# Influence of acidification and liming on metals in lake sediments

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Doctoral Thesis in
Applied Environmental Science

Stockholm 2005

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ISBN 91-7155-056-9 pp. 1-30
Printed in Sweden by Intellecta DocuSys
Cover photograph by Teresia Wällstedt. Lake Årsjön, Tyresta national park.

## Abstract

Emission and precipitation of acidifying substances has caused severe acidification of lakes and streams in Sweden as well as many other countries during the last decades. Also emissions and long-range atmospheric transport of many metals, e.g. As, Cd, Co, Cr, Cu, Hg, Ni, Pb, V and Zn has been extensive during the last decades. This has lead to increased metal concentrations in lakes and streams, as a consequence of atmospheric metal deposition, increased metal transport to surface waters from acidified catchments and increased metal mobility in the water because of the low pH. To counteract the negative consequences of acidification, liming has been used extensively in Sweden since the 1970's, a treatment that has been called one of the largest man-maid manipulations of aquatic ecosystems ever.

The aim of this thesis is to investigate the influence of acidification and liming on deposition of metals to lake sediments, and to look at the fate of metals in sediments during a possible reacidification because of terminated liming.

Studies of both surface sediments and dated sediment profiles sampled from limed lakes included in the Swedish ISELAW programme (Integrated Studies of the Effects of Liming in Acidified Waters) and non-limed reference lakes indicated that liming causes increased sedimentation of many metals. Increased deposition to the sediments was found for Al, Cd, Co, Ni, Fe, Mn and Zn, probably as a direct result of the increased pH. Liming was also found to increase the deposition of As and Cr, but that was probably due to the secondary effect of association to Fe and Mn complexes. No influence of lime treatment on the deposition of Hg, Pb and V to lake sediments could be demonstrated. The studies also indicated that acidification can decrease the deposition of Cd, Fe, Mn and possibly also Co and Zn to the sediments.

The contribution from the used lime products to the metal load in sediments of lakes limed directly on the lake surface was also evaluated. The lime products were found to be an important source for Al, Cu and Ni and a relatively important source for Co, Cr, Hg and V, but do not seem to contribute much to the content of As, Cd, Pb or Zn in lake sediments.

An experimental study of reacidification was performed, where the overlying water columns of sediment cores sampled from one limed and one acidified lake were successively acidified to pH 4.2. The experiment showed that (re)mobilisation of metals, e.g Al, Cd, Mn and Zn, from sediments can occur during reacidification and for Al, the labile inorganic form was increasingly dominating as pH decreased. Sediments of lakes that have been limed directly on the lake surface are greater sources of metals compared to sediments of acidified lakes and reacidification of formerly lime treated lakes may contribute to increased concentrations of these metals in the lake water. Cu, Fe and Pb are less affected by pH changes and consequently the concentrations of these metals will probably not increase in lake water during reacidification.

Altogether, the thesis shows that lime treatment causes increased deposition of many metals to the lake sediments, whereas reacidification may lead to remobilisation of some metals from the sediments with increased lake water concentrations as a result.

# Content

## List of Papers

**I**

**Teresia Wällstedt** and **Hans Borg**
Metal burdens in surface sediments of limed and nonlimed lakes
*Science of the Total Environment 2005;336:135-154.*

**II**

**Teresia Wällstedt**, **Hans Borg**, **Markus Meili** and **Carl-Magnus Mörth**
Influence of liming on the temporal trends of metal deposition to lake sediments
*Manuscript*

**III**

**Teresia Wällstedt**
Contribution from the lime products to the metal burdens in sediments of limed lakes in Sweden
*Submitted to Water, Air, and Soil Pollution*

**IV**

**Teresia Wällstedt** and **Hans Borg**
Effects of experimental acidification on mobilisation of metals from sediments of limed and non-limed lakes
*Environmental Pollution 2003;126:381-391.*

My contribution to the papers are:
**Paper I.** Field sampling during 1999 (10 lakes). Some sample preparation. All ICP analyses. Some Hg analyses. All data processing. Main part in evaluation and writing.
**Paper II.** Field sampling and analyses like Paper I. All data processing. Main part in evaluation and writing.
**Paper III.** Planned the study. All data collection, data processing, evaluation and writing.
**Paper IV.** Took part in the planning of the experiment. Did the field sampling. Performed the experiment. Did the pH and redox measurements. Most of the data processing and evaluation. Main part in writing.

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## Background

### *Short acidification history*

Emissions of acidifying sulphur and nitrogen compounds, from e.g. combustion of fossil fuels, have increased severely during the last century, but already in the 1850's the term "acid rain" was coined by the chemist Angus Smith, referring to the effect that industrial emissions had on the precipitation in the British midlands (cited by Schindler, 1988). At that time, however no one could foresee what a widespread problem this would turn into. One of the first persons to discover and understand some of the causes and consequences of acidification was the Swedish scientist Svante Odén. A fisheries adviser named Ulf Lundin attracted his attention to problems with fish death in streams with low pH on the Swedish west coast. Odén then started to investigate monitoring data on precipitation. In 1967 Odén published an article in the Swedish newspaper Dagens Nyheter, where he described a rapid decrease in pH in precipitation that had occurred during the last years. He also suggested a number of problems that could result from this, e.g. acidification of many lakes and streams with fish death as a consequence, depletion of the base saturation of soils followed by decreases in the forest productivity as well as an increased corrosion of material (Bernes, 1991). One year later, he also published a scientific paper on the subject (Odén, 1968).

In a study of 400 lakes on the Swedish west coast sampled between 1970-1972, Almer et al., (1974) found that 50 % of the lakes had pH values lower than 6, and 22-36 % of the lakes had pH values lower than 5. Data from the Swedish national lake surveys show that the median alkalinity in non-limed lakes continued to decrease from 1972 to 1975, when the lowest alkalinity/highest acidity was recorded in many of the lakes. In some lakes, however, the alkalinity continued to decrease even further and the minimum alkalinity/maximum acidity did not occur until 1985 (Wilander and Lundin, 2000).

Acidification of lakes and streams have since then been reported from many parts of the world, mainly in Northern and Central Europe, Scandinavia, USA, Canada and Russia, but emissions and precipitation of acidifying substances seem to be an increasing problem also in e.g. Japan, China, Korea and India (e.g. Granat et al., 2001; Streets et al., 2001; Klimont et al., 2001).

### *Acid deposition and processes in the drainage area*

As a consequence of the industrial revolution, emissions of sulphur compounds from anthropogenic sources started to increase in the last decades of the 19th century. The increase accelerated after the Second World War because of the sharp rise in the combustion of oil, and the emissions reached its maximum values in the 1970's. As a result of international protocols with restrictions of the $SO_2$ emissions, the acid deposition has decreased in Europe and North America since the early 1970s (Stoddard et al., 2000; Westling and Lövblad, 2000).

Nitrogen emissions increased at a later stage than the sulphur emissions, primarily as a consequence of growth in road transport. In Sweden $NO_3$ deposition culminated around 1990, and has been relatively unchanged since, although a slight decrease can now be observed (Skjelkvåle et al., 2001b).

Soil processes in the catchment are very important in governing the chemistry of a lake. Deposition of sulphate is the primary cause of acidification in most areas, and most forested ecosystems subject to acid deposition contain and export sulphur well in excess of biotic requirements (Reuss and Johnson, 1986).

Sulphate is important for the leaching of base cations, the mobile anion theorem (Reuss and Johnson, 1986). Furthermore, sulphate concentrations in soil/surface water are also regulated by adsorpotion/desorption processes in the mineral soil, which then acts as a buffer. This leads to lag times between decreased deposition and observed sulphate concentration in runoff. The ability to adsorb $SO_4$ on mineral surfaces is pH dependent, the more acidified the soil becomes the more $SO_4$ can be adsorbed (Warfvinge et al., 2000). When deposition decreases, the soil solution concentration also decreases, which leads to desorption of $SO_4$ from the mineral surfaces. This process is fast and seems to be fully reversible (Warfvinge et al., 2000). During recovery, $SO_4$ will also desorb as a result of the increased pH.

