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# The effects of lime treatment in acidified lakes on sediment P sorption and productivity



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## **Abstract**

In the last century fossil fuel combustion has resulted in acidification and elevated metal content in Swedish lakes. To counteract anthropogenic acidification, Sweden began a full scale liming treatment program in the mid 1970's. Even though the pH in lime treated lakes increases after treatment, lake productivity does not always recover. The hypothesis of this study was that increased metal input to the sediment decreases available phosphorus (P) in the water. In this study, sediment cores were taken from three different types of lakes: limed, limed with fertilizer (added P), and acid (reference) lakes in southwest Sweden to investigate the possible link between low production (P availability) and sediment metal content in acidified and limed lakes. Sediment was investigated for metal content and experimental phosphorus (P) additions were conducted to determine P sorption characteristics. Low equilibrium P concentration and high maximum P sorption in the experiments indicates that the sediment will adsorb P from the water column making the already nutrition pore water less productive, driven mainly by high concentrations of aluminium and iron in sediment layers effected by both acidification and lime treatment. There were also indications that lime addition will elevate P sorbing metals in the sediment of acidified lakes, which can lead to less P in the water column. Perhaps making modification (i.e. P addition) to the treatment method is important for success in restoring acidified lakes.

## **Introduction**

### *Acidification*

It has been estimated that over 17 000 of approximately 90 000 lakes in Sweden are acidified due to the increase of emission compounds from combustion of fossil fuels during the last century (Swedish EPA 2006). These compounds, such as sulphur and nitrogen, are deposited on lakes and the soil of the surrounding watershed around lakes, causing acidification of both. In acidified lakes the water chemistry is characterised by depleted alkalinity and low pH, negatively affecting organisms such as fish. Also the nutrients are low in concentration (especially P, the limiting nutrient in these types of lakes (Schindler 1977)) and are often extremely low in these clear water acidic lakes. Unusually high levels of sulphate, dissolved aluminium (Al) and sometimes other metals are found as well (Wällstedt 2005). Primary production is considered to suffer from lack of P rather than from high metal ion concentration in some acidified lakes (Jansson et al. 1986). In any case, acidified lakes experience a decrease in production and are sometimes called dead lakes, because of low productivity. The decrease in production seen in many acidified lakes is generally referred to as oligotrophication.

When acid deposition (both wet and dry) decreases the pH in watershed soils, elevated metal (mainly iron (Fe) and Al) input to acidified lakes can occur (Wällstedt 2005). These metal ions can be directly toxic, but  $\text{Al}^{3+}$  or even the solid  $\text{Al}(\text{OH})_3$  can also react with P in the water and/or near to the sediment. Thereby the formations of Al-bound P (Al-P) are brought to the sediment and the P will be permanently bound unless pH becomes to low. In the case of  $\text{Fe}^{3+}$  or  $\text{Fe}(\text{OH})_3$  it also react with P and forms Fe-bound P (Fe-P) but P can release at potentials below 200 mV when  $\text{Fe}^{3+}$  is reduced to  $\text{Fe}^{2+}$  when oxygen are completed. However, even though a lake is acidified, internal buffering processes (like nitrate and sulphate reduction) can elevate pH near the sediment surface (Ghanström 1985). This can allow for Al and Fe precipitation, potentially increasing the P sorption capacity of the sediment. Therefore, the formation of Al-P and to some extent Fe-P can limit the overall available P in the lake potentially causing oligotrophication. (Huser and Rydin 2005) The study by Huser and Rydin (2005) showed Al-P levels had increased in sediments in recent decades.

### *Liming*

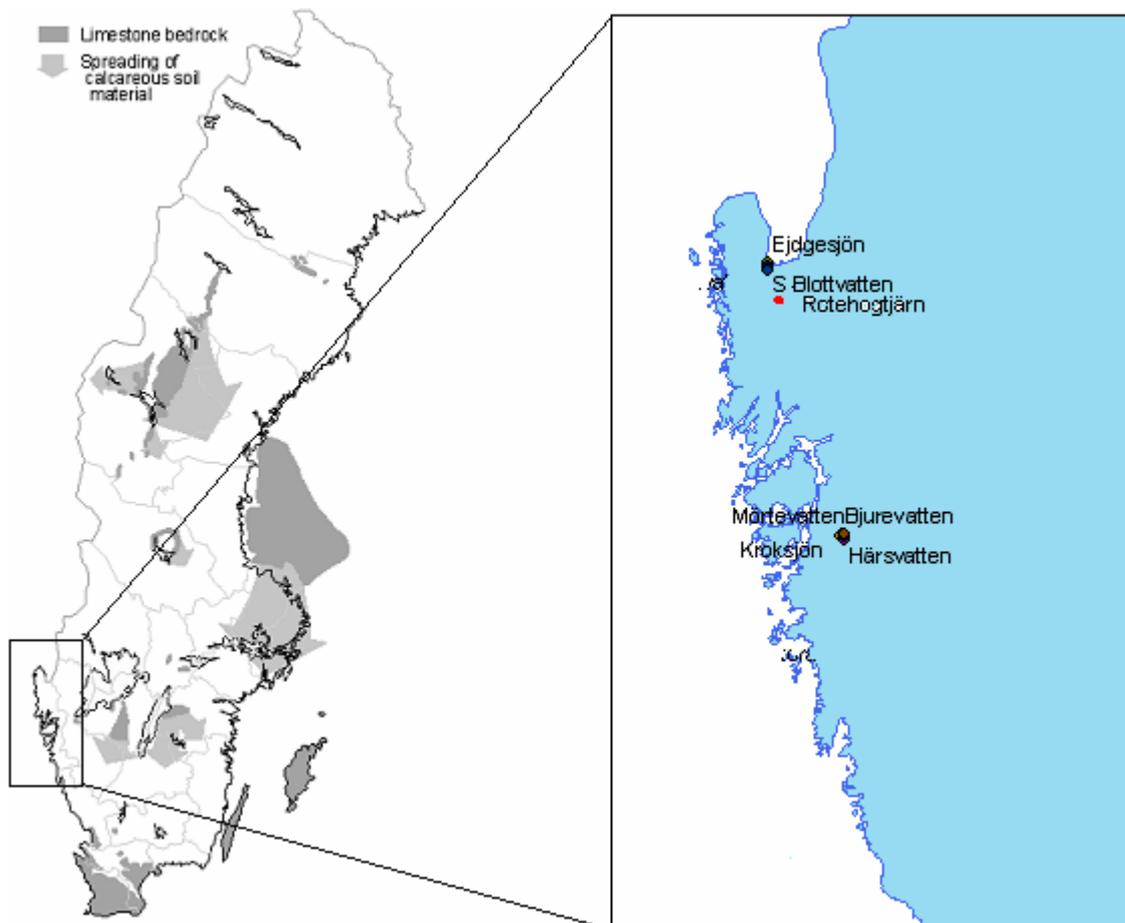
The main restoration technique aimed at reversing acidification is the use of limestone ( $\text{CaCO}_3$ ). Liming of Swedish lakes started in the mid 1970s first on a small scale and on a larger scale in the beginning of the 1980s (Swedish EPA 2006) as a restoration of the anthropogenic (caused by man) acidification of lakes. The most widely used method of spreading lime is to add it directly to the surface water from boats, but helicopters have been used in less accessible areas. The main goal is to counteract the decreasing fish population by raising both pH and alkalinity back to previous levels  $>6.0$  and  $0.05\text{meq/L}$ , respectively (Persson and Wilander 2004).

