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Norvald Fimreite, Bjarne Nenseter and Bjørn Steen

Department of Environmental Sciences

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Telemark College
Post Box 203
N-3901 Porsgrunn
Norway

Telephone: +47 35 57 50 00
Fax: +47 35 57 50 01
Website: <http://www.hit.no/>

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Cadmium concentrations in limed and partly reacidified lakes in Telemark, Norway

Norvald Fimreite, Bjarne Nenseter and Bjørn Steen

Department of Environmental Sciences, Telemark College, 3800 Bø, Norway

Abstract

Cadmium (Cd) concentrations were measured in water and sediments from eight lakes in the acid stressed area of western Telemark, Norway. The lakes were either not limed (group I, n=2), limed once in 1992 (group II, n=4), or regularly since 1982 (group III n=2). Cd concentrations in the lake surface water were generally low as only one sample exceeded the detection limit (0.05 mg/l). The Cd levels in the bottom water were higher and highest in the unlimed lakes. The Cd concentrations in the sediments averaged 1.06, 1.79, and 2.52 µg/g in group I, II, and III respectively, but with much variation within the groups. The Cd levels of the sediment samples, which were collected from the deepest part of the lakes, increased with the depth and with the Fe content in sediments.

Keywords: Cadmium, liming, lakes, sediments, reacidification

Introduction

Severe acidification of Norwegian lakes and rivers during the last four to five decades, has had considerable ecological effects on aquatic life, especially in the southernmost part of Norway where fish populations have disappeared from a number of waters (Hesthagen *et al.* 1994). To counteract the acidification and thereby save remaining fish populations, and to restore biological conditions, liming is considered to be the only remedy and large-scale liming operations are now in progress (Sandøy 1995).

Liming induces rapid precipitation of some important toxic metals like aluminum (Al) and cadmium (Cd) in water (Fimreite *et al.* 1996, Zachariassen & Blakar 1995). Most attention has been devoted to Al, as its toxicity is well documented both from laboratory (e. g. Dickinson Burrow 1977) and field studies (e. g. Dickson 1978). The toxic effects of Cd to a number of aquatic organisms,

including fish, are also documented (Nilsson and Wallgren 1987). Cd ions are relatively mobile and their occurrence is strongly dependent upon pH in the soil-water system (Borg and Johansson 1989). Therefore lake liming normally leads to sedimentation of Cd and consequently decreasing Cd concentrations in the water (Dickson 1980, Wright 1985). Marcus (1988) on the other hand found that liming of 20 American lakes had no effect on the concentrations of Cd, although the mean pH rose from 5.5 to 6.6. Reacidification of sediments has been shown experimentally by Andersson and Gahmstrom (1985) and by Fimreite et al. (1996) when pH dropped below 5. It was especially marked at pH 4.5 or lower. Based on Cd profiles in sediment cores from two acid lakes in Norway Reuther *et al.*(1981) concluded that Cd was mobilized from the sediments when pH in the water declined below 5.

The above findings suggest a pH dependent Cd mobilization from lake sediments that is governed by the range of change in pH and probably other factors as well such as organic carbon and Fe in sediments. The high costs of comprehensive liming projects make discontinuation of some of these probable. This may imply reacidification and probably leaching of Cd from sediments. It is therefore of considerable interest to clarify the extent and rate of such Cd mobilization under field conditions. The present study investigated lakes in Telemark, Norway characterized by heavy acidification caused by acid rain and a geology generating low buffering capacity.