When one equivalent of $SO_4$ is adsorbed on a mineral surface the acidity of the soil solution will decrease, since $SO_4$ adsorption includes adsorption of a cation, generally $H^+$ or 1/3 $Al^{3+}$, which can be thought of as if one equivalent of $H^+$ is consumed. When one equivalent of $SO_4$ is desorbed, one equivalent of $H^+$ will consequently be desorbed again. The process of adsorption thus buffers the soil solution against acidification while the desorption process buffers against recovery (Drever, 1988; Warfvinge et al., 2000).

Nitrogen is an essential nutrient to biota. As long as the ecosystem is N limited, roughly all nitrate and ammonium deposited will be taken up by growing organisms, but when N is deposited in excess of the biological requirements, it has an acidifying effect (Reuss and Johnson, 1986). Several studies indicate that N deposition in e.g. south western Sweden and parts of Canada is close to, or even exceeds, the critical threshold where N-based acidification may occur (Jeffries, 1995; Dise and Wright, 1995; Moldan and Wright, 1998; Magill et al., 2000; Westling and Lövblad, 2000).

One of the most important characteristics of soils in relation to acidification, is the cation exchange pool (Reuss and Johnson, 1986). When acidic substances are deposited on the soil, the $H^+$ added is consumed either by a cation-exchange reaction or by dissolution of an aluminium hydroxide to form $Al^{3+}$ ions that interact with the exchange pool. Initially, the input will be small compared to the amount of cations in the exchange pool and it will actually not make any difference if the cation added is $H^+$ or a base cation (BC). The exchange pool, not the input, will determine the cation ratios in the soil solution (Drever, 1988).

When acid rain continues, the exchange sites will be depleted in BC. There will be a change in solution composition from Ca/Mg dominance to Al dominance and a front will move down the soil column. Above the front the soil solution will be acidic and dominated largely by Al species, whereas below the front exchangeable cations will still be present and the soil solution will be near neutral and dominated by base cations. Considerable time (several decades or even centuries in some cases) could elapse before the input of acidity from acid deposition shows up as acidification of streams or lakes.

Once the soil is acidified, Al will still dominate soil solutions as long as the exchange complexes are dominated by Al species, regardless if the input is $H^+$ or base cations. This means that when acid deposition decreases, the soil solution will still be acidic until enough of the exchange sites are occupied by BC again. Base cations are brought back mainly by the process of mineral weathering, a process that in many parts of Scandinavia is very slow. This severely slows down the recovery from acidification. BC can also be transported to the soil by wet or dry deposition, especially in areas close to the sea (Lövblad et al., 2000).

Depletion of base cations, have been seen in many parts of Scandinavia (Falkengren-

Grerup et al., 1987; Kirchner and Lydersen, 1995). When soils are depleted in base cations any reduction in $SO_4$ and $NO_3$ in the runoff will be followed by a subsequent decrease in BC in the runoff. This prevents an increase in ANC (Acid Neutralising Capacity), and thus counteracts recovery of surface waters. Following the reduced deposition, decreased BC concentrations in lakes and streams have consequently been reported from Scandinavia and North America ( Kirchner and Lydersen, 1995; Mannio, 2001; Skjelkvåle et al., 2001a; Fölster and Wilander, 2002).

As discussed above, processes in the watershed are very important for the effects of acid deposition on surface water chemistry, but also in-lake processes must be considered. In-lake alkalinity generation also contributes to the buffering of acidic substances in the lakes. The contribution of alkalinity from in-lake generation in relation to the alkalinity generation in the catchment can vary substantially between lakes depending on e.g. properties in the watershed and water renewal time. Base cation release from lake sediments and retention of sulphate and nitrate seem to be the most important in-lake alkalinity generating processes (Schindler, 1986; Shaffer et al., 1988; Schindler, 1989).

### *Metal speciation in relation to acidification and liming*

In natural waters trace metals can be present in a number of forms including (a) free metal ions, (b) inorganic complexes, (c) organic complexes (with humic and fulvic acids) or (d) the metals can be associated with colloidal and particulate material as clay mineral, oxides or biogenic material as e.g. algae (Borg, 1995). The speciation of metals is important for the bioavailability and toxicity and the free metal ions are regarded most bioavailable and toxic.

For many metals, decreased pH results in a decreased sorption of metals to particles and decreased complexation to organic material, which leads to an increased portion of the free metal fraction. The dialyzable fraction, including free ionic species, inorganic complexes and perhaps low molecular weight organic complexes of Al, Cd, Mn and Zn has been found to increase with decreasing pH (Borg et al., 2001). For Al, Fe, Mn and Pb complexation with organic substances is important for the regulation and the dialyzable fraction of Pb and Fe has been found to be small (Borg and Andersson, 1984; Borg et al., 2001). The association with colloidal or particulate matter is also an important mechanism with regards to acidification and liming, as will be discussed further down.

### *Transport of metals to lake water*

The supply of metals to surface waters in undisturbed natural systems depend on physical and chemical weathering of rocks and soil in the surrounding catchment. Airborne supply associated with natural geochemical cycles is also important for some elements, e.g. Hg.

Long-range transport of pollutants may influence the concentration of metals in fresh waters in at least three different ways: (1) Enhanced weathering due to acidification, (2) direct atmospheric supply of metals and/or (3) release of metals previously deposited from the atmosphere and temporarily fixed in soils and sediments (Steinnes, 1990). Acidification of soils in the drainage area is of course of great importance for the conditions in a lake. For elements that are major constituents of crustal rocks, e.g. Al, Fe and Mn, enhanced weathering due to acidification is the most important source (Dickson, 1978; Steinnes, 1990).

Atmospheric pollution is often thought of as a problem that started with the industrial revolution, but clear signals of airborne lead pollution from the Greek and Roman cultures 2000 years ago have been found in lake sediments and peat bogs all over Sweden (Brännvall, 2000). Elements characterised as long-range airborne pollutants are e.g. As, Cd, Co, Cr, Cu, Hg, Ni, Sb, Se, Pb, V and Zn (Pacyna et al., 1984; Steinnes, 1990; Berg et al., 1995; Rognerud and Fjeld, 2001).

The supply of acidifying sulphur and nitrogen compounds as well as anthropogenic airborne metals is generally higher in the southern parts of Sweden and Norway compared to the more northerly parts of Scandinavia (Bernes, 1991; Kindbom et al., 2001). The south-north metal gradient is also found in found in surveys of forest mor layer and lake sediments (Johansson et al., 2001; Lithner and Holm, 2003).

Since there is often a close relationship between atmospheric deposition of acids and metals, it can be difficult to know which process that is directly responsible for the elevated concentrations often found in acidified lake water. Lydersen and Löfgren (2002) claim that the atmospheric input is likely to be the causal factor for the relationship between elevated concentrations of Cd, Pb and Zn with pH in acidified waters in Sweden and Norway. Veselý and Majer (1996), on the other hand, found that both pH of the water and atmospheric metal deposition were important parameters regulating Cd and Zn concentrations in lakes in the Czech Republic, while for As the deposition of the element itself is probably more important.

Metals in atmospheric pollution are also deposited in the drainage areas. Acidification of the surrounding soils will contribute to increased transport of many metals to the lakes, and net losses of e.g. Al, Cd, Cr, Ni and Zn have been demonstrated in forest catchments in Sweden (Bergkvist, 1987; Borg and Johansson, 1989). In a literature review, Nelson and Campbell (1991) conclude that inputs of Al and Cd to lakes increase in response to acidification and that elevated aqueous Cd concentrations are more likely due to watershed acidification than to atmospheric deposition of Cd, whereas Pb and Hg in the watershed are relatively unaffected by acidification.

