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Metal burdens in surface sediments of limed and nonlimed lakes

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Abstract

Acidification has been shown to increase the concentrations of many metals in lake water as a result of increased mobility at lower pH, whereas liming has been found to decrease lake water metal concentrations. We hypothesise that increased sedimentation as a result of liming increases the metal burdens in the sediments of limed lakes, but especially those that have been treated directly on the lake surface. We also hypothesise that acidification results in decreased metal burdens in the sediments, whereas near neutral reference lakes and lakes where the lime has been applied on wetlands or upstream have intermediate metal burdens in the sediments.

In order to test the hypothesis, we statistically compare the areal metal and P burdens in the sediments of four groups of lakes: (1) Mainly surface limed lakes, (2) Mainly upstream/wetland limed lakes, (3) Near neutral reference lakes and, (4) Acidified reference lakes. The statistical analysis reveals that the surface limed group have significantly higher areal burdens of As, Cd, Co and Zn in the sediment compared to the acidified reference group, despite large variations within the groups. The investigation indicates that surface liming increases the areal burdens in the sediments of Cd and Pb, probably of As, Ca and Mn and possibly Co and Zn, whereas acidification decreases the areal burdens in sediments of Cd, Fe, Mn and possibly Co, P and Zn. The results of the study confirm the hypothesis.

Keywords: Acidification; Liming; Lake sediment; Metal; P; Burdens

1. Introduction

Emissions of acidifying sulphur and nitrogen compounds have resulted in severe acidification of lakes and streams (e.g., Odén, 1968; Almer et al., 1974; Dickson, 1978; Dillon et al., 1987; Schindler, 1988). Liming has been used extensively in Sweden since the 1970s to counteract the negative effects of acidification (Henrikson and Brodin, 1995). High concentrations of, for example, Al, Cd, Mn, Pb and Zn are found in acidified lake waters, as the solubility of these metals increases at decreasing pH (Dickson, 1978, 1980; Andersson and Borg, 1988; Borg et al., 2001). Liming, on the other hand, causes decreased concentrations of these metals in lake water (Dickson, 1978; Driscoll et al., 1989; Andersson and Holm, 1995; Borg et al., 2001).

As a result of the increased mobility, decreased concentrations of Cd and Zn, for example, are found in the sediments of acidified lakes (Rognerud and Fjeld, 2001). Egeberg and Håkedal (1998) detected increased accumulation rates of Cd, Cu, Pb and Zn in sediments after liming. Increased concentrations of metals such as Cd, Fe, Mn and Zn in sediments after

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liming have also been found by others (Dillon and Smith, 1984; Andersson and Borg, 1988; Driscoll et al., 1989; Andersen and Pempkowiak, 1999; Rognerud and Fjeld, 2001).

Results of several investigations indicate that metals can be mobilised from at least the top 2 cm of surface sediments during (re)acidification (e.g., Andersson and Gahnström, 1985; Arafat and Nriagu, 1986; Gambrell et al., 1991; Matschullat and Wyrobek, 1993; Dickson et al., 1995; Fimreite et al., 1996; Wällstedt and Borg, 2003). A high metal content in the sediment of a limed lake could, thus, be a possible source for increased metal concentrations in the bottom waters if reacidification occurs once liming has ceased.

In recent decades, the acidic deposition has decreased (Kindbom et al., 2001), but it still exceeds critical loads in large areas of southern Sweden (Sverdrup et al., 2002; Rapp et al., 2002). Soil acidification continues (Wilander and Lundin, 2000; Moffat et al., 2002) and many lakes still receive acidic runoff water from the drainage area, especially during periods of heavy rain or snowmelt. In spite of the decreased acid deposition, a recent estimation (Andersson et al., 2002) indicates that 22% of the limed lakes in Sweden may reach pH 5.4 (equals zero alkalinity) or lower if liming ceases. Acidification of the surrounding soils may contribute to an increased transport of many metals to the lakes (Bergkvist, 1987; Borg and Johansson, 1989). When acidic runoff reaches a limed lake, the higher pH will favour the increased precipitation of metals. The increased concentration of suspended particles that result from liming also promotes the scavenging of trace metals through adsorption and coprecipitation (Egeberg and Håkedal, 1998). Consequently, the increased precipitation of metals after liming may contribute to the increased metal burdens in the sediments.

In a study of the whole-lake burdens of cadmium, Powell et al. (2000) found that volumetric concentrations, in contrast to dry weight concentrations, more accurately reflect the spatial distribution of cadmium in surface sediments. They concluded that the 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. Sediments from the shallows are interesting since a relatively higher degree of resuspension and bioturbation will probably enhance the exchange between the sediment and water and thus increase the mobilisation. We have not found any data in the literature that compares metal burdens or volumetric concentrations in sediments between limed and nonlimed lakes.

It might also be possible to distinguish between different liming techniques and between reference lakes with different pH. Egeberg and Håkedal (1998) found that upstream liming increased the accumulation of Cd, Cu, Pb and Zn in lake sediments compared to a nonlimed lake, but that the observed enrichment of Cd was less than that found by Andersson and Borg (1988) in a surface limed lake. We hypothesise 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, especially for metals mainly transported to the lake from the soils of the catchment. Elements originating primarily from deposition directly on the lake surface should not differ between surface limed and upstream/wetland limed lakes. 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 near neutral reference lakes are probably less acidified and thus release less metals. Severely acidified reference lakes could have lower burdens of “airborne” metals in their sediments compared to reference lakes with higher pH, because of the higher metal retention time in the more acidic water. A fact that could counteract this is that the most severely acidified lakes are generally situated in southwestern Sweden where the deposition of acidifying substances as well as the load of airborne metals has been highest (Rühling and Tyler, 2001). Our hypothesis is that liming increases the metal burdens of the sediments, whereas acidification leads to decreased burdens. Areal metal burdens will generally be highest in the surface sediments of lakes limed directly on the lake surface, lowest in nonlimed acidified lakes and intermediate in nonacidified reference lakes and upstream/wetland limed lakes.

2. Materials and methods

2.1. Studied lakes

This study is part of the Swedish national Integrated Studies of the Effects of Liming in Acidified Waters programme (ISELAW), that started in 1989 (Appelberg et al., 1995). Therefore, 20 of the 21 sampled lakes were chosen from this programme. However, many of the limed lakes in this study have been studied with respect to water chemistry and biology since liming started, or even prior to that. Most of the nonlimed reference lakes are included in national monitoring programmes and have been studied for many years.

Unfortunately, four lakes had to be excluded from further calculations. One of the surface limed lakes has recently been found to be naturally acidic at a pH of around 5.3 for the last 3000 years, as interpreted from the diatom flora. During the summers of 1993–1995, pH of the bottom water (7–8 m) frequently dropped below 6, with a minimum pH of 5.61 reached in July which is below the liming goals for water quality (pH 6) that have been set up by the Swedish Environmental Protection Agency. A one-sample *T*-test showed a significant difference ($p<0.05$) between this lake and the rest of the surface limed group, which implies that this lake is probably not representative of the limed lake population in Sweden.

One of the upstream limed lakes has an extremely short turn over time, only 11 days. The addition of lime has been considerable, and a large part of the added lime does not settle until the water has reached the lake. This results in an extremely high calcium content in the sediments close to the inlet, and contributes to the precipitation of metals in the lake instead of in the drainage area as expected in the other lakes in the wetland/upstream limed group.

One upstream limed lake and one acidified reference lake are influenced by former mining activities. The lakes are situated in the "Riddarhytte ore field" which consists of a number of smaller sulphide ore deposits. The mining of iron and copper has been extensive in the area and close to 100 minerals have been found. Mine-tailings are still present on the shores of both lakes.

These four lakes have therefore been excluded from further statistical analyses.

The resulting 17 lakes used in this study are located in the southern half of Sweden (Fig. 1) and they are divided into four groups:

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

Many of the lakes have been limed using a combination of methods. In the group of mainly surface limed lakes, Lakes Stengårdshultasjön, Stora Härsjön and Västra Skälsjön are partly upstream limed and Lakes Stensjön AB and Ejgdesjön have been treated using a combination of all three methods. Lakes Stensjön AB and Stengårdshultasjön have received a relatively large part of the lime on wetlands or in upstream lakes or watercourses and can be regarded as borderline cases. Like most limed lakes in Sweden, none of the lakes in this group have been treated only by direct surface liming, but they are still considered as being mainly surface limed and will, in the further discussions, be referred to as surface limed lakes.