Study area

The lakes are situated in Birtedalsheiane mountains in southern Norway (Figure 1). The area contains many small lakes close to the tree line, about 900 m above sea level. It receives much acid precipitation and has a very low buffering capacity with gneiss and granite as the dominating bedrocks in the catchments (Venugopal 1970). Analysis of water samples collected in 1977 from several localities in the area prior to liming revealed acid lakes with pH ranging from 4.8 – 5.2 (Kiland 1978). The area contains both unlimed and limed lakes, the latter either having been limed once (1992) or frequently from 1982 to 1994. This gave us the opportunity to compare three categories of lakes with respect to liming intensity:

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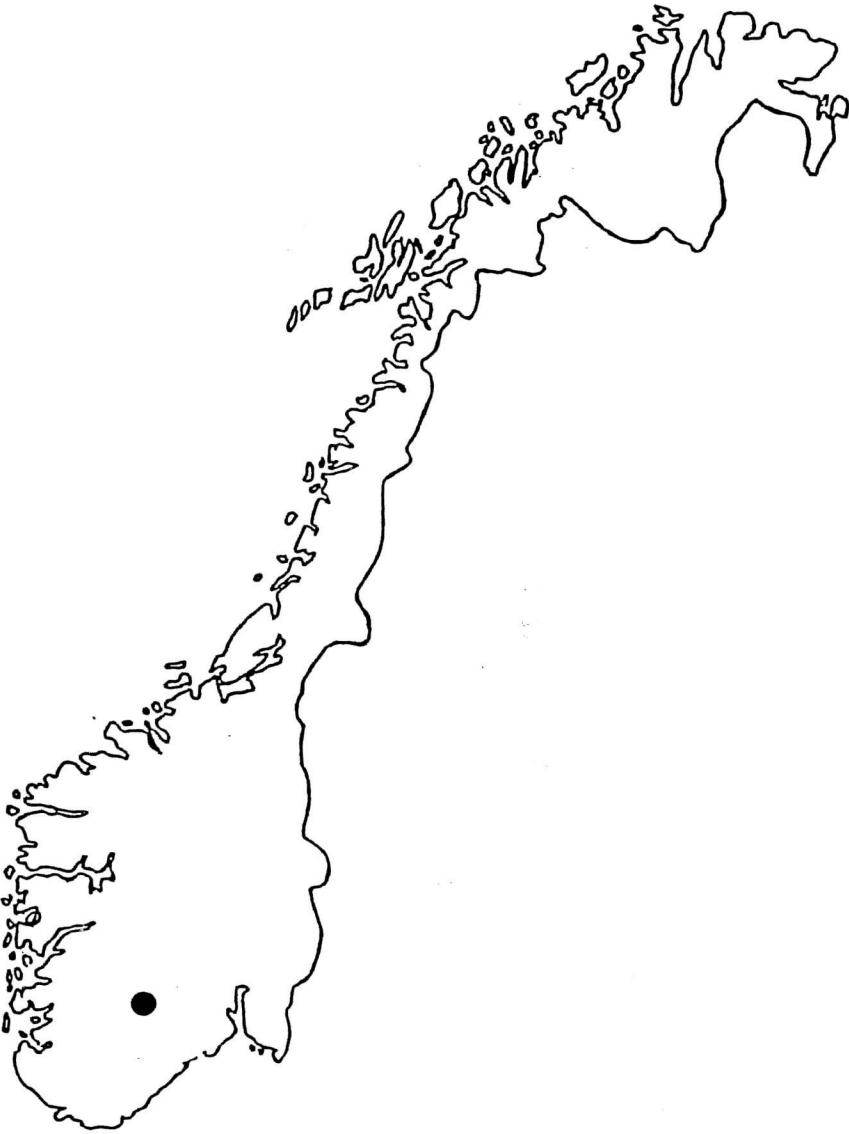


Figure 1. Map of Norway showing the general area of the collecting sites

I. Unlimed lakes, II. Limed once (1992), III. Limed regularly since 1982

The selection of adequate comparable lakes was difficult as the lakes vary considerably with respect to depth, size, catchment area, and the order in which they occurred in the hydrological network. We selected lakes based on geographical nearness and geological uniformity. The morphological and hydrological characteristics of the selected lakes are shown in Table 1 and pH values of the lake waters in Table 2. A short description of the localities in the different categories follows:

Table 1. Morphological and hydrological characteristics of the lakes

Lake (group)	Lake area (km ²)	Catchment area (km ²)	Average depth (m)	Volumem ³ x 10 ⁶	Retention time (yr)
Olavstjørn (I) ^a	0.15	0.85	2.5	0.38	0.45
Stemmetjørn (I) ^a	0.15	1.60	2.5	0.38	0.25
Blakstjørn (II) ^b	0.30	5.50	8.0	2.40	0.46
Hobutjørn (II) ^b	0.23	3.60	4.5	1.04	0.30
N. Kjeldbergjørn (II) ^b	0.20	1.90	4.0	0.80	0.45
Ø. Kjeldbergjørn (II) ^b	0.10	0.70	4.0	0.40	0.60
Sundbekk (III) ^b	0.55	4.20	7.0	3.85	0.97
Øytjørn (III) ^b	0.25	2.05	8.0	2.00	1.03

a. Own measurements

b. Data from Telemark County Adm., Environmental Div.

Table 2. pH of lake waters

Category	Lake	pH	Comments
Group I (not limed)	Olavstjørn	5.00	Outlet 20 July 94
	Stemmetjørn	5.02	Outlet 20 July 94
Group II (limed once)	Blakstjørn	5.30	Outlet 19 July 94
	Hobutjørn	5.45	Outlet 19 July 94
	N. Kjeldbergjørn	5.35	Outlet 19 July 94
		4.56	11 m depth under ice 2 May 94
	Ø. Kjeldbergjørn	5.32	Outlet 19 July 94
Group III (limed regularly since 92)	Sundbekk	6.33	14 m depth under ice 2 May 94
		6.17	Outlet 14 June 94
		6.43	Outlet 13 Oct. 94
	Øytjørn	6.19	Outlet 13 Oct. 94
		6.41	Outlet 13 Oct. 94

Group I. Lake Olavstjørn and Lake Stemmetjørn are two small lakes that served as an untreated control as they have never been limed. They are relatively shallow (average depth 2.5 m). The pH was 5.0 when recorded in the summer 1994 and they contain no fish.

Group II. Lake Blakstjørn, Lake Hobutjørn, Lake Øvre Kjeldbergjørn, and Lake Nedre Kjeldbergjørn were all limed in 1992 and never since. These lakes were originally rich in fish but the fish populations disappeared gradually and the lakes were without fish at the time of liming. Prior to liming the pH was 4.9 in Lake Hobutjørn and Lake Blaktjørn (R. Strand pers. communication). In the summer 1994 the pH was 5.3 - 5.4. In these lakes Brown trout (*Salmo trutta*) was reintroduced after liming and it has been confirmed that the fish population has a satisfactory growth rate (Leif Birger Tovslid pers. communication).

Group III. Lake Sundbekk and Lake Øytjørn have been limed every year since 1982. The trout populations seem to do well in both these lakes (Åni Libjå pers. communication).

The areas of the lakes and their catchments vary somewhat, but there is no reason to believe that these differences per se should affect the Cd levels. However, the ratio of drainage area to lake size (

D/L) may be of significance as a small lake draining a relatively large catchment may allow more leaching of elements, included Cd, to the lake. On the other hand the hydrological turn over time of the water will be lower in such a lake. D/L in the present study varied between 5.7 (Olavstjørn) and 18.3 (Blakstjørn).

Materials and methods

Sampling Samples were collected from three stations the deepest parts in each lake. Water samples were retrieved from 1 m below surface and 1 m above bottom, respectively, using a Ruttner water collector. Surface sediment samples down to about 5 cm were collected from each station using a grab sampler. Dates of collection were 18 - 20 July 1994. The water samples were immediately preserved with 1ml 7M HNO₃ and stored in glass bottles at 4°C until analysis. The sediment samples were put in polyethylene bags and stored in a refrigerator. All bottles and bags used for storing samples were earlier acid-washed and rinsed with distilled water.

Analytical procedures

Cd concentrations were determined by atomic absorption spectrophotometry with graphite furnace techniques. The instrument used was a Perkin Elmer AAS-3100. Water samples were analyzed using a HGA-600 graphite furnace. Cd in the sediment samples was determined by atomic absorption using flame technique. The sediment samples were dried to constant weight before being analyzed and the Cd concentrations are therefore referred to as µg Cd/g sediment d.w.