During the last decades the atmospheric deposition of metals as well as the acid deposition has declined. The deposition has decreased markedly in Sweden from 1968/71 to 1995 and the south-north gradient over the country has been declining since the 1970's (Rühling and Tyler, 2001; Kindbom et al., 2001).

### *Liming*

Lime treatment has been called one of the largest man-maid manipulation of aquatic ecosystems ever. Since liming counteracts acidification it has been extensively used in Sweden, first in a small scale since 1976 and since 1982 in a larger scale (Swedish Environmental Protection Agency, 1981). In Sweden about 7500 lakes have been limed at least once and about 6500 lakes are continuously being treated. About 11000 to 12000 km's of running water have also been limed. This operation has included almost 50% of the acidified lakes but only a small part of the acidified streams (Dickson W. and Brodin, 1995; Swedish Environmental Protection Agency, 1997).

Lime treatment has been carried out using a couple of different methods. The most widely used method is liming directly on the lake surface. Other techniques that have often been used are liming in upstream lakes or in running waters by lime dosers or liming of wetlands in the drainage area. Small scale experimental lime treatment of soils in the drainage area has also been performed (Larsson and Westling, 1997; Akselsson et al., 2000).

### ***Transport of metals to lake sediments***

When run-off water from acidic catchments, with elevated metal concentrations reaches a limed lake or when an acidified lake is being limed, the higher pH will favour an increased precipitation of metals that are sensitive to pH changes. The increased pH value combined with increased concentrations of suspended particles also promotes scavenging of trace metals through particle - dissolved trace metal interactions.

The liming agents also commonly include a few percents of clay minerals. High concentrations of Fe associated with these clay mineral particles suggest that the surface properties of these particles are governed by coatings of amorphous Fe(III)-hydroxides precipitated during dissolution of the carbonate particles. Adsorption by Fe(III)-hydroxides has long been considered an important mechanism for controlling trace metal concentrations in natural waters and trace metals may also be incorporated by coprecipitation with the Fe(III)-hydroxides (Egeberg and Håkedal, 1998).

Also Al and Mn oxides/hydroxides play an important role in the regulation of trace metal concentrations in lake water and the transport to the sediments. When ionic Al species supplied by acidic tributaries reach a lake with higher pH, they are hydrolysed and form Al oxyhydroxides. These fresh colloidal Al oxyhydroxide flocs have large surface areas (Kopacek et al., 2001), which means that they have a large adsorbing ability. Mn oxides are also likely to be formed after liming, since Mn speciation is highly pH dependent (LaZerte and Burling, 1990).

Significantly elevated concentrations of As, Cd, Cu, Hg, Ni, Pb and Zn, most likely caused by anthropogenic atmospheric deposition, have been found in surface sediments in Swedish and Norwegian lakes. For the majority of these elements the highest degree of impact is observed in the southern part of the countries with a pronounced decrease with latitude (Rognerud and Fjeld, 2001; Johansson et al., 2001). In the Norwegian study, a statistical analysis found a positive borderline effect of surface liming on the differences between Cd concentrations of surface and reference sediments (Rognerud and Fjeld, 2001) and increased concentrations of Al, Cd, Cu, Fe, Mn, Ni, Pb and Zn sediments after liming have also been found in other studies (Dillon and Smith, 1984; Andersson and Borg, 1988; Driscoll et al., 1989; Egeberg and Håkedal, 1998; Andersen and Pempkowiak, 1999; Rognerud and Fjeld, 2001).

According to the above discussion, metals can be precipitated to the sediment as a direct consequence of the increased pH after liming. They can also be transported to the sediment as a result of coprecipitation with or adsorption to lime particles or oxides/hydroxides of e.g. Al, Fe and Mn that are formed after liming. An additional important process is precipitation with organic matter.

### ***Reacidification***

What will happen if liming is terminated? Is there a risk of reacidification, and what effects can be expected in case of reacidification?

It is difficult to predict the risk of reacidification in view of the decreased sulphur deposition over the last decades, but a recent estimation, considering the decreased S deposition, indicates that 22% of the limed lakes in Sweden may reach pH 5.4 (equals zero alkalinity) or lower if liming ceases (Andersson et al., 2002).

There has been concern about what could happen with the metals in the sediments during a possible reacidification, but few studies of the effects of reacidification have been made. In a study by Dickson et al. (1995), reacidification as a result of intentionally terminated liming from 1986-1989 of Lake Rävekärrs Långevatten in the south west of Sweden lead to a severe pH decrease to values below 5. In the meantime, concentrations of Al, Cd and Zn increased substantially in the water column. In an earlier reacidification study in Lake Lysevatten, also in the south west of Sweden, pH decreased to around or below 5 during 1983, 9 years after the liming in 1974 (Andersson et al., 2002).

In a more recent reacidification study where the liming was intentionally terminated in Lake Trehörningen south east of Stockholm, the terminated liming, after a final treatment in 1991, resulted in a decrease in annual mean pH from 7.1 (similar to a limed reference lake) to 6.1 (similar to a non-limed reference lake in the same area) in 1999. From 1997-1999 pH during the spring flood dropped well below 5.5 and in 1998 and 1999 labile inorganic Al reached peak values over 100 µg/l (Edberg et al., 2001). Spring flood pH below 5.5 and labile inorganic Al over 100 µg/l were also measured in this lake during 2000 to 2004 (F. Edberg, personal communication). The labile inorganic aluminium concentrations can be compared to the lowest biological risk levels of 25-75 µg/l suggested by Rosseland et al. (1990).

During experimental acidification of Little Rock Lake (Wisconsin, USA), Brezonik et al. (2003) found elevated concentrations in the lake water of dissolved Mn, Fe, Al, Cd, Zn and Pb. They ascribe the increased concentrations of dissolved Cd and Pb to reduced scavenging by settling particles at lower pH, whereas the increased Zn concentration was ascribed to a combination of reduced settling and desorption from the sediments. For dissolved Al, the concentration in the reference basin was governed by equilibrium with gibbsite, but the acidified basin was undersaturated relative to gibbsite, probably as a result of pH disequilibrium between the water column and the sediments.

In a literature study, Lydersen and Löfgren (2002) claim that it is unlikely that enhanced remobilisation of metals from the catchment or the sediment will occur when formerly limed waters reacidify. Rather, they expect the concentrations in surface waters to be lower than before the liming started because of the reduced atmospheric input of both strong acids and metals during the last decades.

Laboratory experiments have indicated that metals could be remobilised from the sediments during reacidification (Arafat and Nriagu, 1986; Gambrell et al., 1991; Matschullat and Wyrobek, 1993; Fimreite et al., 1996), whereas Nelson and Campbell (1991) in their literature review conclude that remobilisation from lake sediments seem improbable due to the steep pH gradient at the sediment/water interface.

## Summary and discussion of the Papers

### *Study area and sampling, Papers I-III*

Lakes from the Swedish national ISELAW-programme (Integrated Studies of the Effects of

Liming in Acidified Waters) were sampled. All lakes that are used in the studies are located in the southern half of Sweden (Figure 1) and they are divided into 4 groups:

1) Mainly surface limed lakes
2) Mainly upstream or wetland limed lakes
3) "Near neutral" reference lakes ($pH \geq 6.0$)
4) Severely acidified reference lakes ($pH \leq 5.5$)

In Paper II we wanted to compare the metal deposition to lake sediments before and after the limed period in the sediment cores. Therefore, possible changes in metal deposition had to be detected. This means that the mixing of the sediment because of resuspension or bioturbation should not be too large, since that would prevent detection of trends in metal deposition to the sediment, whether caused by acidification, liming or changes in atmospheric deposition. The sediment profiles should also be subject to reliable dating so that the layers representing different time periods could be separated. These criteria left 11 suitable lakes for the study (Figure 1). Among these lakes, only one upstream limed lake was left. Therefore, all limed lakes were combined into one group.

