Al, vu	21.5	10.37	5	8.12	10	0	<10
2011-06-14	3	Al, vu	20.4	10.44	5.1	6.78	27	176	203
2011-06-22	3	Al, vu	19.1	10.18	5.1	8.28	5	0	18
2011-06-27	3	Al, vu	21.9	11.12	5.1	8.34	14	18	32
2011-07-06	3	Al, vu	19.8	11.14	5.1	8.5	13	0	13
2011-07-11	3	Al, vu	22	11.08	5.2	8.55	17	-1	16
2011-07-19	3	Al, vu	22	10.4	5.2	8.58	16	25	41
2011-07-29	3	Al, vu	22	10.42	5.3	8.68	41	2	43
2011-08-04	3	Al, vu	21.9	10.35	5.3	8.67	61	-3	58
2011-08-08	3	Al, vu	21.3	9.58	5.3	8.73	65	-3	62
2011-08-18	3	Al, vu	20.1	10.04	5.3	8.7	27	29	56
2011-08-26	3	Al, vu	19.6	10.26	5.3	8.66	24	49	73
2011-09-02	3	Al, vu	18.2	9.86	5.3	8.66	5	0	61
2011-09-07	3	Al, vu	17.4	9.55	5.3	8.49	23	35	58
2011-09-15	3	Al, vu	15.7	9.48	5.3	8.24	25	25	50
2011-09-23	3	Al, vu	13.8	9.42	5.3	8.01	16	32	48
2011-09-28	3	Al, vu	13.2	10.22	5.3	8.11	16	18	34

Average simplified seawater composition (moles/l) assumed in all models

```
SOLUTION 1
      units  moles/l
      pH  8.28     charge
      temp 5
      Na  0.078
      Cl  0.07
      C(4) 0.001350
      SO4 0.004
      Si    0.0002
      Driscoll  0.000017
      # equivalent to around 5 ppm organic carbon
```

List of additional aqueous species:

```
3Al+3 + 4 H2O = Al3(OH)4+5 + 4 H+
        log_k   -13.7
        delta_h 39.89   kcal
        -analytic       226.3740.0      -18247.8        -73.597
# Hedlund  et al. 1997 at 0.1 M
Al+3 + SO4-2 = AlSO4+
        log_k   3.84
        delta_h 2.29 kcal
# Thermo VisMinteq
Al+3 + 2SO4-2 = Al(SO4)2-
        log_k   5.58
        delta_h 3.11 kcal
# Thermo VisMinteq
2Al+3 + CO3-2 + 2 H2O =  Al2(OH)2CO3+2  + 2H+
        log_k   4.31
        delta_h 2.29 kcal
# Hedlund  et al. 1997 at 0.1 M
13Al+3 + 32H2O = Al13(OH)32+7 + 32H+
     log_k   -109.7
    delta_h 44.06   kcal
# Plyasunov and Grenthe 1994
Al+3 + H4SiO4 = AlOSi(OH)3+2 + H+
     log_k   -2.38
     delta_h 44.06   kcal
# Pokrovsky 1996
H4SiO4 = H3SiO4- + H+
     log_k   -9.81
     delta_h 8.935   kcal
     -analytical 6.368      -0.016346  -3405.9
# Grenthe et al. 1992
H4SiO4 = H2SiO4-2 + 2H+
     log_k   -23.14
     delta_h 29.714  kcal
     -analytical 39.478     -0.065927  -12355.1
# Grenthe et al. 1992
H4SiO4 + 6F- + 4H+ = SiF6-2 + 4H2O
     log_k   30.18
     delta_h -16.26  kcal
# Minteq
SwedenH3 = SwedenH3
     log_k   0
     delta_h 0       kcal
# definition of two different triprotic acids
```

```
DriscollH3 = DriscollH3
        log_k   0
        delta_h 0       kcal
# adapted from Driscoll et al. 1994
# 10 mg/l equals 0.0000458 moles   4.58 umol charge per g
DriscollH3  = DriscollH2-  + H+
         log_k   -3.04
# adapted from Driscoll et al. 1994
DriscollH2- = DriscollH-2  + H+
         log_k   -4.51
# adapted from Driscoll et al. 1994
DriscollH-2  = Driscoll-3  + H+
         log_k   -6.46
# adapted from Driscoll et al. 1994
Al+3 + Driscoll-3 = AlDriscoll
        log_k   7.9
# adapted from Driscoll et al. 1994
Al+3 + Driscoll-3  + H+ = AlHDriscoll+
        log_k   12.6
# adapted from Driscoll et al. 1994
```