Several studies have shown the effects of liming acidified lakes have varied and show that acidified lakes undergo further oligotrophication (Broberg 1984; Kopáček et al. 2000) even though pH increases. Reports showing a decrease in P concentrations after liming of lakes (Persson and Appelberg 2001; Blomqvist 1999) indicate removal of P from these lakes. This may result in a further decline in productivity. Liming reduced total-P in the water by 30%, from  $9.3$  to  $6.6 \mu\text{g P/l}$  in the Swedish lake Njupfatet (Blomqvist et al., 1995), and made P the only growth limiting factor for phytoplankton (Pettersson and Blomqvist 1992), placing negative pressure on productivity in the lake.

The higher pH in limed lakes will favour increased precipitation of metals that are responsive to changes in pH (Al and Fe). With continued input to the lake from the acid watershed soil, Fe and Al can precipitate with organic matter and the already limited P to the sediment: during elevated pH. As ionic Al and Fe species hydrolyse and form colloidal hydroxides, they can coagulate dissolved organic carbon and adsorb orthophosphate in the water column (Kopáček et al. 2000). The Al and Fe hydroxides settle and can enhance the P sorption capacity of the sediment. The higher concentration of Al oxyhydroxides in the surface sediment may reduce P released to the water column after orthophosphate discharge from Fe oxyhydroxides during anoxia, because Al hydroxides are indifferent to redox changes. Thus, I hypothesize that liming of acidified lakes will increase the ability of the sediments in acidified lakes to bind P from the water column. Since P is the limiting nutrient in such systems, the reduction in available P will have a negative effect on productivity in the lake.

## Background

In this study, sediment was taken from seven lakes: two were acidic, three were acidic-limed and two were acidic-limed and had been fertilized (Table 1). These lakes are situated in the south-west part of Sweden and are heavily affected by atmospheric deposition and the watershed soils are low in buffering capacity (Figure 1 and Figure 2). The limestone in the map weathers easily and acts as protection against acidification.



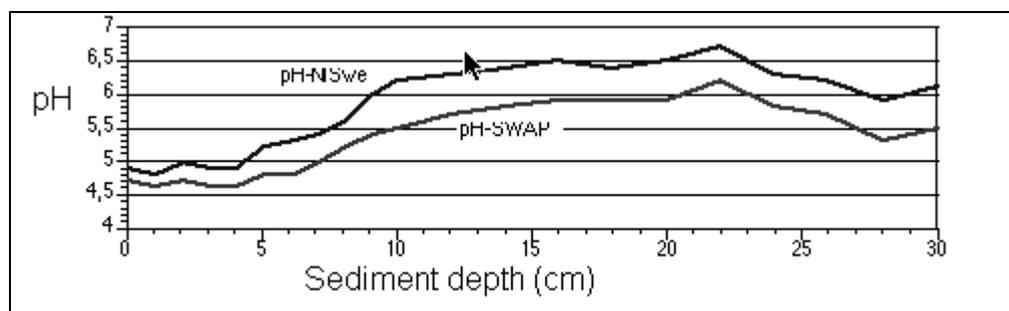
**Figure 1.** Calcareous soils and rocks in Sweden.

**Figure 2.** Map over sampled lakes.

### Acidic lakes

Lakes Härsvatten and Rotehogstjärn are part of a monitoring program called IKEU by Sveriges Lantbruks Universitet (SLU) initiated in 1983 that includes periodic sampling of general water chemistry of lakes across Sweden annually. The pH of the two acidified lakes is, as expected, low. Statistics from 1989 to 1993 show on an average of 5.28/5.03 surface/bottom water pH for Lake Rotehogstjärn and 4.42/4.47 pH for Lake Härsvatten surface and bottom water (IKEU, 2006). The surface water (0.1 – 2.5 m) of Lake Rotehogstjärn has a total P (TP) concentration average of 14.3  $\mu\text{g/l}$  with a standard deviation (SD) =  $\pm 4.7$ . Mean metal content is 492  $\mu\text{g/l}$ , SD =  $\pm 187$  for Fe, and 296  $\mu\text{g/l}$ , SD =  $\pm 124$  for Al. Alkalinity is near zero (avg. 0.003 mekv/l). The catchment and surface area of Lake Rotehogstjärn are 3.43  $\text{km}^2$  and 0.17  $\text{km}^2$  respectively. The surrounding area is mainly forest and wetland (66% and 18%). The lake has a maximum depth of 9.4 m, mean depth 3.4 m and water retention time of  $\sim 110$  days. It is located in the south-western Sweden, close to the Norwegian border (Figure 2).