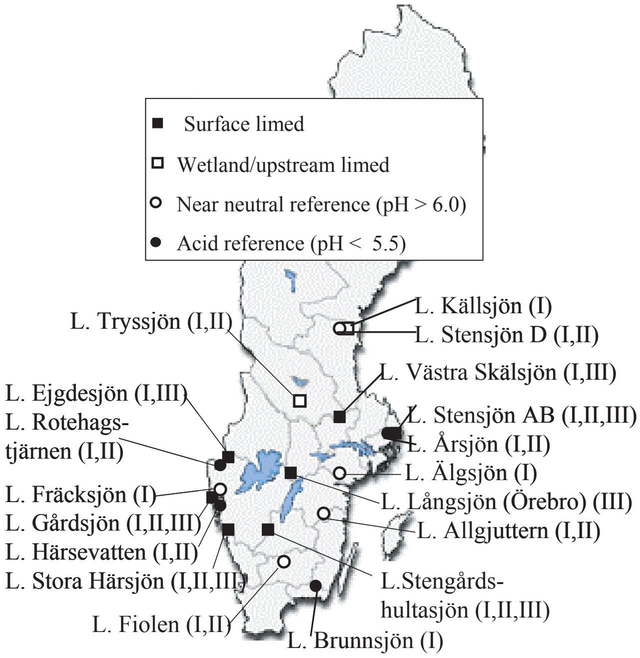

**Figure 1.** *Sampled lakes in Sweden. The inclusion of the respective lakes in Papers I, II and III are indicated by the roman numerals.*

Generally 15-20 surface sediment samples were collected from each lake. The number of samples collected from each morphometric depth interval (0-2 m, 2-4 m, etc.) was in approximate proportion to the relative contribution of that depth zone to the whole lake area (Paper I). At least one core from the deepest part of each lake was also sampled (Paper II). The cores were sectioned in the field.

Total $HNO_3$-digestable amounts of Al, As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, V, Zn, Ca and also P were determined using Inductively Coupled Plasma (ICP) Atomic Emission Spectrometry (Varian Vista-PRO Ax, which is an ICP equipped with a CCD camera, often called ICP-OES). Hg was determined by Flow Injection Analysis Cold vapour AAS (Perkin Elmer 305 B) with $SnCl_2 * 2H_20$ as a reductant.

### *Summary of Paper I*

The aim of this study was to compare metal burdens in surface sediments of limed and nonlimed lakes. Our hypothesis was that liming increases the metal burdens in the sediments, whereas acidification leads to decreased burdens, so that areal metal burdens would generally be highest in the surface sediments of lakes limed directly on the lake surface, lowest in non-limed acidified lakes and intermediate in non-acidified reference lakes and upstream/wetland limed lakes. This was based on the assumption that liming directly on the lake surface will precipitate the metals in the lake, whereas upstream liming or liming on wetlands should precipitate some metals before they reach the lake, and hence give lower burdens in the sediments. Near neutral reference lakes are likely to receive less metals from the drainage area compared to surface limed lakes and acidified reference lakes, since the soils surrounding these lakes are probably less acidified and thus release less metals. Severely acidified reference lakes should have lower metal burdens in the sediments, because of the higher metal retention time in the more acidic water.

Powell et al. (2000) suggest that whole lake burdens of sediment components should be evaluated based on volumetric concentrations so as not to underestimate the potential reservoir of contaminants in the shallow areas of a lake. We have not found any data in the literature that compares metal burdens or volumetric concentrations in sediments between limed and non-limed lakes.

A statistical comparison of areal metal burdens (g m$^{-2}$, 2 cm) in the surface sediments, assumed to represent the limed period, of four groups of lakes, (1) Surface limed lakes, (2) Upstream/wetland limed lakes, (3) Near neutral reference lakes and, (4) Acidified reference lakes, was carried out (Table 1).

**Table 1.** *Differences in areal burdens of metals and P, Dry Substance (DS)% and Loss on Ignition (LOI)% between groups. ANOVA,* ***$p<0.05$ (bold)*** *and $p<0.1$. Significance of the differences found was calculated with Post Hoc Tests, Tukeys test (equal variances) or Tamhanes test (unequal variances). Additional significant differences found using T-test ($p<0.05$) are also shown within parentheses.*

| | **S L**[a] | **U/W L**[a] | **N N R**[a] | **A R**[a] |
|---|---|---|---|---|
| **S L >** | ---- | Al, **As, Cd,** Ni, **P, (Zn)** | **As**, (**Cd**, **Pb**) | **As, Cd,** Co, **Zn,** (Al, Fe, Mn, Ni, **P**, **Pb**, DS) |
| **U/W L >** | | ---- | | |
| **N N R >** | | | ---- | (Cd) |
| **A R >** | **LOI** | | **(LOI)** | ---- |

[a] **S L** = Surface Limed, **U/W L** = Upstream/Wetland Limed, **N N R** = Near Neutral Reference, **A R** = Acidified Reference

The statistical analysis revealed that the surface limed group had significantly higher areal burdens of As, Cd, Co and Zn in the sediment compared to the acidified reference group. The surface limed group also had significantly higher burdens of As compared to the near neutral reference group and the results indicated that surface liming can increase the areal burdens of Cd and Pb, probably also of As, Ca and Mn and possibly Co and Zn (Table 1). The results of the investigation also indicated that acidification can decrease the areal burdens of Cd, Fe, Mn and possibly also Co, P and Zn in the sediments.

### *Summary of Paper II*

The aim of this study was to investigate more thoroughly if the deposition of metals to lake sediments is increased by lime treatment. Our hypothesis was that liming causes increased sedimentation of elements for which the mobility is influenced by pH e.g. Al, Cd, Zn, Co and Ni, whereas elements that are less influenced by pH fluctuations e.g. Cu, Hg and Pb are much less affected by lime treatment.

The sediment profiles were dated with $^{210}$Pb using the CRS (Constant Rate of Supply) and CIC (Constant Initial Concentration) methods, but also using $^{137}$Cs and total Pb concentration peaks, assumed to represent 1986 and 1970 respectively, as chronostratigraphic markers.

In order to separate the effects of lime treatment from those of temporal trends in air-borne metal deposition, metal concentrations were normalised using Cu, an evaluation found to emphasise the effects of liming on the sedimentation of metals (Figures 2 and 3). The metal/Cu ratios before and after liming, or for the corresponding time intervals for non-limed lakes, were compared by calculating the enrichment factors between the time periods before and after liming: $[(\mathrm{Me/Cu})_{\mathrm{after}}/(\mathrm{Me/Cu})_{\mathrm{before}}]$, in the following referred to as Cu-Normalised Enrichment Factors (Cu-NEF).