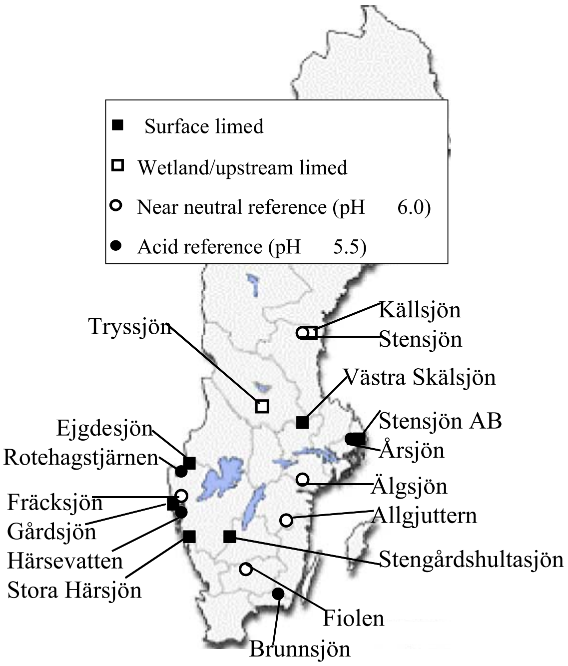


Fig. 1. Sampling locations in Sweden.

In the upstream/wetland limed group, Lakes Tryssjön and Källsjön have been treated with a combination of upstream and wetland liming.

Separation of the nonlimed reference lakes is more straightforward. Five of the reference lakes have an annual mean water pH above 6.0. With respect to pH, they do not differ from the limed lakes in this study and the pH is not below the liming criteria for Swedish lakes (Swedish Environmental Protection Agency, 2002). The other four reference lakes all have an annual mean water pH below 5.5, which must be considered severely acidified (Table 1).

2.2. Sampling

The limed lakes in this study have been treated for 13–22 years. As the average sedimentation rates for forest lakes in Sweden have been reported to be around 0.5–2 mm per year (El-Daoushy and Johansson, 1983), the top 2 cm of the sediments probably cover this period. Besides, they offer enough material for analysis as well as representing the layer that could be affected by a possible future reacidification.

All sediments were sampled with a Limnos type gravity corer. The tube is made up of Plexiglas “rings” that have a height of 1 cm each, a feature that eases slicing of the sediment cores in the field. The sampler was lowered slowly to cautiously penetrate the sediment by the sampler’s own weight. Tilting was not allowed and only cores with visually undisturbed sediment–water interfaces were used for the study.

Generally, 15–20 surface sediment samples and 3–4 cores were collected from each lake, but only the surface samples are treated in this paper. The number of samples collected from each morphometric depth interval (0–2, 2–4 m, etc.) was in approximate proportion to the relative contribution of that depth zone to the whole lake area. However, in some of the lakes, parts of the epilimnetic zone could not be sampled because of features on the bottom, such as large rocks or gravel. The areas that couldn’t be sampled varied between 1–5 m depth, from a few up to nearly 50% (mean = 22%) of the whole lake area, for the different lakes. It was assumed that these uncorable areas did not accumulate any metals.

The samples were placed in preweighted, acid-washed polypropylene vessels. The cups were stored in the dark in a cold-storage bag with freeze elements, which were exchanged regularly to maintain a low temperature, and frozen within 1–4 days (mostly 1–2 days) after sampling.

Table 1
Lake characteristics

Lake	Main “method”	Drainage area (A_d) (km^2)	Water area (A_0) (km^2)	A_d/A_0	Turn over time (years)	Maximum water depth (m)	Mean water depth (m)	Mean bottom water pH (95–99)	First liming	Altitude
Stengårdshultasjön	S L	78.6	4.89	16.1	0.8	26.8	7.1	6.6	1981	223.9
St Härsjön	S L	22.7	2.64	8.6	2.4	42.0	14.1	6.9	1977	90.4
Gårdsjön[a]	S L	2.11	0.31	6.8	1.5	18.5	4.9		1981	113.8
Ejgdesjön	S L	3.60	0.86	6.4	2.0	28.6	7.0	6.6	1982	143.4
Stensjön AB	S L	7.75	0.39	19.9	2.0	20.6	9.1	6.4	1978	35.1
Västra Skälsjön	S L	1.04	0.41	2.5	6.0	18.7	7.4	6.3	1977	233
Tryssjön	U L	12.0	0.30	40.0	0.50	19.6	7.2	6.1	1981	345
Källsjön	W L	16.4	0.22	74.5	0.28	17.4	7.1	6.3	1984	232
Fiolen	N N R	3.82	1.64	2.3	5.2	10.5	3.8	6.2	–	226
Allgjuttern	N N R	0.85	0.19	4.5	12.6	40.7	11.4	6.0	–	126.3
Fräcksjön	N N R	4.26	0.28	15.2	0.8	14.5	6.0	6.0	–	58.3
Älgsjön	N N R	3.96	0.36	11.0		6.0		6.3	–	49
Stensjön Delsbo	N N R	3.65	0.57	6.4	2	8.5	4.2	6.1	–	268
Brunnsjön	A R	2.61	0.11	23.7	1	10.6	5.3	5.4	–	98.4
Härse-vatten	A R	2.03	0.18	11.3	0.9	26.2	5.7	4.7	–	130
Rotehagstjärnen	A R	3.43	0.17	20.2	0.3	9.4	3.4	5.2	–	120.5
Årsjön	A R	1.70	0.16	10.6	1.4	8.0		5.3	–	>35

Surface Limed (S L), Upstream/Wetland Limed (U/W L), Near Neutral Reference (N N R), Acidified Reference (A R).

[a] Not included in the ISELAW programme.

2.3. Chemical analyses

All samples were freeze dried before analysis. No size fractionation of the sediment material was made, since we wanted to analyse the metal content in the sediment regardless of particle size.

0.5 g of the freeze-dried samples were digested with 20 ml 7 M HNO_3 for 1 h under pressure at 120 °C and the digests were filtered through 0.45-μm membrane filters, according to Swedish Standard Method SS 028150. The filtrate was diluted to 50 ml with ultrapure water (MilliQ) and stored in acid washed polypropylene bottles. Procedural blanks were also prepared, using the same routines as for sample preparation.

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 Simultaneous ICP-AES and SPS-5 autosampler). Hg was determined by Flow Injection Analysis, cold vapour AAS (Perkin Elmer 305 B) with $SnCl_2 \cdot 2H_20$ as a reductant.

Standards and blanks with the same acid concentrations as the samples were prepared from commercially available stock standard solution and ultrapure water. The curve fit (r^2) of the standards were all close to one (generally 0.998–1.000). Triple measurements were performed on each sample, and in the ICP-AES multiple wavelengths were generally used in order to detect interferences. Fe interfered with the Cd detection (overlapping peaks in the emission spectrum), which was compensated for by mathematical correction in the instrument software (Varian Vista-PRO).

Separate samples were dried at 105 °C for 24 h to determine the total dry substance (DS) and then ignited at 550 °C for 2 h to determine the content of organic material as Loss on Ignition (LOI).

All sample containers and laboratory glassware were acid washed and rinsed with ultrapure (MilliQ) water before use. Acids and standard solutions used in the digestion and analysis were of suprapur or PA quality.

2.3.1. Quality assurance and precision

Detection limits were calculated from the analytical results of the procedural blanks. The detection limit for each metal was set to the mean values of the blanks plus three times the standard deviation of the blanks, increased to an even figure (Table 2). Mo was excluded from further calculations since for many of the lakes more than 50% of the samples had concentrations below the detection limit. A few Cd concentrations were also below the detection limit.