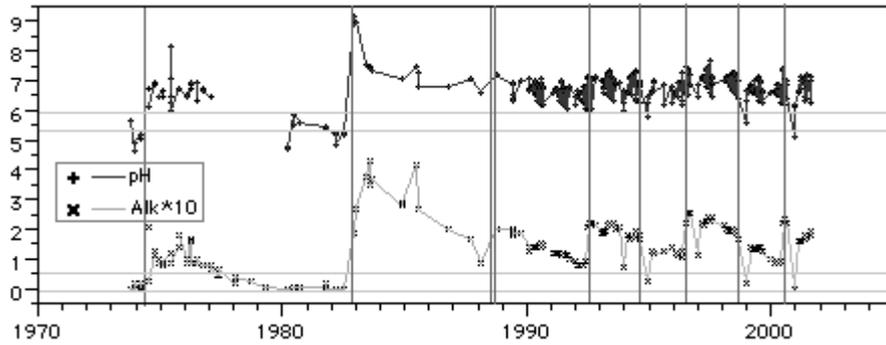
Lake Härsvatten is located in south west of Sweden 30 km north of Gothenburg and has a catchment area of 2.03  $\text{km}^2$  with mostly pine forest and a lake area of 0.19  $\text{km}^2$ . Maximum depth is 26.2 m but mean depth is only 5.7 m and it has a retention time of  $\sim 330$  days. The TP in the lakes surface water averaged 5.1  $\mu\text{g/l}$  (SD =  $\pm 2.5$ ) between 1985 and 2005. Secchi depth and pH averaged 9.4 m and 4.6 with SD  $\pm 2.3$  and  $\pm 0.2$  respectively during the same period. Figure 3 shows the calculated pH as historical review. Al and Fe concentration content in the water fluctuated greatly during the seasons but averaged 420  $\mu\text{g/l}$  (SD =  $\pm 125$ ) and 73  $\mu\text{g/l}$  (SD =  $\pm 23$ ) respectively, while alkalinity was stable and below zero, averaging -0.042 mekv/l (SD =  $\pm 0.016$ ).



**Figure 3.** A sediment core from Lake Härsvatten with estimated historical pH.

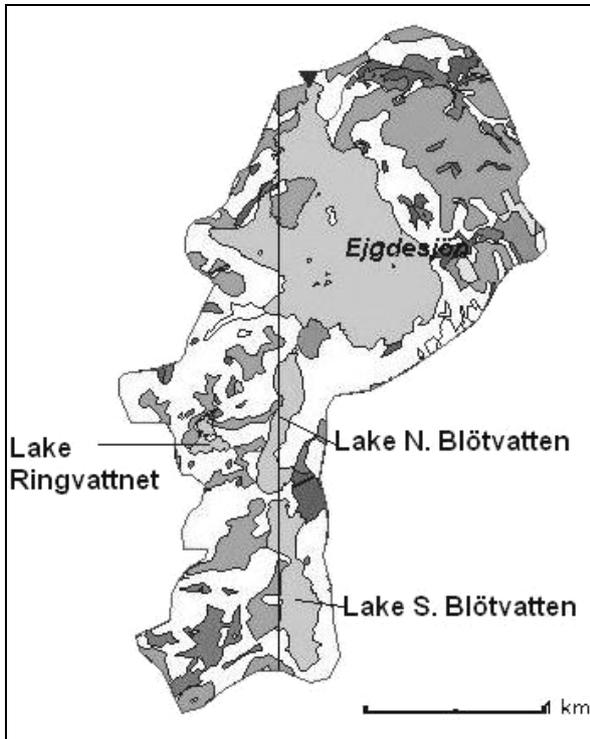
### Limed lakes

Lake Ejdjesjön is also monitored by the IKEU program. The lake is located at the Norwegian border in proximity to Lake Rotehogstjärn and has an area of 0.86  $\text{km}^2$  and a catchment area of 3.6  $\text{km}^2$  (Figures 2 and 5) including mostly woodland and lakes. Prior to liming, the pH averaged 5.2 and mean alkalinity was 0.009 mekv/l. Currently it has pH of 7.0, SD =  $\pm 0.4$  and the alkalinity has improved to an average 0.18 mekv/l, SD of  $\pm 0.07$  in the surface water (IKEU 2006). TP at beginning of the restoration was 5  $\mu\text{g/l}$  and was 4.7, between 1997 and 2005, SD =  $\pm 2.4$ . Mean value of Al concentration in the surface water is 82.6  $\mu\text{g/l}$ , SD =  $\pm 28$ , while the Fe content was 79.4  $\mu\text{g/l}$  but fluctuating here as well (SD =  $\pm 133$ ).



**Figure 4.** Historical pH and alkalinity data for Lake Ejgdesjön (IKEU 2006).

Lake Ejgdesjön was first limed in 1974 with 250 tons of lime but re-acidification occurred four years after dosage so the same amount was added in the year 1982. To keep pH level more constant, dosage was decreased and additions became more frequent (Figure 4). In total the lake has directly receive almost a thousand ton of lime between 1974 and 2002. One important aspect is that other lakes included in this catchment have been limed. The lakes include Ringvattnet, which is a small lake and has only received approximately 10 tons between 1994 and 2003 (prior data unavailable). Södra Blötvattnet has been limed with more than 160 tons between 1974 and 2003. Both these lakes exit into Norra Blötvattnet, which has also been limed (approximately 50 ton between 1988 and 2003; prior data unavailable), and thereafter exits into Lake Ejgdesjön. Thus, the lake could receive more lime-affected water than expected. This could explain what happen in late 1982 when ph reach a maximum of over 9, seen in Figure 4. Lake Södra Blötvattnet is as prior mention included in lakes Ejgdesjön catchment (Figure 5) but is not monitored by IKEU.



**Figure 5.** Lake Ejgdesjön catchment (SLU 2006)

Stora Bjurevatten is a large (estimated approximation 0.33 km<sup>2</sup>) and shallow (max. depth ~7 m) lake in Stenungsunds kommun in the same region as Lake Härsvatten (Figure 2). Historical data for this lake are not available.

### *Limed fertilized lakes*

Monitoring data are not available for these lakes but they have both received lime and have had phosphorus additions as well (Hans Hultberg 2006). The lakes are located near Lakes Härsvatten and Stora Bjurevatten (Figure 2) and have been moderately limed. Lake Mörtevatten has received 33 ton between 1978 and 2003. Lake Kroksjön (approximated area 0.05 km<sup>2</sup>) feeds into Lake Mörtevatten (approximated area 0.03 km<sup>2</sup>) and has received 47 tons of lime between 1978 and 2002.

### **Materials and methods**

Sediment cores were collected in May of 2006 in the south west side of Sweden (Figure 1) with a Willner gravity corer. To make sure that the sediment taken represented the lakes accumulation zone, it was obtained from the deepest hole in each lake. A polyethylene cylinder (40 cm long and with an inner diameter of 6.3 cm) was used to collect each sediment core which were then sliced every cm the first 10cm and then every two cm thereafter. Dry weight was calculated after freeze-drying at -30 °C. Sediment dating was attempted by analyzing for cesium (Cs). Date estimation can be made by locating the peak of Cs activity which is assumed to mark the Chernobyl accident in 1986.