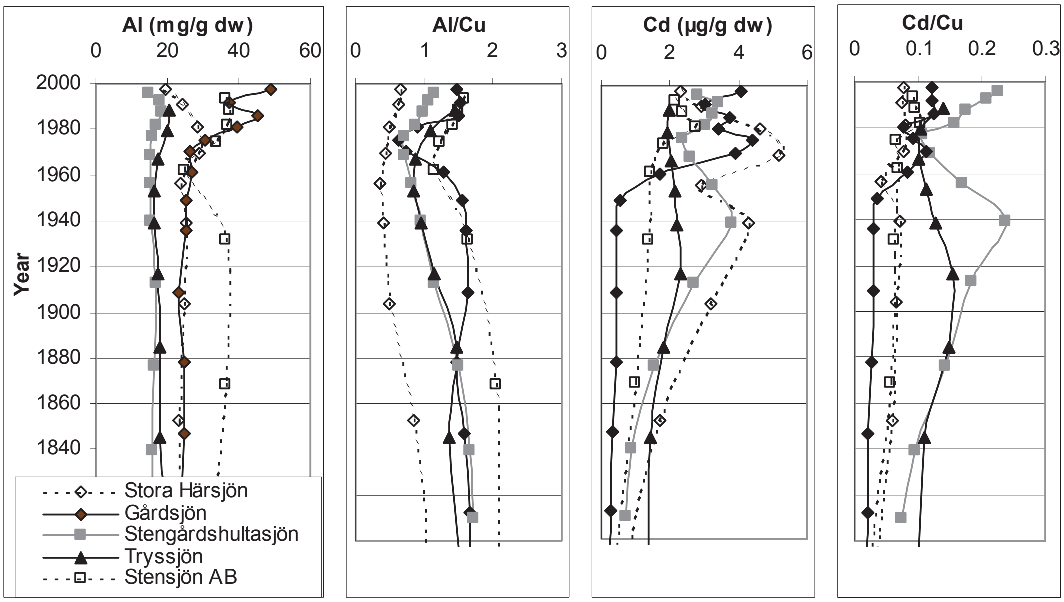

Figure 2 a-d. *Concentrations and Metal/Cu ratios versus sediment age for Al and Cd in limed lakes.*

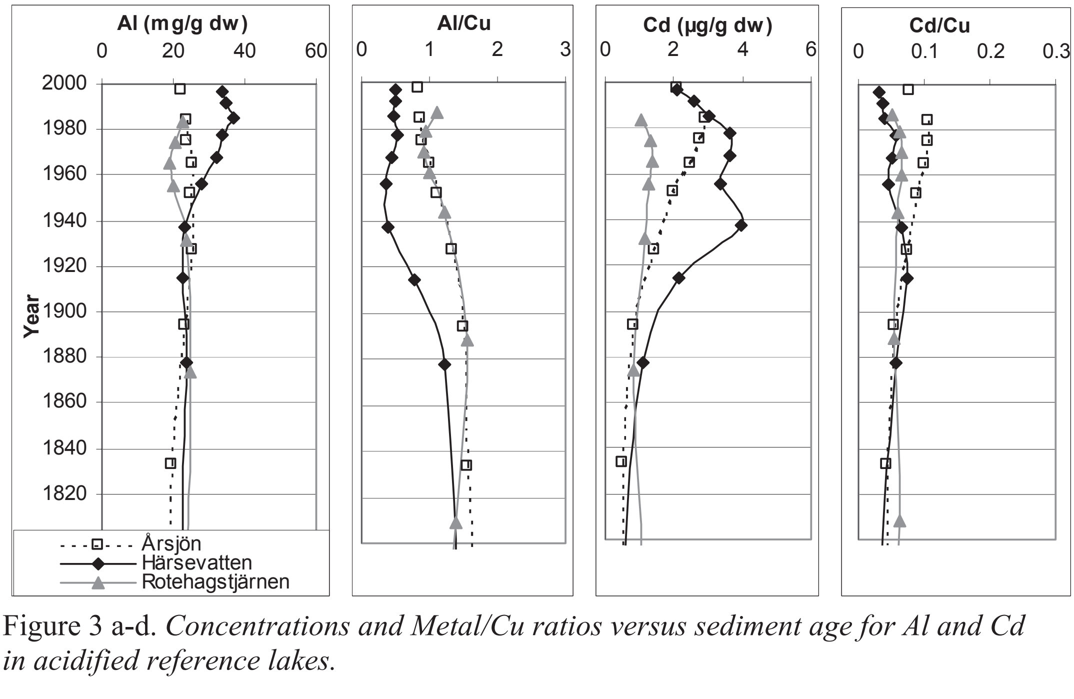

Figure 3 a-d. *Concentrations and Metal/Cu ratios versus sediment age for Al and Cd in acidified reference lakes.*

Differences between the three lake groups were analysed with One-Way ANOVA and subsequent Post Hoc tests (Tukeys test and Tamhane's T2 test for equal and non-equal variances respectively). A Principal Component Analysis (PCA) was also performed on the Cu-NEF with inclusion of some other variables, such as LOI (content of organic material), geographical location (as x- and y-coordinates) and sulphate deposition.

Liming was found to have a direct effect on the sedimentation of Al, Cd, Co, Fe, Mn, Ni and Zn to lake sediments, resulting in higher deposition to the sediments of limed lakes compared to nonlimed reference lakes. Liming also had a secondary effect on the deposition of As, Cr and Co, which was governed by the increased deposition of Al, Mn and Fe. Even though no significant difference was found in the statistical analysis, liming also clearly increases the deposition of Ca to the sediments, whereas no effect of lime treatment on the deposition of Hg, P, Pb and V to the sediments could be demonstrated.

## *Summary of Paper III*

During the comparison of total metal burdens in the sediments of limed and non-limed lakes (Paper I), we found that there was a very limited knowledge about how large quantities of different metals that are added directly to the lakes via the used lime products. Therefore, a study was initiated, with the aim to quantify the amounts of different metals added by the lime treatment to the lakes investigated in Paper I.

Data about lime products were collected through personal communication with the Swedish County Administrations, municipalities, liming companies and private persons that have been organising lime treatments throughout the years. It was not possible to obtain data of the metal concentrations in the lime products for all lime treatments. Therefore, mean concentrations with standard deviations as well as minimum and maximum concentrations for each metal in 'average lime' were estimated, and the amount of each metal that had been applied directly on the lake surface was calculated (Figure 4). These amounts were then compared with the total metal burdens in the surface sediments of limed lakes, calculated in Paper I.

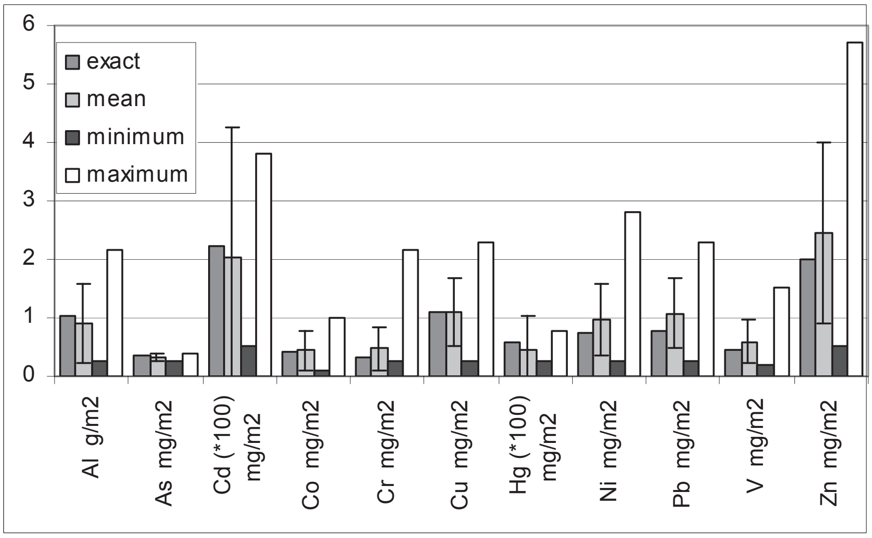

**Figure 4.** *Amounts of different metals added with the lime to the sediments of Lake Långsjön in Örebro County. Exact amounts calculated from addition of lime from known sources, mean values with standard deviations as well as min and max values calculated from 'average lime'. (Note that the amounts of Cd and Hg are multiplied with 100).*