For quality assurance, reference material was analysed with every batch of samples. Two types of

Table 2
Analytical precision and recovery from certified material using HNO_3 digestion

Detection limit (μg g^{-1} ds)		Certified material (n=6)				Internal reference (n=21)	
		Certified concentration (μg g^{-1} ds)	Relative standard deviation (%)	Recovery (%)	Relative standard deviation (%)	Measured concentration (μg g^{-1} ds)	Relative standard deviation (%)
Al	60	22,600	1.0	23	11	34,320	6.0
As	0.3	66	–	90	3.6	13.0	3.7
Ca	30	29,000	–	82	10	5499	4.6
Cd	0.05	10.2	7.5	73	2.7	7.38	4.1
Co	0.08	10.1	3.0	29	1.8	50.6	3.4
Cr	0.7	29,600	4.8	87	2.6	39.2	4.4
Cu	0.5	109	8.9	81	4.6	36.9	3.9
Fe	150	113,000	5.4	73	7.0	48,300	3.3
Hg	0.1	–	–	–	–	0.198	7.1
Mn	10	785	6.3	69	12	1870	3.4
Ni	0.7	45.8	3.2	54	3.2	40.0	3.8
P	50	–	–	–	10	1601	7.4
Pb	0.5	714	2.0	66	3.8	71.6	4.1
V	0.1	23.5	15.0	35	32	56.4	5.5
Zn	2	1720	5.0	63	3.0	167	3.4

reference material were used, including one certified reference material (river sediment, NIST 1645, Washington DC) and one internal reference sample (lake sediment). Only a few analyses were performed on the certified material, because for many elements the concentration in this material differed considerably from those of the samples. The concentrations in the internal reference material were much closer to the concentrations in the samples.

Around 70–90% of the certified concentrations were recovered for most elements (Table 2). Only 23% of the certified value of Al was measured, however, probably because most of it is bound in the sediment in the form of minerals that do not dissolve during HNO_3 digestion. The recovery of Ni, V and Zn was also somewhat low. All elements discussed in this paper were, however, in the acceptable range according to the internal reference sample and, most importantly, the reproducibility was satisfactory, with relative standard deviations generally in the range 3–6% (Table 2).

2.4. Calculations

The bulk density (g cm^{-3}) of each surface sample was calculated from the weight fractions of water, organic material (LOI) and minerogenic material (DS-LOI), where the densities were assumed to be 1.0, 1.2 and 2.6 g cm^{-3}, respectively (Håkanson and Jansson, 1983). Volumetric concentrations (mg cm^{-3}) of the elements in each surface sample (wet sediment) were calculated from the wet-weight concentration (mg g^{-1} ww) and bulk density of the respective sample, and the volumetric concentrations were used to calculate the areal burdens. Areal burdens are defined as being the mass of each element in the uppermost 2 cm of sediment per unit of lake area (g m^{-2}, 2 cm) and the final numbers obtained are thus measurements of the metal burden in the 2 cm surface sediment layer of each lake, averaged on a whole-lake basis.

Sediment focusing and other in-lake processes could cause a relationship between water depth and volumetric concentration. When calculating the areal metal burden for a lake, the different volumetric concentrations at different depth intervals must be considered. The mean volumetric concentration for each depth zone of the lake (e.g., 0–2 m) was calculated, prorated by the proportion of the lake which that depth zone comprised, corrected for the uncorable (nonaccumulating) area and summed to give a whole-lake surface content, referred to as a weighted mean areal burden. The area of each depth zone was assumed to have a standard deviation equal to 5% of the area. Standard deviations for the mean volumetric concentrations were calculated using the same process, following the principles of propagation of uncertainties during addition and multiplication with standard deviations.

2.5. Statistical method

Differences in areal burdens between groups were analysed with One-Way ANOVA. When significant differences between groups ($p < 0.05$ or $p < 0.1$) were found in the ANOVA, subsequent Post Hoc tests (Tukeys and Tamahanes tests for equal and nonequal variances, respectively) were used for the relevant elements to identify the differences between the respective groups (SPSS for Windows, 11.0.0, SPSS) Normally, a *T*-test would have been used to identify significant differences between groups. A problem with the *T*-test is, however, that it doesn't correct for the fact that multiple comparisons are being made. However, it seems very unlikely, that the many more significant differences we found using the *T*-test compared to the Post Hoc test are only caused by a random variation. Therefore, the results found in the *T*-test will also be reported, but not considered as truly significant.

3. Results

3.1. Correlations between element concentrations and water depth

The mean bulk densities varied between 1.03–1.10 g cm^{-3}, with minimum values from 1.01–1.04 g cm^{-3} and maximum values from 1.04–1.25 g cm^{-3} for the different lakes. The highest densities were found in samples from shallow areas of the lakes, containing a high fraction of minerogenic material.

Significant correlations (Spearman correlations, $p < 0.05$) between water depth and dry-weight concentrations (μg g^{-1} ds) were found for 56% of the cases (one case = one metal in one lake). These correlations were mostly positive (44% of all cases, 80% of the significant cases) with higher concentrations at larger water depths. Fewer significant correlations, only 36% of the cases, were found between water depth and volumetric concentrations. These correlations were often negative (28% of all cases, 78% of the significant cases). This implies that although the dry-weight concentrations are often lower for shallower areas compared to deeper areas, the volumetric concentrations are often higher as a result of the lower water content and higher bulk density.

3.2. Differences in areal metal burdens between groups

For most elements, areal burdens differed between the lakes within each group but significant differences between groups (ANOVA, $p < 0.05$) were still found for As, Cd, P, Pb, and Zn and for Loss on Ignition (LOI) (Tables 3 and 4, Fig. 2a–f).

If a lower significance level ($p < 0.1$) was accepted in the ANOVA, differences between groups were also found for Al, Co, Fe, Mn and Ni and for dry substance (DS). The subsequent Post Hoc tests revealed significant differences between groups, as presented in Table 3. Surface limed lakes showed higher areal burdens of the elements As, Cd, Co and Zn, compared to acid reference lakes. Furthermore, surface limed lakes had higher burdens of As than near neutral reference lakes, and higher burdens of Al, As, Cd, Ni and P, compared to the lakes treated by upstream or wetland liming (Table 3).

Table 3
Differences in areal metal burdens and in P, DS% and LOI% between groups

	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)	–

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 Tamahanes test (unequal variances). Additional significant differences found using T-test ($p < 0.05$) are also shown within parentheses.

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

If an independent T-test was used instead of the Post Hoc tests, significantly higher burdens of Al, Fe, Mn, Ni, P, Pb and Dry Substance were found in the surface limed lakes compared to the acidified reference lakes (Table 3).

4. Discussion

4.1. Areal burdens

In a study of Cd burdens in lake sediments, Powell et al. (2000) concluded that expression of concentrations on a dryweight basis does not accurately reflect the spatial distribution of cadmium in surface sediments of the study lakes. It may support the misconception that shallow-water sediments contain substantially less cadmium than sediments in deeper areas. Moreover, dryweight concentrations underestimate shallow-water sediments as potential sources of biologically available cadmium. Volumetric concentrations, however, more accurately reflect the spatial distribution of cadmium in surface sediments and emphasise the potential reservoir of cadmium in the shallow areas of a lake. This was also shown in our study, where dry-weight concentrations were positively correlated to water depth in most cases, whereas volumetric concentrations were more often negatively correlated to water depth. These results are expected and are related to the general influence of depth on the water content and LOI of the sediment of most lakes. Consequently, the total reservoir of metals in surface sediments in the littoral zone was relatively large. This may have ecological implications since metals in sediments in shallow areas probably have a higher potential of exchange with the water column since these sediments are more likely to be influenced by bioturbation and resuspension, for example.