To determine metal content, sediments were digested at high temperature and pressure in 50% nitric acid and then Ca, Al and Fe were measured using inductively coupled plasma emission spectrometry (ICP) at wavelengths  $\lambda = 315.887, 167.078$  and  $259.941$  respectively.

In order to determine maximum sediment P sorption capacity, orthophosphate (KH<sub>2</sub>PO<sub>4</sub>, pH=6.5) was added to sediment (~200 mg wet weight) in 15mL polypropylene tubes samples in concentration range 0, 0.04, 0.08, 0.10, 0.20, 0.50, 2.5, 10, 50 and 100mg/L. Ionic strength of all P solutions was 1 mM through the addition of NaCl. Samples were shaken and kept in the dark for 48 h. P was analyzed using the ammonium molybdate method according to Murphy and Riley (1962).

Water was collected from each lake using a Ruttner sampler and dissolved oxygen was measured with an oxygen meter probe (WTW Oxi 340i/SET) just above the sediment surface. Water samples were analyzed for pH with a Crison micro pH 2001-meter and TP was measured according to Menzel and Corwin (1965).

A Langmuir equation was used to acquire maximum P sorption ( $B_{max}$ ) (Figure 6):

$$y = \frac{B_{max} x}{K_d + x} \quad \text{With:} \quad \begin{array}{l} B_{max} = \text{maximum number of binding sites} \\ K_d = \text{concentration of ligand to reach half maximal binding} \end{array}$$

Equation 1. Langmuir model used to fit sorption data in this study.

This equation is used to fit specific binding data (y) as a function of ligand concentration (x).

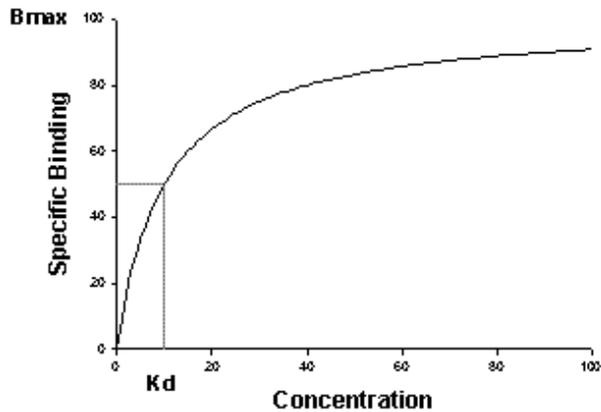


Figure 6. Example of a one site saturation ligand binding.

Equilibrium phosphorus concentration (EPC) is determined by using the linear portion of the P sorption graph where the function crosses the x axis where P sorption = 0 ( $R^2 \geq 0.9$ ), or where no release or uptake of P by the sediment occurs. If the P concentration in the lake water is higher than the EPC value, P uptake should occur. If the lake water P concentration is lower, then P release is expected.

The upper 5 cm of sediment was analyzed for both EPC and maximum sediment P sorption. A lower sediment layer was chosen to represent pre-liming conditions and was analyzed for EPC and maximum P sorption as well.

## Results

General water quality results from sampling in early May 2006 are shown in table 1.

Table 1. Study lakes include acidified (reference), limed, and limed + fertilized lakes. May 2006.

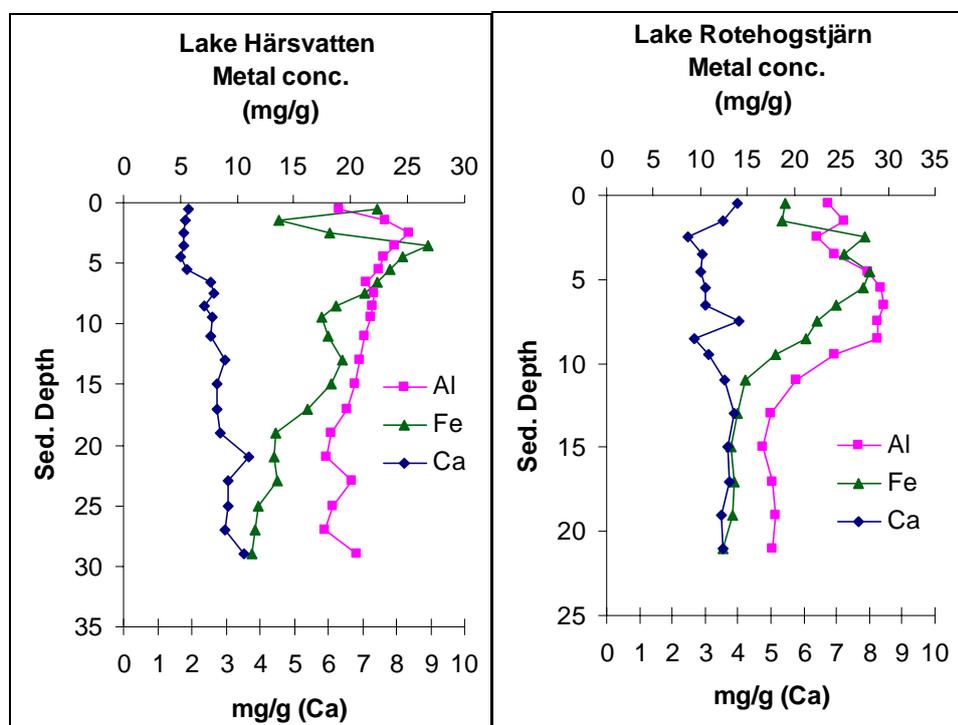
Lakes	Coordinate s X-Y = RT 90 2.5 gon V	Secchi (m)	Core depth (m)	pH Surface/ Bottom	Total phosphorus Surf./Bott.	Dissolved oxygen at bottom
<b>Acidic</b>						
<i>Rotehogstjärn</i>	652902- 125783 643914-	1.5	8.5	5.0/5.0	13.67/12.6 2	2
<i>Härsvatten</i>	127698	4.3	23.5	4.5/4.7	3.86/5.26	2.1
<b>Acidic-limed-P</b>						
<i>Kroksjön</i>	644120- 127686 644140-	5.3	13	6.4/6.3	3.51/14.02	<1
<i>Mörtevatten</i>	127682	3.3	7	6.3/6.2	5.61/5.96	4.8
<b>Acidic-limed</b>						
<i>Ejgdesjön</i>	653737- 125017	5	25	6.2/6.2	4.56/3.16	7
<i>Södra Blötvattnet</i>	653497- 125002	3	24.3	6.6/6.5	4.21/4.21	0.5
<i>Stora Bjurevatten</i>	644061- 127578	3.2	6.6	6.7/6.7	5.96/4.91	-

The dating result were inconclusive in most cases do to small amounts cesium detected. Except for Lake Ejgdesjön, the date of the Chernobyl accident has been estimated with help of good judgments.