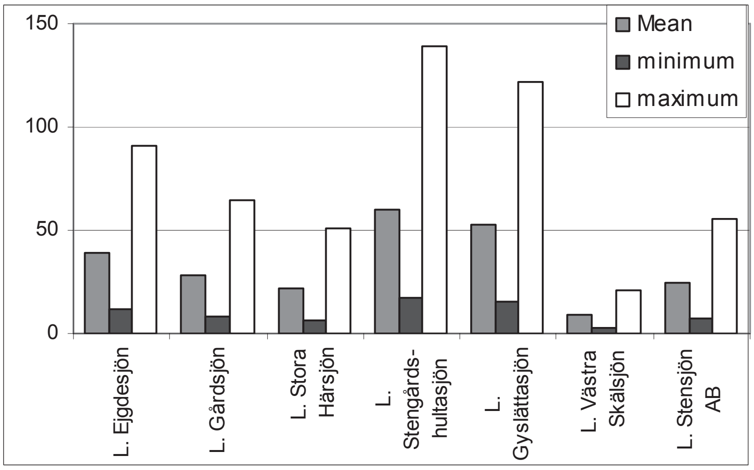

**Figure 5.** *Mean, minimum and maximum contribution from lime products (calculated from 'average lime'), in % of the total Al burdens in 2 cm surface sediments.*

The calculated contribution from the lime products to the total metal burdens suggest that the lime is an important source for Al, Cu and Ni (exemplified with Al, Figure 5). For these three metals, about 30-50 % of the total content in the surface sediments could originate from the used lime products. The lime seems to be a relatively important source also for Co, Cr, Hg and V, where about 10-20 % of the total content in the surface sediments could originate from the lime products. The lime products do not seem to be very important for the burdens of As, Cd, Pb and Zn in lake sediments. For these metals, the lime products seem to have contributed only about 5-10 % of the total burdens in surface sediments.

### *Summary of Paper IV*

The objective of this study was to assess the acidification effect on the mobilisation of metals from sediments of limed and non-limed lakes. Most published experiments have been performed on homogenised sediments (Arafat and Nriagu, 1986; Matschullat and Wyrobek, 1993; Fimreite et al., 1996). Homogenisation might, however, influence the mobility, since mixing of the sediments probably has a substantial effect on the redox potential and also changes the particle surface area that comes into contact with the (re)acidified water. Our hypothesis was that remobilisation of metals from the surface sediments can occur also under more undisturbed natural conditions, by diffusion, as a result of a lowered pH in the overlying water during reacidification.

In order to study the influence of pH on the mobilisation of metals from lake sediments, intact sediment cores with overlying water were sampled from one acidified lake, Lake Årsjön (Figure 1) and one lime treated lake, Lake Långsjön, situated in the same area. The overlying water of two cores from each lake was successively acidified to pH 4.2 over a period of 3 months, while two cores from each lake were kept as references.

In the reference columns the concentrations of all studied metals decreased or remained unchanged, except for Cd in the Lake Långsjön columns, which increased slightly. Cu and Fe concentrations were unchanged or decreased also in the acidified columns. Concentrations of Pb were also unchanged or decreased during the first 9 weeks, but increased significantly in the acidified columns from Lake Långsjön when pH had decreased below 5. Al and Zn concentrations increased in the acidified columns from both Lake Årsjön and Lake Långsjön whereas Cd and Mn concentrations increased significantly only in the acidified columns from the limed Lake Långsjön.

For Al, the labile inorganic form was increasingly dominant as pH decreased. At the end of the experiment $Al_i$ represented about 70% of the total Al concentration in the acidified samples. In the acid treated samples from the limed lake, the initial concentrations of Al, Cd, Mn, Pb and Zn in the overlying water were generally lower and the final concentrations were higher than in the acid treated samples from the acidified lake.

Log concentrations of Al, Cd, Mn and Zn were plotted against pH in the overlying water of the acidified cores from Lake Långsjön and Lake Årsjön (exemplified with Al and Cd, Figure 6). Both log Zn and log Cd could be fitted to a linear curve, which indicates an exponential release from the sediments. $Al_{tot}$, on the other hand, showed a larger increase over the last four weeks. It can be concluded that during the experimental period of 3 months, the concentrations of these metals did not reach a steady state and the rate of mobilisation did not decrease. For Cd and Zn, the concentrations in the water were considerably higher in the Lake Långsjön columns compared to the Lake Årsjön columns at the same pH and this was also true for $Al_{tot}$ concentrations when pH was less than about 5.

According to the redox potential, the sediments were oxidised to a depth of about two centimetres by the end of the experiment. A comparison of sediment pH in acidified and reference cores indicated that the uppermost 2 to 3 cms were affected by the acidification.

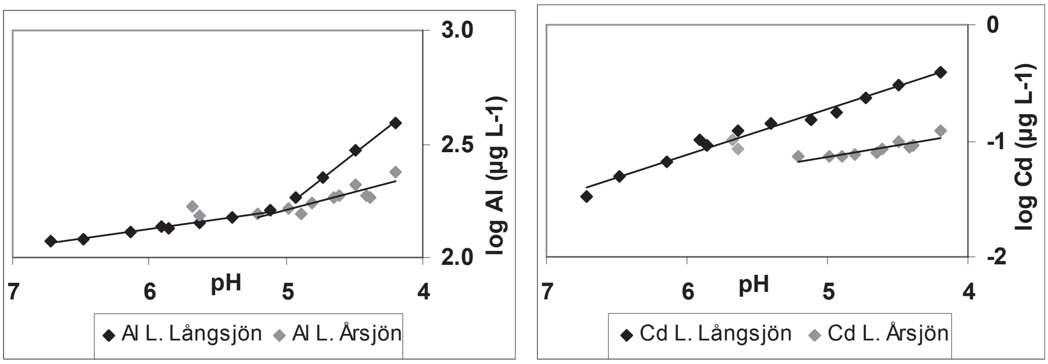

Figure 6A-B. *Logarithms of the mean metal concentrations versus pH in the overlying water of the two acidified cores from Lake Långsjön and Lake Årsjön.*

Altogether, the experiment showed that mobilisation of metals from sediments can occur and the results indicated that mobilisation could contribute to increased concentrations of metals in lake water during reacidification of formerly lime treated lakes.

## *Discussion*

Based on the results in Paper I and II it seems evident that liming increases the deposition of As, Ca, Cd, Co, Mn and Zn to lake sediments.

For Cd, Co, Mn and Zn, increased sedimentation as a result of liming was expected. Cd, Zn and Mn have often been studied with respect to pH changes as a result of acidification and liming and are well known to be highly controlled by pH. Elevated concentrations of both Cd, Mn and Zn in sediments after liming have been found in several investigations (Dillon and Smith, 1984; Andersson and Borg, 1988; Driscoll et al., 1989; LaZerte and Burling, 1990; Egeberg and Håkedal, 1998; Andersen and Pempkowiak, 1999; Rognerud and Fjeld, 2001). Co has not often been studied in view of acidification and liming, but Granéli and Haraldsson (1993) found a clear inverse relationship between pH and Co in river water. In a whole-lake experiment with radionuclides (Schindler et al., 1980), the proportion of Co in particulate phase decreased and the dissolved phase increased in acidic conditions. Co is also influenced by the diagenetic cycling of Fe and Mn (Belzile et al., 2004), and the elevated concentrations of Co found in limed lakes compared to nonlimed reference lakes in Papers I and II are thus probably due to a combination of the pH dependence of Co and a covariation with Mn and Fe.