4.2. Differences between groups

4.2.1. Aluminium

Enrichment of Al in sediments as a result of mobilisation in the catchment and subsequent precipitation in the limed lake with higher pH is probable, as

Table 4

Weighted mean areal burdens (with standard deviations in parenthesis)

Lake name	Al (g m^{-2}, 2 cm)	As (mg m^{-2}, 2 cm)	Ca (g m^{-2}, 2 cm)	Cd (mg m^{-2}, 2 cm)	Co (mg m^{-2}, 2 cm)	Cr (mg m^{-2}, 2 cm)	Cu (mg m^{-2}, 2 cm)	Fe (g m^{-2}, 2 cm)
Ejgdesjön	17.72 (2.4)	36.88 (11.02)	2.89 (0.46)	2.23 (0.57)	23.48 (7.86)	54.05 (11.88)	18.42 (3.46)	49.37 (27.80)
Gårdsjön	28.79 (6.67)	36.42 (12.26)	7.78 (2.68)	2.95 (0.71)	26.19 (3.14)	20.89 (4.56)	24.10 (6.07)	53.54 (20.89)
St Härsjön	25.53 (4.07)	43.68 (14.05)	33.56 (33.49)	3.87 (0.73)	46.29 (11.03)	22.47 (4.51)	41.53 (7.36)	90.36 (24.65)
Stengårdshultasjön	9.12 (1.99)	20.43 (5.11)	6.41 (3.10)	2.89 (0.99)	30.55 (12.44)	6.53 (1.16)	8.03 (1.45)	107.06 (26.79)
Västra Skälsjön	26.75 (4.61)	58.18 (18.24)	15.09 (4.89)	3.17 (0.72)	32.66 (10.05)	21.57 (3.28)	25.45 (4.09)	125.36 (65.69)
Stensjön AB	29.81 (5.74)	30.64 (8.59)	7.01 (1.28)	2.57 (0.55)	69.80 (21.01)	34.35 (6.85)	18.08 (3.50)	120.94 (30.57)
Mean, surface limed group	**22.95 (8.01)**	**37.70 (12.69)**	**12.12 (11.24)**	**2.95 (0.56)**	**38.16 (17.40)**	**26.64 (16.07)**	**22.60 (11.13)**	**91.11 (33.08)**
Tryssjön	8.90 (2.85)	12.69 (6.42)	3.93 (1.17)	1.93 (0.85)	27.56 (13.37)	5.58 (1.82)	5.66 (1.82)	122.12 (58.63)
Källsjön	5.12 (0.83)	19.04 (3.29)	2.91 (0.37)	0.38 (0.06)	6.92 (1.03)	3.93 (0.75)	3.16 (0.51)	31.33 (5.48)
Mean, upstream/ wetland limed group	**7.01 (2.67)**	**15.86 (4.49)**	**3.42 (0.73)**	**1.16 (1.10)**	**17.24 (14.59)**	**4.75 (1.16)**	**4.41 (1.77)**	**76.72 (64.19)**
Fräcksjön	36.08 (9.48)	14.22 (7.01)	7.04 (2.50)	3.29 (0.58)	49.23 (20.50)	32.46 (7.75)	18.85 (2.78)	64.03 (24.78)
Fiolen	14.85 (2.94)	9.85 (1.30)	3.67 (0.34)	1.59 (0.35)	7.32 (1.30)	15.80 (2.16)	17.36 (1.54)	28.00 (3.62)
Allgjuttern	11.10 (0.8)	20.79 (3.15)	4.47 (0.62)	1.48 (0.20)	18.39 (3.54)	9.23 (0.77)	16.95 (1.52)	75.44 (15.42)
Älgsjön	26.33 (5.98)	6.04 (0.86)	6.26 (0.78)	1.27 (0.15)	21.51 (3.35)	32.03 (6.93)	34.21 (5.53)	39.26 (6.09)
Stensjön Delsbo	8.67 (1.17)	17.06 (4.17)	2.57 (0.34)	1.50 (0.20)	9.25 (1.58)	7.94 (1.12)	7.45 (1.01)	138.64 (28.12)
Mean, near neutral reference group	**19.41 (11.52)**	**13.59 (5.82)**	**4.80 (1.84)**	**1.83 (0.83)**	**21.14 (16.80)**	**19.49 (12.02)**	**18.96 (9.64)**	**69.07 (43.25)**
Rotehogstjärnen	14.78 (3.19)	5.66 (1.01)	3.02 (0.93)	0.63 (0.27)	6.38 (1.84)	13.75 (2.67)	12.74 (2.85)	14.73 (2.75)
Härsevatten	10.78 (2.77)	18.38 (6.89)	0.73 (0.36)	0.69 (0.18)	3.64 (1.89)	14.91 (5.09)	18.51 (4.06)	29.85 (13.39)
Brunnsjön	8.85 (1.26)	6.02 (0.84)	2.89 (0.38)	0.66 (0.11)	5.42 (0.72)	6.94 (0.92)	11.78 (1.74)	24.97 (3.99)
Årsjön	10.84 (2.18)	10.64 (5.54)	2.72 (1.02)	1.09 (0.35)	19.42 (11.49)	13.79 (3.09)	12.43 (3.25)	26.48 (14.39)
Mean, acidified reference group[c]	**11.31 (2.49)**	**10.17 (5.92)**	**2.34 (1.08)**	**0.77 (0.22)**	**8.72 (7.23)**	**12.35 (3.65)**	**13.86 (3.12)**	**24.01 (6.51)**

Lake name	Hg (mg m^{-2}, 2 cm)	Mn (g m^{-2}, 2 cm)	Ni (mg m^{-2}, 2 cm)	P (g m^{-2}, 2 cm)	Pb (mg m^{-2}, 2 cm)	V (mg m^{-2}, 2 cm)	Zn (mg m^{-2}, 2 cm)
Ejgdesjön	0.17 (0.06)	9.13 (5.12)	9.99 (1.85)	0.77 (0.12)	144.83 (29.18)	26.02 (3.95)	216.24 (44.36)
Gårdsjön	0.26 (0.07)	5.26 (1.16)	21.14 (3.38)	1.17 (0.35)	186.14 (52.27)	38.37 (8.96)	317.10 (59.1)
St Härsjön	0.28 (0.03)	39.42 (18.99)	26.53 (4.19)	1.40 (0.23)	192.55 (33.91)	55.17 (9.51)	362.63 (53.34)
Stengårdshultasjön	0.11 (0.02)	57.68 (20.74)	9.75 (3.12)	0.92 (0.15)	66.50 (17.71)	23.05 (4.23)	178.74 (47.61)
Västra Skälsjön	0.34 (0.03)	9.62 (2.54)	14.48 (1.94)	1.54 (0.43)	266.14 (59.96)	45.87 (8.84)	263.02 (40.75)
Stensjön AB	0.23 (0.04)	16.99 (6.74)	25.96 (5.26)	1.51 (0.25)	94.91 (19.57)	55.49 (10.11)	335.74 (67.16)
Mean, surface limed group	**0.23 (0.08)**	**23.01 (20.95)**	**17.97 (7.62)**	**1.22 (0.32)**	**158.51 (72.39)**	**40.66 (14.05)**	**278.91 (71.99)**
Tryssjön	0.14 (0.04)	27.28 (16.73)	4.14 (1.48)	0.70 (0.22)	55.56 (18.85)	30.78 (9.52)	146.73 (56.16)
Källsjön	0.07 (0.01)	9.85 (10.54)	1.63 (0.31)	0.60 (0.07)	10.70 (1.50)	19.93 (2.77)	27.91 (4.27)
Mean, upstream/ wetland limed group	**0.10 (0.05)**	**18.56 (12.33)**	**2.89 (1.77)**	**0.65 (0.07)**	**33.13 (31.72)**	**25.35 (7.67)**	**87.32 (84.02)**
Fräcksjön	0.24 (0.05)	5.36 (3.61)	28.60 (11.45)	1.67 (0.50)	78.30 (15.22)	58.69 (19.88)	390.97 (130.17)
Fiolen	0.08 (0.02)	0.47 (0.17)	10.24 (2.37)	1.84 (0.23)	67.44 (9.59)	26.20 (6.30)	165.20 (33.38)
Allgjuttern	0.13 (0.02)	10.58 (5.06)	9.83 (1.13)	0.86 (0.07)	58.85 (6.92)	22.80 (1.99)	85.35 (9.93)
Älgsjön	0.20 (0.04)	1.38 (0.20)	28.09 (5.53)	1.38 (0.16)	50.85 (7.82)	47.93 (7.96)	206.58 (35.41)
Stensjön Delsbo	0.13 (0.02)	11.78 (3.95)	4.59 (0.52)	0.88 (0.13)	53.91 (8.31)	27.95 (4.44)	103.59 (15.12)
Mean, near neutral reference group	**0.16 (0.06)**	**5.91 (5.17)**	**16.27 (11.25)**	**1.33 (0.45)**	**61.87 (11.12)**	**36.71 (15.73)**	**190.34 (122.16)**
Rotehagstjärnen	0.31 (0.38)	0.18 (0.06)	10.76 (2.54)	0.98 (0.14)	35.59 (8.07)	26.83 (5.52)	75.83 (33.39)
Härsevatten	0.23 (0.04)	0.15 (0.10)	6.86 (2.19)	0.69 (0.15)	95.33 (22.33)	28.30 (7.16)	52.74 (12.79)
Brunnsjön	0.14 (0.02)	0.15 (0.02)	4.37 (0.63)	0.76 (0.13)	34.28 (5.64)	29.91 (5.01)	29.63 (5.21)
Årsjön	0.16 (0.03)	2.89 (2.43)	10.14 (2.14)	0.70 (0.20)	70.81 (14.39)	21.40 (4.01)	76.35 (26.43)
Mean, acidified reference group	**0.21 (0.08)**	**0.84 (1.37)**	**8.03 (2.98)**	**0.78 (0.13)**	**59.00 (29.54)**	**26.61 (3.70)**	**58.64 (22.25)**

pointed out by Norton and Kahl (1991). 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). Surface limed lakes are likely to receive more Al from the drainage area compared to upstream/wetland limed lakes, where some of the aluminium probably precipitates before it reaches the lake. The liming agent itself also