#### Acidic Lakes

Lake Härsvatten pH and TP are shown in Table 1. The lake water was acidic with top and bottom pH of 4.5 and 4.7. TP was low and was 3.9 and 5.3  $\mu\text{g/l}$  at the top and bottom respectively. Lake Rotehogstjärn pH was similar at surface and bottom at 5.0 and TP concentrations were 13.7 $\mu\text{g/l}$  at the surface and 12.6  $\mu\text{g/l}$  at the bottom (Table 1)

Fe and Al concentration in these lakes are shown in Figures 3a and 3b. Fe content peaked at 3.5 cm at 27 mg/g while Al content peaked at 2.5 cm at 25 mg/g.



**Figure 3.** Metal content (dry weight) in sediments (cm) of lakes Härsvatten (a) and Rotehogstjärn (b), were Al and Fe on the upper x axis, Ca on the bottom x axis.

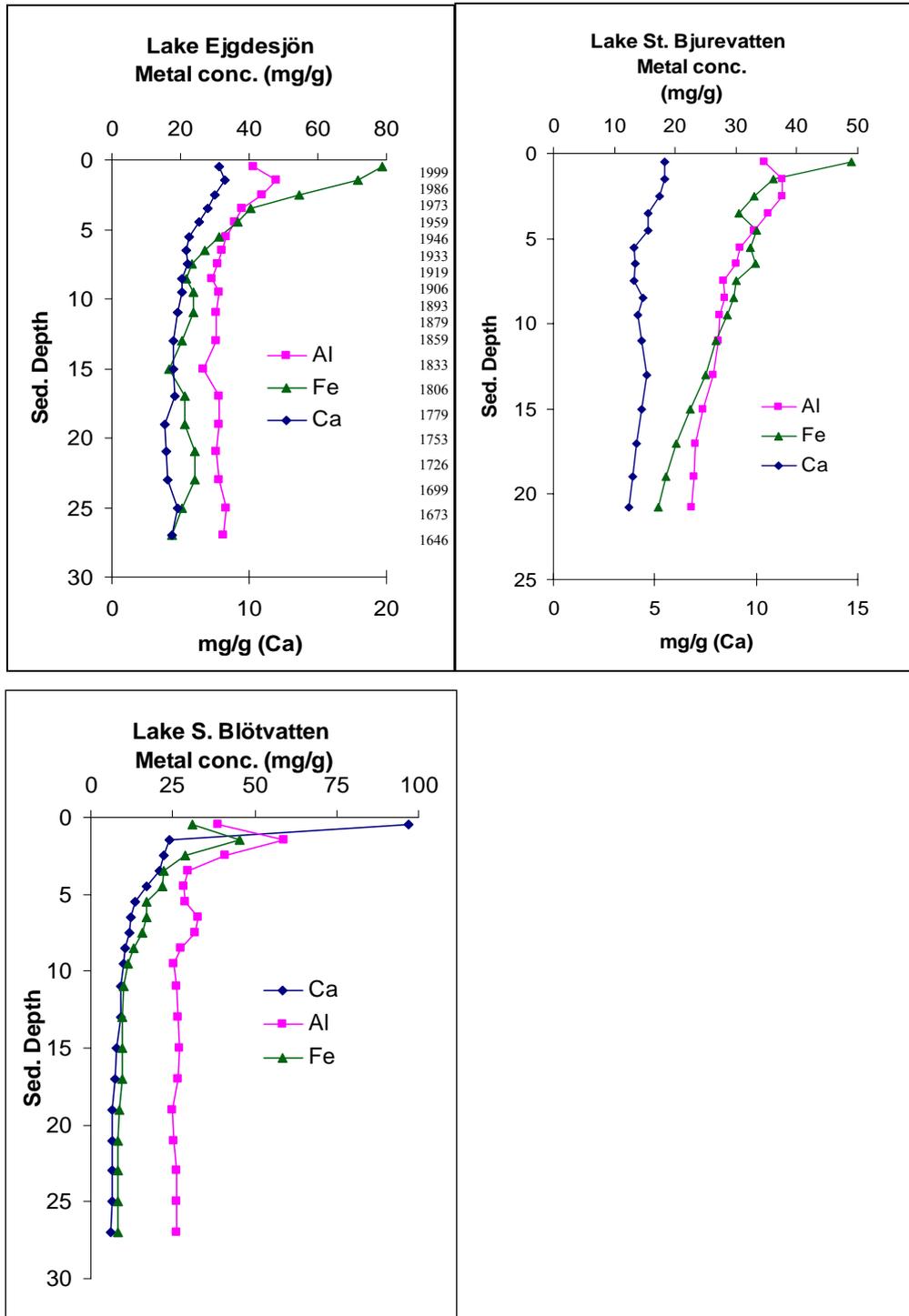
Max P sorption varied in the upper sediments of Lake Härsvatten ranging from a low of 4.7 mg/g to a high of 23.5 mg/g. The deep sediment had a lower max P sorption at 4.5 mg/g. Average EPC in the top 5cm of sediment was 4.3 $\mu\text{g/l}$  and was 28.1 $\mu\text{g/l}$  at 16 cm depth. In Lake Rotehogstjärn the max P sorption range from 5.4 to 10.9 mg/g in the top sediment layers, while at 16 cm sediment depth it was 3.8 mg/g. EPC averaged 6.2 $\mu\text{g/l}$  in the surface sediments and 9.7 $\mu\text{g/l}$  in the sample taken at 14cm depth.