Sediments have been found to be a major sink for As in lakes, where As is scavenged from the water column as a result of coprecipitation with hydrous oxides of Al, Fe and Mn. A clear similarity between sediment profiles of As and Fe was found in a study by Belzile et al. (2004). The binding of As to these oxides is also more efficient at higher pH, and the increased deposition of As to the sediments of limed lakes is thus probably due to the increased sedimentation of Al, Mn and Fe combined with the more efficient binding of As to these components in a limed lake with higher pH.

In Paper II, we used Cu-Normalised Enrichment Factors (Cu-NEF) in order to get a more sensitive measure of the influence of pH changes as a result of liming on the metal deposition to the sediments. The idea of normalisation with respect to Cu was to separate the effects of lime treatment from the effects of changes in atmospheric deposition, and thereby emphasise the liming effects.

Like most other airborne metal pollutants, the main anthropogenic emission sources of Cu are metal industry and combustion of fuels (Pacyna et al., 1984). It is thus reasonable to assume that Cu deposition has followed the general trend for metal deposition before 1970. The atmospheric deposition of Cu has also generally followed the same decreasing trend after around 1970 as other heavy metals. The decrease in atmospheric deposition of Cu has been similar to the decrease for Zn, but somewhat smaller compared to e.g. Pb, Cd, Ni and V (Rühling and Tyler, 2001; Kindbom et al., 2001). This means that the effect of changed metal deposition can not be completely compensated for, but probably substantially reduced, by normalisation with respect to Cu.

Furthermore, the mobility of Cu is not very influenced by pH changes in the pH-range (around 4,5-7,5) prevailing in the studied lakes. A number of studies have shown that Cu is much less affected by pH changes due to acidification and liming compared to e.g. Al, Cd, Mn and Zn (Borg and Andersson, 1984; Borg, 1987; Borg et al., 1989; Veselý and Majer, 1996; Hindar et al., 2003; Brezonik et al., 2003; Paper IV).

Consequently, we believe that normalisation with Cu can be used to highlight the effects of liming.

In Paper II but not in Paper I we found significant differences between the group of limed lakes compared to non-limed reference lakes for Al, Fe and Ni. In Paper I, differences for these elements can be found if looking at the results of the T-test (Table 1), which was regarded not truly significant. The differing results of the two investigations are probably due to the more sensitive method using Cu-NEF, used in Paper II.

Nickel is known to be influenced by pH changes, with higher mobility at lower water pH (Borg, 1995) and Andersen and Pempkowiak (1999) found that Ni concentrations in the sediment increased more than 30 times above the background concentration after the liming of Lake Terjevann.

Also Al has a higher mobility at lower pH. When ionic Al species, supplied by acidic tributaries, reach a lake with higher pH they are hydrolysed and form Al oxyhydroxides (Kopacek et al., 2001). Enrichment of Al in sediments as a result of mobilisation in the catchment and subsequent precipitation in the limed lake with higher pH is therefore probable (Norton and Kahl, 1991), although not that easy to detect because of the high natural background. Fe is also mainly transported to the lake water via mobilisation in the catchment. The increased pH when the acidic drainage water reaches a limed lake probably facilitates a higher degree of oxidation and complex formation. Subsequent precipitation of these complexes is probably enhanced through sorption onto particles introduced with the lime (Andersen and Pempkowiak, 1999) and increased accumulation of Fe in sediments after liming have been reported previously (Dillon and Smith, 1984; Driscoll et al., 1989; Andersen and Pempkowiak, 1999).

In Paper I we found higher burdens of Pb in the surface limed lakes compared to the non-limed reference lakes, but in Paper II no differences between the groups were found for Pb. The difference documented in Paper I is probably due to the general deposition pattern with higher deposition of both acidifying substances and metals over the southern part of Sweden, whereas in Paper II this effect was filtered out when normalising with Cu.

In neither of Papers I or II, could any difference in metal deposition to the sediments of limed lakes compared to non-limed reference lakes be demonstrated for Hg, P or V

In Paper I, we could also see different influence of the lime treatment due to different liming methods, reflected as higher areal burdens of e.g. Al, As, Cd and Ni in the sediments of lakes limed directly on the lake surface compared to lakes that have been limed in upstream lakes or watercourses or on wetlands in the drainage area (Table 1). In fact, the group of upstream/wetland limed lakes in this study did not have significantly higher burdens of any measured metal in the surface sediments compared to the reference lakes, whereas the differences between the surface limed group and the reference groups were substantial. It should be noted, however, that the group of upstream/wetland limed lakes contained only two lakes, hence statistical significances are difficult to obtain. Still, significant differences were found between the group of surface limed lakes compared to the group of upstream/wetland limed lakes. The difference between the two groups of limed lakes could be due to at least four different reasons; 1) Liming of upstream lakes and watercourses or wetlands in the drainage area probably induces precipitation of metals before the water reaches the investigated lake, hence less metals are transported from the drainage area to upstream/wetland limed lakes compared to surface limed lakes. 2) The upstream/wetland limed lakes in the study are situated further to the north compared to the surface limed lakes and thus receive less metals from airborne deposition, as a result of the general deposition pattern over Sweden. 3) The used lime products contain clay minerals and other particulate matter, which enhance adsorption and coprecipitation of metals in the water column. 4) The lime products used contain various amounts of metals that could also contribute to the metal burdens in sediments of limed lakes and especially in lakes limed directly on the lake surface.

During the evaluation of Paper I we found, however, that the knowledge about the contribution from the lime products to the metal load in limed lake sediments was very limited. Therefore a study of the metal content in lime products was initiated (Paper III). Since it was not possible to obtain data of the metal concentrations in all lime products used ever since the liming started, rough estimates had to be used. Mean concentrations with standard deviations as well as minimum and maximum concentrations for each metal in ‘average lime’ were calculated. The mean values and standard deviations were calculated by taking simple mean values of every known concentration data of each metal in lime products. This means that lime from sources where I have been provided with data on the metal concentrations from several liming occasions have been weighted higher than lime from sources where I have data from only one or a few occasions. It is likely that lime from the higher weighted sources are used more often and therefore should be more important when calculating the mean value, but since there is no information on how often different lime products are used it isn’t possible to calculate any exact mean value or to know how correct this weighting really is. However, for Lake Långsjön in Örebro County, data on the metal concentrations in all lime products ever used were provided, and exact amounts of metals added to the lake could be calculated. The calculated exact value for each metal is relatively similar to the mean value calculated from ‘average lime’, and it is also within the range of the standard deviations (Figure 4), which indicates that the calculated mean values are reasonable estimates for the metal amounts added with the lime products.

The metal amounts added with the lime products were then compared with the total metal burdens in the surface sediments, calculated in Paper I. This comparison suggests that the lime is an important source for Al, Cu and Ni. For these three metals, the mean values based on ‘average lime’ indicate that about 30-50 % of the total content in the surface sediments could originate from the used lime products. The lime seems to be a relatively important source also for Co, Cr, Hg and V, for which about 10-20 % of the total content in the surface sediments could originate from the lime products. The metal content in the lime products does not seem to be very important for the burdens of As, Cd, Pb and Zn in lake sediments. For these metals, the lime products used seem to have contributed only about 5-10 % of the total burdens in surface sediments.

These results indicate that the difference in Al and Ni burdens between surface limed lakes and non-limed reference lakes shown in Paper I could, to some extent, be caused by the contribution from the lime products. The lime products used could also have contributed to the increased Co burdens in sediments of surface limed lakes, but did probably not cause the elevated burdens of Cd, Pb, As or Zn that were found in Paper I.

In Papers I-III, we have shown that lime treatment increases the deposition of many metals to the lake sediments. As mentioned before, there has been concern about what could happen if the liming is terminated. Is there a risk of reacidification, and in that case, what will be the effect on the metals previously deposited to the sediments?