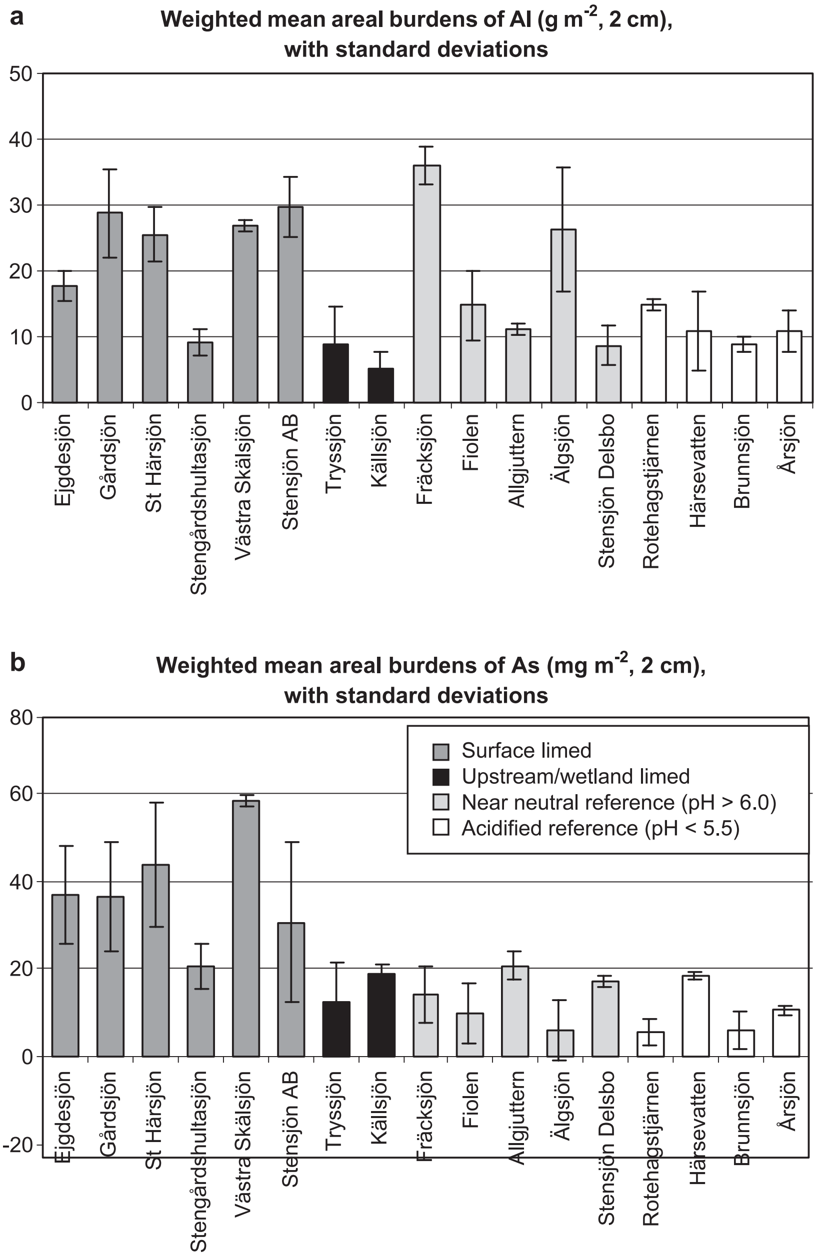
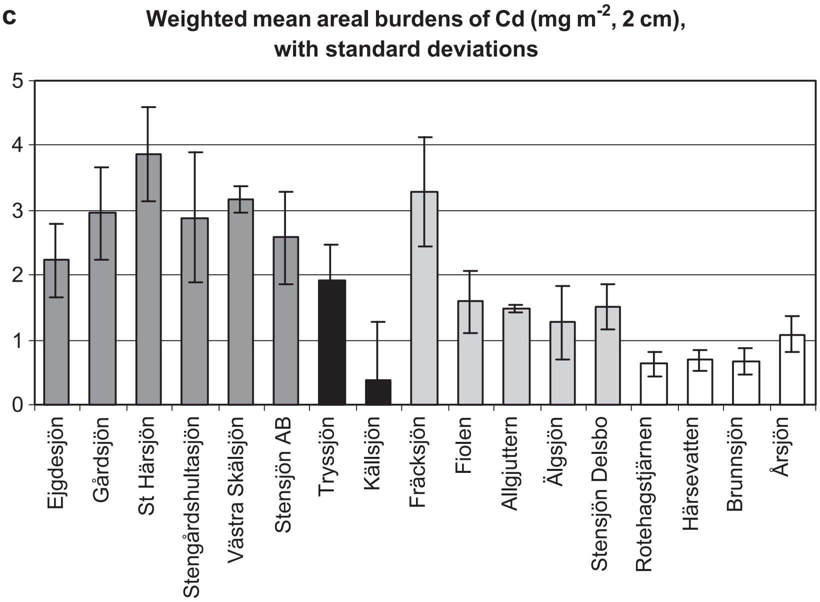


Fig. 2. (a–f) Areal burdens of Al, As, Cd, Co, Ni and Pb with standard deviations, calculated from weighted mean values. The lakes are sorted from west to east (left to right) within each group.



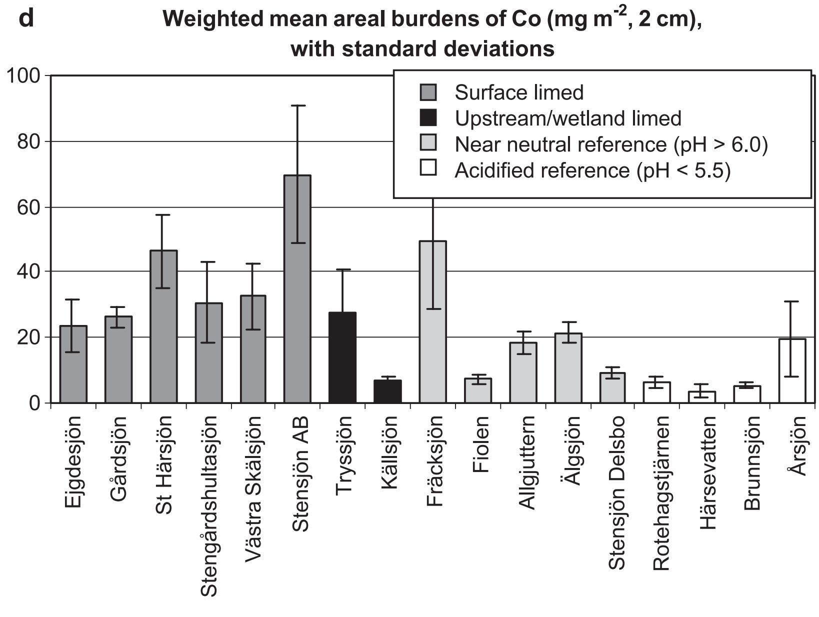


Fig. 2 (*continued*).

contains up to 2% Al in the form of Al_2O_3 (William Dickson, Swedish EPA, personal communication), which could also contribute to the higher burdens in sediments of surface limed lakes. Acidified reference lakes should receive Al from the drainage area in the same range as the surface limed lakes, but the lower pH in the water probably counteracts precipitation to some extent.