#### Limed Lakes

Lake Ejgdesjön pH was 6.2 in the whole water column from the samples taken in this study. TP was 4.56  $\mu\text{g/l}$  at the surface but was lower near the bottom at 3.16  $\mu\text{g/l}$ . Lake Södra Blötvattnet had a pH of 6.6 and 6.5 at the top and near the sediment surface, respectively. Measured TP was 4.2 $\mu\text{g/l}$  in the whole water column. The shallowest lake, Lake Stora

Bjurevatten had a pH of 6.7 overall and TP was 5.96  $\mu\text{g/l}$  at the surface and 4.91  $\mu\text{g/l}$  at the foot of the lake. (Table 1)

Fe and Al concentrations were higher in the surface sediment at the layers affected by lime and lower below this depth (Figure 5). Fe was 79 mg/g at 0.5 cm and an estimated background of a mar 17 mg/g at 16 cm and Al had a maximum at 1.5 cm with 48 mg/g compared with 27 mg/g background in Lake Ejdgesjön.



**Figure 5.** Al, Fe and Ca dry weight (DW) concentrations in sediments (cm) of Lake Ejdgesjön (a), Lake St. Bjurevatten (b) and Lake Södra Blötvattnet (c) ink dating of Ejdgesjön.

Also in Lake St. Bjurevatten Fe was higher than Al reaching 49 mg/g in the first cm slice while a background value of 22 mg/g been estimated. Al was in 1.5-2.5 cm 38 mg/g and 25 mg/g in the older sediment taken at 16 cm depth. Because of the increase in Ca in the first cm sample the proportion of Al and Fe to the total amount of sediment taken from Lake S. Blötvattnet is skewed. This lake had its peak of Al and Fe at 1.5 cm of 59 mg/g and 45 mg/g while background was 27 mg/g and 10mg/g, respectively.

Maximum P sorption in the surface sediment of Lake Ejdeshjön was 3.0 mg/g at the lowest and 4.8 mg/g at the highest. The deeper sample had a max P sorption of 1.6 mg/g. The average EPC in the 1-5 cm sediment depth was 8.7µg/l and EPC at 16 cm depth was 19.8µg/l. In Lake Södra Blötvattnet the top few centimetres had a max P of 21.6 mg/g and 4.0 mg/g in a steady decline and 3.9mg/g in the lower taken sample with. The average EPC value of the surface sediment was 13.9µg/l and 33.6µg/l in the deeper sediment. Lake Stora Bjurevatten EPC values were 3.0 µg/l and 5.9 µg/l in the top and at 16 cm in the sediment, respectively. The sediment had a maximum P sorption of 6.5 mg/g to 2.3 mg/g in first 5 cm and 2.6 mg/g at the deeper sample taken.

#### *Limed and fertilized lakes*

In the limed and fertilized lakes group, Lake Kroksjön had low TP concentration in the surface water (3.5 µg/l) and an elevated amount closer to the sediment (14.0 µg/l). pH at the same locations were 6.4 and 6.3 respectively. Lake Mörtevatten had similar pH values at the surface water and above the sediment of 6.3 and 6.2. The TP concentrations of 5.6 µg/l and 6.0 µg/l, top and bottom respectively suggest low nutrition concentration in the water.

The metal content of the sediment is shown in Figure 6. where substantial levels of Al and even Fe during the liming period can be seen. In Lake Kroksjön, maximum Al was detected at 1.5cm at 44 mg/g and was lower (this isn't a background value, that should be estimated with multiple values in the deep sediment) at 16 cm (22 mg/g). The Fe was at its uppermost level of 30 mg/g at 3.5 cm, three times as much as the level found at 16 cm (12 mg/g). Metal content fluctuated greatly in Lake Mörtevatten sediment but the trend seen in Figure 6 (b) shows that metal concentrations have increase when compared to the pre-liming period. Both Al and Fe peaked in the sediment at 0.5 cm at 26 mg/g and 19 mg/g respectively, while background concentrations were approximately 16 mg/g and 7 mg/g respectively.

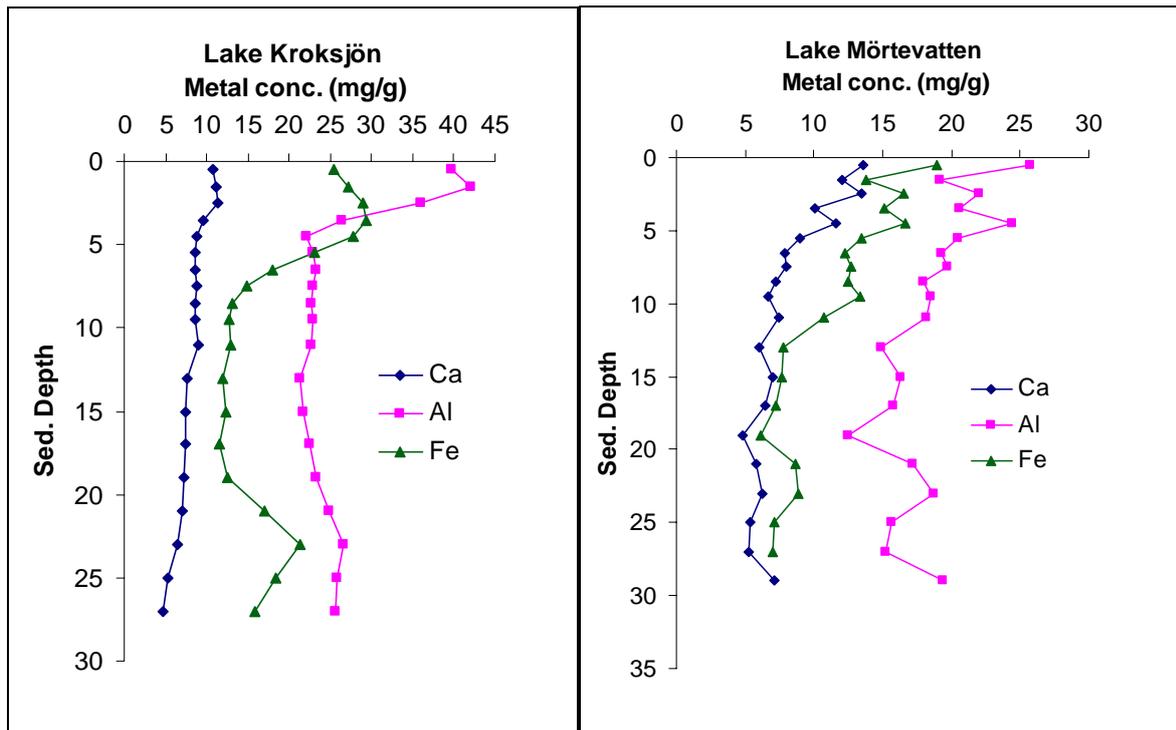


Figure 6. Metal concentration (dry weight) in sediments (cm) of Lakes Kroksjön (a) and Mörtevatten (b).