In the experiment presented in Paper IV, pH 4.2 was chosen as the end point, representing severely acidified lakes. In view of the decreased sulphur deposition over the last decades, it is unlikely that pH of Swedish lakes today would generally reach 4.2 during a reacidification of previously limed lakes, but even though the acidifying deposition has decreased, it still exceeds critical loads in large areas of southern Sweden (Warfvinge and Sverdrup, 1995; Sverdrup et al., 2002; Rapp et al., 2002). A natural lake will receive acidic water also from the drainage area, especially during periods of heavy rain or snowmelt, and it is quite clear that the run-off from many catchments is still acidic. Exchangeable Mg has continued to decrease and exchangeable Al has increased in the B horizon of soils throughout Sweden over the last decade, indicating that soil acidification has penetrated to even greater depths during this period (Wilander and Lundin, 2000). Continued soil acidification during the last decade has also been found in Norway (Kvaalen et al., 2002; Moffat et al., 2002). Altogether, this indicates that reacidification in the case of terminated lake liming is not that unlikely and a recent estimation Andersson et al. (2002) indicates that 22% of the limed lakes in Sweden may reach pH 5.4 or lower if liming ceases, in spite of the decreased S deposition over the last decade.

Mobilisation of metals from lake sediments as a result of (re)acidification has been considered unlikely due to the steep pH gradient at the sediment water interface (Nelson and Campbell, 1991). However, in our study the sediment pH was found to be influenced by the acid addition down to a depth of 2 to 3 cm. Consequently, the lowered pH in the surficial sediment layers should allow a mobilisation of metals from the sediments, which we also found. Further, the single study (Andersson, 1985) referred to by Nelson and Campbell (1991) actually showed pore water pH of 4.8 to 5.8 down to a sediment depth of 4.5 cm, reaching pH above 6 only at 8.5 cm depth. Consequently, the increasing pH gradient between overlying water and sediment may not be so steeply increasing in acidified lakes (c.f. in situ study by Schiff and Anderson, 1986), thereby providing conditions for metal mobilisation from surficial sediments.

In our experiment Al, Cd, Mn and Zn were mobilised during reacidification and higher metal concentrations were reached in the water column of the limed lake compared to the non-limed lake. This indicates that during acidification to the same pH, the sediments of limed lakes mainly treated directly on the lake surface may be a greater source of metals than sediments from lakes that have not been limed, which seems probable considering the results of Papers I and II. The highest metal concentrations will probably be reached in the bottom water close to the sediment surface, which is supported by the results of the reacidification studies in Lake Rävekärrs Långevatten where concentrations of Al, Cd and Zn increased, in the near bottom water after reacidification (Dickson et al., 1995) and in Lake Trehörningen, where the terminated liming resulted in decreased pH and increased concentrations of e.g. labile inorganic Al, with peak values over 100 µg/l in 1997-2004 (Edberg et al., 2001; F. Edberg personal communication).

## Conclusions

- Liming causes increased deposition to the sediments of Al, Cd, Co, Ni, Fe, Mn and Zn as a result of the increased pH
- Liming also causes increased deposition to the sediments of As, Co and Cr probably a secondary effect, mainly resulting from association to Al, Fe and Mn complexes.
- No influence of lime treatment on the sediment deposition of Hg, Pb and V to lake sediments could be demonstrated.
- Acidification can decrease the deposition of Cd, Fe, Mn and possibly also Co and Zn to the sediments.
- Besides the liming technique or pH of the water, the sediment metal content is influenced by other factors, e.g. the deposition gradient of airborne metals, and the metal content in the used lime products.
- Cu can be used to normalise the effects of changes in atmospheric deposition and highlight the effect of lime treatment on temporal trends of metal deposition to lake sediments.
- The used lime products can be an important source for Al, Cu and Ni in sediments of lakes that have been limed directly on the lake surface and a relatively important source for Co, Cr, Hg and V, but do not seem to contribute much to the content of As, Cd, Pb or Zn in lake sediments.
- Sediments of limed lakes with oxidising conditions may be a source of e.g. Al, Cd, Mn and Zn during reacidification and remobilisation may contribute to higher concentrations of these metals in lake water during reacidification of formerly lime treated lakes.
- Cu, Fe and Pb are less affected by lowered pH and consequently, the concentrations of these metals will probably not increase during reacidification, unless pH reaches extremely low levels.

## Future research suggestions

It is still disputed whether reacidification could be expected in Sweden in case of terminated liming. The decreased acidic deposition today should decrease the risk, but on the other hand the recovery of lakes is generally very slow and soils in the drainage areas are still acidic. Furthermore, large parts of Sweden still receive acidic deposition well above the calculated critical load. The risk of reacidification should thus be further evaluated and possible long-term consequences should be studied. Special emphasis should be put on the labile inorganic form of Al, which has often been pointed out as the most hazardous element during possible reacidification.

During the evaluation of the $^{210}$Pb dated sediment profiles in Paper II, the calculated ages of profiles from two lakes did not at all agree with ages assumed from $^{137}$Cs and total Pb peaks. These two lakes are among the lakes in the study that have been most severely acidic ($pH < 5$). Since the mobility of Pb increases at pH values below about 5, the sedimentation of $^{210}$Pb could be decreased in severely acidified lakes and it might thus be wrong to assume a constant rate of supply or a constant initial concentration, which the $^{210}$Pb dating models do. This should be studied further to elucidate if the dating problem in these lakes was just a coincidence or if $^{210}$Pb dating is not suitable for sediments in severely acidified lakes.

## Tack

Hans Borg som har varit min handledare under de här åren. Nästan alltid tillgänglig för att svara på frågor och diskutera resultat och otroligt snabb på att läsa manusutkast. Stort tack!

Rolf Hallberg, biträdande handledare fram till licen.

Markus Meili, tack för dateringshjälp och för massor av åsikter, funderingar och förslag.

Magnus Mörth. Tack för hjälpen med ICP-analyserna och för mycket stöd och hjälp under slutspurten.

Tack också till alla som har hjälpt mig med provtagningar, analyser och annat på lab, Ann-Marie (många uppslutningar blev det!), Elisabeth, Hanna, Jörgen, Karin H, Pia och Tomas W.
Bosse, tack för hjälp med datortrassel och för assistans med jämviktsberäkningar.
Göran, tack för diskussioner om metaller och deras beteende.

Alla inom IKEU. Tack för hjälp med datainsamling, givande diskussioner och trevligt sällskap på konferenser och seminarier.

Jag vill också tacka alla mina trevliga rumskamrater genom åren, Frida, Cilla, Ellen, Eva U-T, Hanna, Jenny, Ulrika och exjobbare. Tack för trevliga diskussioner om forskning och mycket annat och för att ni (i alla fall de flesta av er) är bättre än jag på att vara tysta så att andra kan koncentrera sig ;-)

Självklart vill jag också tacka alla övriga medarbetare på Mm, alla doktorandkollegor och hela ITM för roliga fester, lunch- och fikasällskap och allmänt trevlig stämning.

Sen vill jag också tacka mina vänner utanför ITM. Jessika och Cicci, tack för att ni finns där och för att ni har stått ut med mina oändliga utläggningar om livet som doktorand. Eva och Helena, det har varit jätteroligt med doktorandkompisar utanför institutionen, alla jämförande diskussioner och långa luncher. Tack också till mina nyingledarkollegor som har stått ut med min myckna frånvaro den sista tiden utan att klaga.

Ett stort tack till ”mina tre familjer” för allt stöd, god mat, semlor, barnpassning, fika, semestrar och mycket annat. Speciellt tack till Josef och Anton, ni gör det lätt att släppa jobbet och tänka på annat när man kommer hem.

*Tack för finansiellt stöd*
Naturvårdsverket/IKEU
Resestipendier från A E W Smitts stipendie- och understödsstiftelse samt C.F. Liljevalch J.ors stipendiefond.

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