Increased concentration of Al in sediment is, however, not easily demonstrated because of the high natural background concentrations. This may explain why differences in areal burdens between

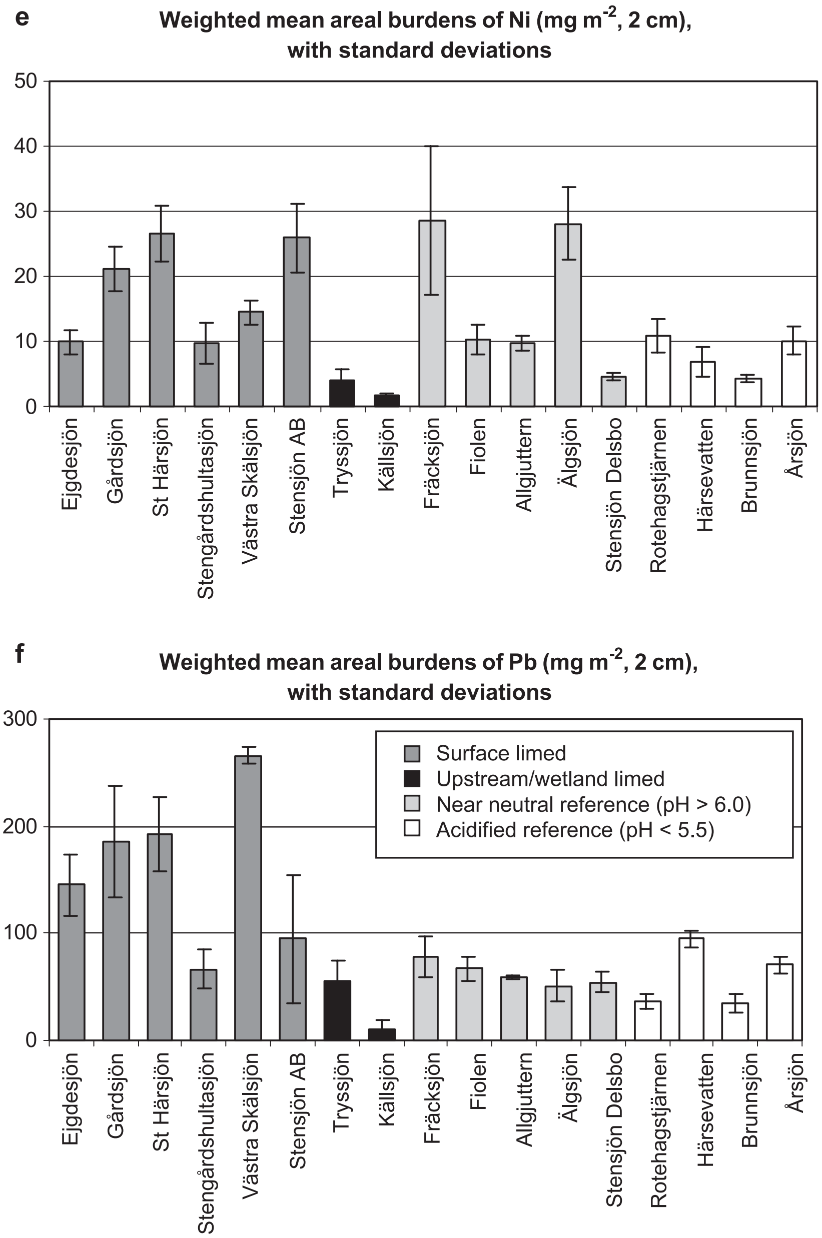


Fig. 2 (*continued*).

groups are significant only at the $p<0.1$ level in the ANOVA. We found, however, as expected from the discussion above, higher areal burdens of Al in the surface limed lakes compared to the upstream/wetland limed lakes and the acidified reference lakes (Tables 3 and 4, Fig. 2a).

4.2.2. Arsenic

The dominating species of As in oxic fresh water is the negative arsenate ion $HAsO_4^{2-}$. Because of the negative charge, and unlike most other metals, it has a greater mobility at higher pH, similar to Mo and V (Lithner et al., 2000). Limed lakes could therefore be expected to have lower burdens of As in the sediment compared to acidified lakes. On the other hand, aerial deposition has been suggested to be the most important factor for elevated As concentrations in lake waters (Veselý and Majer, 1996). Sediments constitute the major sink for As in many aquatic ecosystems, where hydrous oxides of Al, Fe and Mn participate in the immobilisation of As species. The relative efficiency of As binding to these components is a function of pH and redox potential. Immobilisation of As species by metal hydrous oxides is more efficient at higher pH levels (Pierce and Moore, 1982; Mushak, 1985). In this study, the areal burdens in the surface limed lakes are higher compared to both reference groups (Table 3, Fig. 2b). The increased As burdens is probably, at least partly, a result of elevated atmospheric As deposition, since many of the surface limed lakes in this study are situated in SW Sweden where the atmospheric metal deposition is highest (Kindbom et al., 2001). This, combined with coprecipitation with the oxides and hydroxides that are formed because of the lime addition contribute further to the increased As level in surface sediments.

4.2.3. Cadmium and zinc

To a great extent, the partitioning of Cd and Zn is influenced by pH changes, and elevated concentrations of both Cd and Zn in sediments after liming have been found in several investigations (Andersson and Borg, 1988; Driscoll et al., 1989; Egeberg and Håkedal, 1998; Andersen and Pempkowiak, 1999; Rognerud and Fjeld, 2001). As expected, higher burdens of Cd and Zn were found in the surface limed lakes compared to the acidified reference lakes in this study (Tables 3 and 4, Fig. 2c). The surface limed lakes also showed higher areal burdens of Cd than the near neutral reference lakes which in turn had higher burdens than the acidified reference lakes, although these differences are significant only if the *T*-test is used. These results agree well with the hypothesis presented in the introduction.

4.2.4. Calcium

As a result of the repeated addition of lime, one would have expected a difference in areal burdens of calcium between the limed lakes and the nonlimed lakes and especially between the groups of surface limed lakes and that of acidified reference lakes. The calcium burden was also found to be markedly higher in the surface limed group compared to all the other groups (Table 4) but large within-group variation gives a large standard deviation, which counteracts a significant difference between this and the other groups.

4.2.5. Cobalt

Only a few studies report results for Co with reference to liming and acidification. Rognerud and Fjeld (2001) found no effects of liming on dry-weight concentrations of Co in lake sediments, whereas 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 acid conditions.

Our results show that the areal burden of Co in the sediments was higher in the surface limed group compared to the acidified reference group (Tables 3 and 4, Fig. 2d), which seems reasonable according to the discussion above.

4.2.6. Iron and manganese

Increased accumulation of Fe in lake sediments after liming has been found in previous investigations (Dillon and Smith, 1984; Andersen and Pempkowiak, 1999). Andersen and Pempkowiak (1999) ascribe the increased accumulation of Fe to the formation of oxyhydroxides in the lime treated water. They state that the increased pH probably facilitates a higher degree of oxidation of possible ferrous complexes introduced by drainage water and that the precipitation of these complexes are probably enhanced through sorption onto particulate matter introduced with the lime.

In our study, the areal burden of Fe was higher in the surface limed group compared to the acidified reference group (Table 3). Table 4 reveals, however, that the areal burden of Fe was relatively uniform in all groups except in the acidified reference group, which has a lower burden. This indicates that it might be the acidification that reduces the areal burden of Fe in sediments rather than the lime treatment that increases the areal burden.

Mn oxides are also likely to be formed after liming, since Mn speciation is highly pH-dependent (LaZerte and Burling, 1990), and increased dry-weight concentrations of Mn in sediments after liming have been reported previously (Dillon and Smith, 1984; Driscoll et al., 1989; Andersen and Pempkowiak, 1999). In this study, the mean areal burdens of Mn were higher in both limed groups compared to the nonlimed groups, indicating that liming might increase the Mn burdens (Table 4), although no significant difference was found (Table 3).

The mobility of both Fe and Mn is largely controlled by the redox potential in the pore water of the surface sediments and the water layers near the bottom, where reducing conditions favour an increased release of dissolved species. However, in the oligotrophic forest lakes used in this study, the oxygen levels are generally high enough to keep the sediments oxidised throughout most of the year, even in the deepest part of the lake. Furthermore, the surface sediment samples were collected at different depth intervals, covering most of the lake area. Thus, in our case, the influence of reduced conditions on Fe and Mn mobility is probably minor.