In the P addition experiment for Lake Kroksjön, the P sorption reach a maximum of 11.5 mg/g and minimum of 6.7 mg/g in the top sediment layers, while the 16 cm layer had only 1.5 mg/g maximum P sorption. This lake sediment also had EPC values of 4.3  $\mu\text{g/l}$  and 31.6  $\mu\text{g/l}$  in the surface (1-5 cm) and 16 cm sediment depth samples, respectively. The maximum P sorption of Lake Mörtevatten did not reach higher than 7.0 mg/g but was as low as 2.7mg/g in the first few cm, whereas the sample taken deeper down had a max P of 1.4 mg/g. EPC value averaged 5.6  $\mu\text{g/l}$  in the surface sediment and 5.5 $\mu\text{g/l}$  further down (16 cm).

## Discussion

All the lakes included in this study had substantially lower EPC values than some other studies looking at P sorption in sediment (Appan and Wang 2000; Koski-Vähälä and Hartikainen 2001). Appan and Wang (2000) showed that the tropical Kranji reservoir, Singapore had EPC values above 1.5 mg/l and maximum P sorption values between 2.3 and 10.3 mg/g. According to the authors, a high concentration of Al in the surrounding watershed soils might be the explanation for the relative high sorption capacity seen in the reservoir. In the study conducted by Koski-Vähälä, the authors looked at how different pH values affect the release of P from sediments in the Finnish Lake Tuusulanjärvi. The EPC value seems to increase with higher pH, however all the results were above EPC values found in this study.

In one other study (Pant et al. 2001), river sediment from redwood forest area was investigated and also had much higher EPC values (50  $\mu\text{m/l}$  and 750  $\mu\text{m/l}$  under oxic and anoxic condition) than what was found in this study. Whereas for maximum P sorption, a much lower value was found (0.13 mg/g and 0.03 mg/g for oxic and anoxic conition) then what was determined in this study. Fe and Al concentration found in the sediment of the river were also lower (maximum values of 3.9 mg/g and 1.2 mg/g, respectively) then the lowest value in the Swedish lakes in this paper.

Similar results to this study were found in another acidified lake (Lake Plešné, Kopáček et al. 2000) that had 13.8 mg/g maximum P sorption in the top sediment and 6.5 mg/g maximum P sorption deeper sediment (not affected by acidification). In Lake Plešné, the metal content of the sediment reach higher values in the most upper layers, but they are steady and do not peak like the metal content of the lakes in this study. The exception was Al, which increased in the upper layers of the sediment core in Lake Plešné, similar to Al content in most of the lake sediment analyzed in this study. Maximum Al and Fe concentrations were 48 mg/g and 8.8 mg/g, respectively, in the study by Kopáček et al. 2000.

Only a few lake sediments in this study had an Al concentration as high as that found in Lake Plešné, but at the same time much more Fe was present in the sediments. This could suggest anoxic condition in the Lake Plešné or different metal content in the watershed is reason for this. The lakes investigated in this study have higher P binding metal content in the sediment, both Al and Fe, and this could be one reason why EPC is extremely low and maximum P sorption is high. If the lakes in this study go anoxic in the summer months, P sorption will be limited due to release of P from Fe in the sediment.

In order to gain a more accurate picture or comparison of these lakes, it is necessary to separate out the studied lakes by geographic area because differences in the watershed soils may affect sediment composition. Tables 2-3 show differences in the maximum P sorption for the lakes in this study. Table 2 shows that surface sediment (affected by lime) had 3.2 times the maximum P sorption found in deeper sediments in limed lakes from the northern group. Only a 1.85 times increase in maximum P sorption was found in the acidified lakes. However, Table 3 shows no difference in maximum P sorption change (from surface to deeper sediments) between the acidic and limed lakes. For the fertilized lakes, the data shows that even the extra P added to the lakes did not decrease the ratio of maximum P sorption (4.6) between the surface and deeper sediments (not affected by lime or P addition).

Table 2. The average maximum P sorption of the northern group lakes (Figure 2).

North Avg. max P sorption	Acidic	Limed
Top	7.03	8.18
~16 cm	3.80	2.55

Table 3. The average maximum P sorption of the southern group lakes (Figure 2).

South Avg. max P sorption	Acidic	Limed	Limed + P
Top	6.94	4.04	6.75
~16 cm	4.52	2.59	1.48

EPC values were always lower in the surface sediment than in the deeper layers, indicating stronger P sorption characteristics (Tables 4 and 5). This is likely due to the fact that even in non-limed lakes, Al and Fe have been shown to increase during acidification (Huser and Rydin 2005). All lakes in this study showed elevated concentrations of Al and Fe in the sediment, however, limed lakes had some of the highest values for Al and Fe.

In the northern limed lakes (Table 4), EPC ratio (between surface and bottom sediments) was less than half while in the acid lakes it was more than 2/3. This indicates that the limed lake sediments P sorption strength is increasing by a greater amount when compared to the sediments from deeper layers not affected by lime treatment or acidification.

The surface EPC values for the southern lakes (Table 5), indicate that limed lakes have lowest EPC values and the limed and added P lakes have the highest. It appears as the added P

increase the EPC while just liming lakes lowering it, as suspected in the hypothesis. Comparing the EPC ratio between the acidic and fertilized lakes, the values (0.15 and 0.27, respectively) shows that EPC has decreased more in the acid lakes than in the limed plus P lakes.

This could mean that P addition can facilitate a higher EPC value which means the sediments P uptake will be less active. This could be positive because even though the lakes have been limed and probably have more Al and Fe if the EPC is actually higher than that seen in the acidic lakes and returns to pre-acidification and liming range.