4.2.7. Lead

The mobility of Pb is generally only considered to be affected by pH changes at relatively low pH levels (Borg and Andersson, 1984), and therefore the increased areal burdens of Pb in the surface limed lakes compared to the reference lakes in this study were not expected (Tables 3 and 4, Fig. 2f). On the other hand, a relatively strong negative correlation between Pb concentrations and pH in lake water was found in a Swedish–Norwegian lake survey (Lydersen and Löfgren, 2000). A contributing factor may be the atmospheric deposition pattern of Pb, which in Sweden and Norway generally coincides with the deposition of acidifying substances. Another explanation for the higher sedimentation of Pb may be the liming agent itself, which in one study was found to be the most important source of Pb (Egeberg and Håkedal, 1998). Furthermore, the lime treatment may increase the coprecipitation of Pb with Fe and Mn hydroxides. In a laboratory experiment, Pb was readily adsorbed to Mn and Fe oxides and organic material (Dong et al., 2000) and both Fe and Mn oxides are likely to be formed after liming, as discussed above. The increased areal burdens of Pb in the sediments of the surface limed group are probably caused by a combination of the factors discussed above.

4.2.8. Nickel

Ni is also known to be influenced by pH changes, with higher mobility at lower water pH (Borg, 1995). Net losses of Ni from acidified soils have been found in Sweden (Bergkvist, 1987) and in the study by Andersen and Pempkowiak (1999), Ni concentrations in the sediment increased more than 30 times above the background after the liming of Lake Terjevann. When the drainage water from an acidified catchment reaches a surface limed lake, Ni precipitates as a result of the higher pH, a process not occurring to the same extent in acidified reference lakes. For the group of upstream/wetland limed lakes it seems probable that a large portion of Ni is retained in the catchment. With reference to this, the higher areal burden of Ni in the surface limed group compared to the upstream/wetland limed group (Table 3, Fig. 2e) and the acidified reference group (Table 4), found in this study, was expected.

4.2.9. Phosphorous

P concentrations in acidified lake water seems to be regulated largely by adsorption or coprecipitation with Al (Dickson, 1978; Kopacek et al., 2001). When ionic Al species supplied by acidic tributaries reach a lake with higher pH, particulate Al-oxyhydroxide flocs can be formed. These flocs have large surface areas and strongly adsorb ortophosphate. P can also be coprecipitated as Al-hydroxo-phosphate complexes (Kopacek et al., 2001).

In this study, the surface limed lakes have higher areal burdens of P compared to the upstream/wetland limed lakes and the acidified reference lakes (Tables 3 and 4). The near neutral reference lakes also have higher P burdens than the upstream/wetland limed lakes, and the acidified reference lakes, although none of the differences are significant (Tables 3 and 4). Surface limed lakes are likely to receive more Al from the drainage area compared to upstream/wetland limed lakes, where some of the Al and P probably precipitate before it reaches the lake, which can be an explanation for the higher P burdens in surface limed lakes compared to upstream/wetland limed lakes. This does, however, not explain why near neutral reference lakes have higher P burdens than the upstream/wetland limed lakes. One answer to this question might be that the near neutral reference lakes probably have less acidified catchments than the limed (former acidified) lakes. P can be retained in acidified soils in the drainage area as a result of the precipitation as $AlPO_4$ (Persson and Broberg, 1985). This is probably an important mechanism, since high concentrations of Al in the soil solution are characteristic of acidified areas. Thus, more P may be exported from the catchment of near neutral reference lakes compared to acidified catchments. Acidified reference lakes probably receive P and Al in the same range as surface limed lakes but the lower pH may to some extent counteract precipitation in the lake.

If P is regulated by Al, the same differences should be seen when comparing the P and Al burdens for the groups of lakes, and in this study we also find a covariaton of these elements, reflected as higher areal burdens of P and Al in sediments from surface limed lakes and near neutral reference lakes compared to upstream/wetland limed lakes and acidified reference lakes (Tables 3 and 4).

4.2.10. Content of organic matter

The content of organic matter, expressed as Loss on Ignition (LOI), was found to be higher in the acidified reference group compared to surface limed lakes and near neutral reference lakes (Tables 3 and 5). The acidified reference group also had a slightly higher organic content compared to the upstream/wetland limed group (Table 4). Many authors have reported an increased transparency of the water as a consequence of acidification (Almer et al., 1974). One reason for this is probably precipitation of humic substances with aluminium (Dickson, 1978), which may be one explanation for the higher content of organic material in the sediment of the acidified lakes. An additional explanation may be a decreased degradation rate of organic matter in the acidic environment (Andersson, 1985).

4.2.11. A_d/A_0

The ratio between drainage area and lake area (A_d/A_0) should be an important factor for the areal burdens of elements that are transported from the catchment to the lake. In this study, the upstream/wetland limed group had a considerably larger A_d/A_0 compared to the other groups, although the difference was not significant (Tables 3 and 5). The upstream/wetland limed group also had a (insignificantly) shorter turn over time compared to the other groups (Tables 3 and 5). Large A_d/A_0 and short turnover time is often the reason why a lake is limed on wetlands or in upstream lakes or watercourses. This treatment method is more efficient than surface liming, since the lime in the latter case would be quickly consumed and the lake would frequently need reliming, which is more costly and probably causes rapid fluctuations in the water chemistry.

The most likely effect of a large A_d/A_0 is the increased areal burdens of metals that are transported from the drainage area and hence a positive correlation between A_d/A_0 and the burdens of for example Al, Cd, Mn and Zn could be expected. Blais and Kalff (1993) found that the Cr and Ni burdens in lake sediments increased with A_d/A_0 until A_d/A_0 values of about 20 were reached, whereas Zn and Pb retention in the soils were considered almost complete. Bergkvist (1987) found net losses of Al, Cd, Cr, Mn, Ni and Zn from acidified soils whereas Cu and Pb were accumulating in the soil. The different conclusions regarding Zn in these two studies can be explained by the fact that the lakes and thus probably also the drainage areas in the first study were not acidified. Dillon and Evans (1982)

Table 5
Statistics for some potentially influencing factors

Element	Group*	N	Mean	Standard deviation
Dry substance (%)	S L	6	5.86	1.65
	U/W L	2	3.21	0.69
	N N R	5	5.52	1.61
	A R	4	3.73	0.71
Loss on ignition (%)	S L	6	30.69	5.06
	U/W L	2	38.45	0.52
	N N R	5	33.20	6.20
	A R	4	43.62	6.75
Turnover time (years)	S L	6	2.27	1.54
	U/W L	2	0.45	0.06
	N N R	4[a]	5.15	5.30
	A R	4	0.90	0.45
A_d/A_0	S L	6	11.13	7.51
	U/W L	2	55.25	17.47
	N N R	5	8.28	5.53
	A R	4	16.34	6.36

*Surface Limed (S L), Upstream/Wetland Limed (U/W L), Near Neutral Reference (N N R), Acidified Reference (A R).

[a] Lake Älgsjön, turnover time not known.

found no relationship between Pb burden and A_d/A_0 in nine lakes. They concluded that there was no significant input of Pb from the watersheds and that the Pb retention capacity of the lakes did not vary. Their results indicated that the only significant input of Pb to the lakes resulted from atmospheric deposition directly on the lake surfaces. Similar results have been found by other authors (e.g., Evans and Rigler, 1985; Borg and Johansson, 1989). According to this discussion, the upstream/wetland lakes in this study, showing a higher A_d/A_0, should receive higher loads of, e.g., Al, Cd, Cr, Mn, Ni and Zn from the drainage areas compared to the other groups. On the other hand, we have already argued that upstream or wetland liming causes the precipitation of metals transported from the drainage area before they reach the lake and hence give lower metal burdens in the sediments compared to surface liming. In this study, a large A_d/A_0 does not coincide with high areal burdens, which indicates that the effect of large A_d/A_0 is either relatively small or is counteracted by some other mechanism, e.g., trapping of metals before they reach the lake, as a result of the lime treatment.

4.2.12. General differences between the four groups of lakes

As discussed above, the largest differences in areal metal burdens were found between the surface limed group and the acidified reference group. The reason for this is probably a combination of increased burdens because of the surface liming and decreased burdens because of the acidification.

It is also interesting to compare the near neutral reference group to the other groups. In this study, the near neutral reference group is the group that comes closest to what can be called a "normal case"; that is, the lakes in this group are not limed and are influenced less by acidification than the other lakes.

The surface limed group had significantly higher areal burden of As compared to the near neutral reference group, indicating an influence by the lime treatment. Although not statistically significant, the areal burdens of Ca, Cd, Co, Mn, Pb and possibly Zn were also higher in the surface limed group compared to the near neutral reference group, indicating that for these elements surface liming may also cause increased areal burdens.

Differences, although not significant, between the near neutral reference group and the acidified reference group were found for Al, Ca, Cd, Fe, Mn, Ni, Zn and possibly also P and V, indicating that acidification may cause lower areal burdens of these elements.

Long-range airborne transport of metals has influenced the deposition pattern over Sweden, reflected as a decreasing S–N gradient. That pattern was most pronounced when metal emissions were higher, i.e., in the 1960s and 1970s. During the 1980s and 1990s, the slope of the gradient has decreased successively, as a result of decreased metal emissions in Europe, and this trend is documented, e.g., in the repeated surveys of metals in land mosses (Rühling and Tyler, 2001). Our study lakes are primarily located in the southernmost part of the country (Lat < 60 N), and the period influenced by lime treatment is about 20 years. Data from the moss surveys from 1970–1995 indicate a moderate variation within that area. Lead showed 30%, 14%, and 22% difference between minimum and maximum concentrations for three subregions in S Sweden in 1970, 1985, 1995, respectively. For Cd and Hg, 20% and 9–14% variation was found in 1985 and 1990, respectively, while Zn showed a 5% variation (Rühling and Tyler, 2001). Considering the good correlation between atmospheric deposition and metal concentrations in moss, these variations may also be expected in the deposition data for metals (Rühling et al., 1987). This is also confirmed when comparing the bulk deposition of Pb, Cd and Zn from three precipitation monitoring sites in S Sweden. Results from 1985–1990 show a spatial variation of about 11%, 19%, and 14% (CV) within the region (Swedish precipitation monitoring programme, http://www.ivl.se/db).

In our investigation, the near neutral reference group is somewhat biased to the east compared to the surface limed group, and some of the difference in metal burdens in the sediments might therefore be explained by the difference in metal deposition. The differences in metal burdens between the surface limed group and the near neutral reference group are, however, much larger than the differences in atmospheric metal deposition, 38%, 30%, 61% and 32% for Cd, Hg, Pb and Zn, respectively. Furthermore, significant correlations between weighted mean volumetric metal concentrations and the *x*-coordinate for each lake, representing the east–west geographical location, were found only for the near neutral reference group and the differences between that subgroup and the surface limed group are much larger than the differences within the near neutral reference group of lakes (exemplified with Pb in Fig. 3).

Conclusively, these results indicate that the difference in atmospheric deposition within S Sweden, would have a relatively minor influence on the observed difference in sediment load of metals between the studied lakes, especially during the last decade before sampling.

The lakes are also influenced by the runoff water from the catchment areas, carrying metals that also partly originate from airborne deposition on the catchments. Data on runoff chemistry for the studied catchments does not exist. Earlier studies on 15 small catchments in Sweden showed that for elements such as Zn and Cd, 60–95% originated from runoff, and was primarily influenced by soil pH of the catchment. Elements such as Pb, Cu, and Hg, originated to a lesser extent from the catchment, and were more influenced by humus concentrations (Borg and Johansson, 1989). The pH of the soil solution in the catchments may especially influence the load of Cd and Zn to the study lakes. The lakes are located in coniferous forest catchments in southern Sweden, where spatial variation of the pH of the forest soil is relatively small; 4.15–4.30 in the O-horizon and 4.85–5.05 in the B-horizon (http://www-markinfo.slu.se). The influence of soil pH of the catchment on the sediment deposition of these metals in our study lakes should thus be relatively small.

4.3. Other features that influence the metal burdens in the sediment

4.3.1. Contribution from the liming agent

All liming products that are used in Sweden contain various amounts of metals. Nowadays, the maximum concentrations allowed are regulated, but when the liming activities started, some lime products could have high concentrations of, e.g., Cr. In a study of Lake Terjevann (Andersen and Pempkowiak, 1999) some metals, including Al, Fe and Mn in the lime, contributed to the increased accumulation in the sediment. However, the metal concentrations in the sediment considerably exceeded the measured concentrations in the lime. Furthermore, lack of correspondence between the maximum concentrations of Ca and trace elements in the sediments indicated that the lime was not the main source.

Another study (Egeberg and Håkedal, 1998) found that enhanced scavenging of dissolved metals from the water phase at liming caused most of the accumulation of Cd and Zn in the sediment, whereas the liming agent itself was the most important source for Pb. For Cu, both sources were of equal importance. The effect of the various liming products on the metal burdens in the sediments of surface limed lakes is thus not fully understood, and should be investigated further.

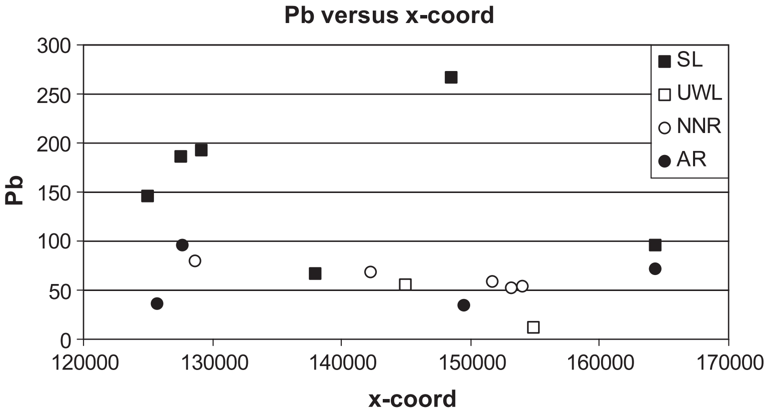


Fig. 3. Weighted mean volumetric concentrations of Pb vs. *x*-coordinate (geographical location where a lower *x*-value means further to the west).

4.3.2. Sedimentation rates and other morphological factors

The effect of acidification and liming on sedimentation rates has been discussed. It has been argued that acidification might decrease the sedimentation rate as a result of a lower in-lake production whereas liming might increase the sedimentation rate. Andersen and Pempkowiak (1999) found that the sedimentation rate in Lake Terjevann in southern Norway increased from 1.27 ± 0.20 mm year^{-1} before liming started to 5.7–8.0 mm year^{-1} after liming. A potentially higher sedimentation rate in limed lakes means that the 2 cm layer used in this study could reflect a shorter period of time in the limed lakes than in the acidified lakes, which might contribute to a dilution effect. The atmospheric deposition of many metals has also decreased over the last few decades (Kindbom et al., 2001; Rühling and Tyler, 2001), implying that the 2-cm layer in the acidified lakes may contain metals that have been deposited over a longer period of time, compared to the limed lakes, and also over a period when the metal concentrations in the deposition were higher than today. This has, however, to be investigated further, with an accurate dating of sediment cores from limed and nonlimed lakes, before any conclusions can be made.

There are, of course, also other features besides liming techniques and pH of the reference lakes that differ between the lakes. Minerals and soil type in the drainage area, altitude, forestry and other factors may also be important to the metal burdens in the sediments.

5. Conclusions

A statistical comparison of areal metal burdens in the sediments of four groups of lakes: (1) Surface limed lakes, (2) Upstream/wetland limed lakes, (3) Near neutral reference lakes and, (4) Acidified reference lakes has been carried out.

The statistical analysis reveals 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 indicate that surface liming can increase the areal burdens of Cd and Pb, and probably also of As, Ca and Mn and possibly Co and Zn.

The results of the investigation also indicate that acidification can decrease the areal burdens of Cd, Fe, Mn and possibly also Co, P and Zn in the sediments.

Besides the liming technique or pH of the water, the metal burdens of the sediments are influenced by other factors, e.g., the deposition gradient of airborne metals, also contributing to the variation among the studied lakes.

The results agree relatively well with the hypothesis that there are generally highest areal burdens in the surface sediments of lakes that have been limed directly on the lake surface, lowest areal burdens in nonlimed acidified lakes and intermediate areal burdens in nonlimed, nonacidified reference lakes and upstream/wetland-limed lakes.

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