Table 4. Average EPC values for the northern group lakes

North EPC Avg.	Acidic	Limed
1-5 cm	6.2	11.3
~16 cm	9.7	26.7

Table 5. The average EPC values of the southern group lakes

South EPC Avg.	Acidic	Limed	Limed+P
1-5 cm	4.3	3.0	5.0
~16 cm	28.1	5.9	18.6

Liming acidified lakes imitates the conditions similar to the lake restorations technique based on the addition of Al-salt to the eutrophic lakes. Metals that are soluble in the water column, like Al and Fe, will precipitate when the pH is increased. This will provide sorption sites for P at the sediment surface. It is difficult to separate out the increased Al and Fe due to acidification and liming but in the lakes in this study, Al and Fe were elevated in the limed lakes, especially when compared to non-limed acidic lakes (Figure 7), and the difference between maximum P sorption in the top sediment and the sample taken below was generally higher as well.

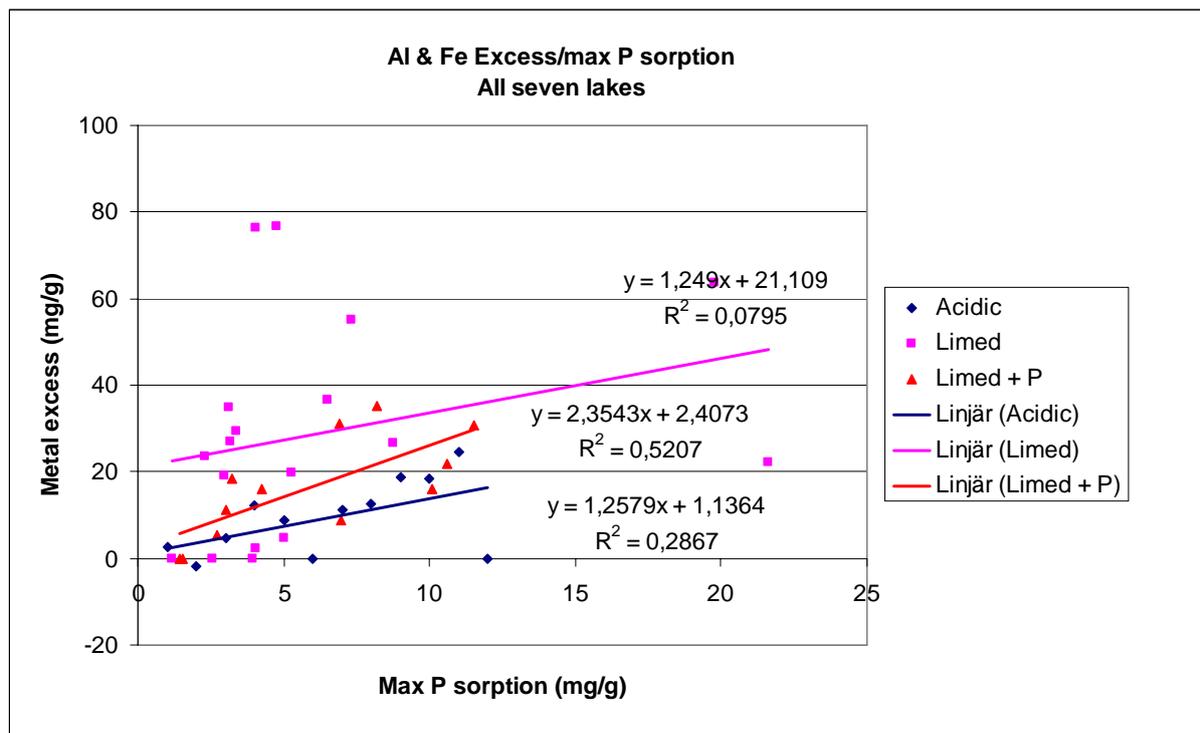


Figure 7. Excess metal (Al and Fe) with max P sorption, all lakes.

The line for lakes with P added in Figure 7 has a higher slope which means that for a given amount of excess metal, max P sorption is less when compared to the other system. This could mean that sediment metals have already bound with the extra added P in these lakes, rendering the P-sorption “site” occupied. Also, in both limed systems, excess metals are higher than in the acidic, non-limed lakes.

In the lakes included in this study maximum P sorption was always higher in the surface sediment affected by lime treatment than in the deeper layers not affected by treatment. Excess Al and Fe increased in these layers, likely due to a combination of chemistry changes caused by liming (higher water pH and continued watershed inputs) and long term affects of acidification (Huser and Rydin 2005). EPC was lower in the surface and higher in the deeper sediments. This indicates that the surface sediments (both from limed and non-limed lakes) are strongly sorbing P from the water column, in most cases, since water column TP concentrations (at least from this study) were mostly above the EPC values.

Again, it is difficult to separate out the effects from acidification alone and those from liming, but this study indicates that liming exacerbates nutrient limitation. Additional Fe and Al input to the sediment decreased EPC values and increased maximum P sorption relative to background conditions in most lakes in this study.

The concern that this acidification will render affected lakes, “dead lakes” was the reason for the lime program initiative. Species like crustaceans and other benthic animals as well as acid sensitive macrophytes perish due to acidification and acid tolerant, usually less desirable, species increase. Liming increases the pH of lakes so that natural flora and fauna may return. However, this study shows that even though pH in these lakes may have increased, nutrients may have decreased in the water column. This means that the natural productive state in these lakes might not come back unless nutrient levels return to normal as well.

The potential impact of liming and higher sediment P-binding metal content could limit production in the long term. This study has shown that higher sediment metal concentrations lead to greater P sorption. This can lead to lower P availability and limit production in the acidic lakes and the problem may be even worse in limed lakes. It is very clear that excess metal is higher in the limed lakes and those metals will probably bind with P. However this study included only seven lakes and a larger study is needed to fully comprehend the effect this has on productivity. The liming method may need to incorporate fertilization in some cases when Al and Fe availability are high if restoration is to be successful in these acidified lakes.

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<http://info1.ma.slu.se/IKEU/>

Figure 3.

<http://info1.ma.slu.se/gp/HAERSVAT.WWW/pg4.html>

Figure 4

[http://info1.ma.slu.se/ma/www\\_ma.acgi\\$StationC&ID=StationData&S=1137](http://info1.ma.slu.se/ma/www_ma.acgi$StationC&ID=StationData&S=1137)

Figure 5.

<http://info1.ma.slu.se/IKEU/ejgde.www/pg2%2C5.html>

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[Oxi probe: WTW = Wissenschaftlich – Technische Werkstätten]