Organic content in the sediments was determined by two different techniques (A and B below) in order to obtain the most reliable results. A. Total organic carbon (TOC) was determined by a TOC analyser (Carlo Erba - Total Carbon Monitor model 400/P). Digested sediment samples were diluted before analysis. The results are presented in mg C/g sediment d.w. B. Determination of organic content measured as the difference between dry matter and ignition residues. Results are presented as per cent loss by ignition.

Fe in sediments. As a correction to TOC determined by loss of ignition, the content of iron should be considered (Rannem and Hongve 1980). The rationale is that Fe₂O₃ attracts water which will be included in the loss of ignition value thereby enhancing it. If there is much Fe₂O₃ · 3H₂O in the

sediment the error will be significant and the following formula is suggested as a correction : $OC = 0.52 (LI - 0,48 \times Fe)$, where OC = organic carbon, LI = loss of ignition, and Fe = per cent Fe in the sediment. Fe was determined by atomic absorption using flame techniques.

pH determination . A Copenhagen Radiometer with a combination electrode was used for determining pH.

Statistics. We followed Miller and Miller (1989).

Results

pH relationships

The pH measured in July 1994 in the two unlimed lakes (group I) was 5.0. Among the lakes in group II the pH varied between 5.3 and 5.5. These lakes, that were limed once (1992), were less acidic than they were prior to liming and 0.3 - 0.6 pH units above those in group I. For the two regularly limed lakes the pH was measured to 6.2. Even in the spring/early summer after snowmelt and acidic episodes their pH values exceeded 6 (Table 2).

Cadmium in water

Since the detection limit was 0.05 µg/L all values below this limit are reported as < 0.05 µg/L. The samples collected from 1 m below the surface were very low in Cd content regardless of lake category, and with only one value (from Hobutjønn) above the detection limit (Table 3). The Cd levels in the bottom water were higher in all lake groups and highest in the unlimed lakes, which very clearly exceeded the others (ANOVA, $P < 0.05$). Differences between the Cd levels from groups I and II there were not statistically significant. The pH of the unlimed lakes was only about 0.3 pH units lower on average.

Cadmium in sediments

The Cd concentrations in sediments were highest in the group III with an average of 2.52 µg/g as compared to 1.79 µg/g in group II and 1.06 µg/g in group I, respectively (Table 3). These averages, however, conceal considerable variation within the groups. In group II, Lake Blakstjørn stood out markedly from the others by having very high levels. The samples from this lake were collected from 22 m depth in contrast to the other samples that were taken from much lesser depths (Figure 2). It is

also a marked difference between the two lakes in group III. Regression analysis of Cd concentrations as a function of depth confirmed a significant relationship ($p < 0.01$, Figure 2).

Table 3. Cadmium in the water and sediment samples ($\bar{X} \pm SD$)

Group	Lake	Cd in water ($\mu\text{g/L}$)		Cd in sediments ($\mu\text{g/g d.w.}$)
		1 m depth	1 m above bottom	
I	Olavstjørn	< 0.05	0.16 ± 0.06	1.16 ± 0.58
I	Stemmetjørn	< 0.05	0.15 ± 0.05	0.97 ± 0.15
II	Blakstjørn	< 0.05	0.06 ± 0.04	3.39 ± 0.14
II	Hobutjørn	0.06 ± 0.06	0.07 ± 0.05	1.36 ± 0.54
II	N. Kjeldbergtjørn	< 0.05	0.05 ± 0.04	0.75 ± 0.08
II	Ø. Kjeldbergtjørn	< 0.05	0.07 ± 0.04	1.66 ± 0.86
III	Sundbekk	< 0.05	0.09 ± 0.06	1.61 ± 0.21
III	Øytjørn	< 0.05	0.05 ± 0.05	3.43 ± 0.18

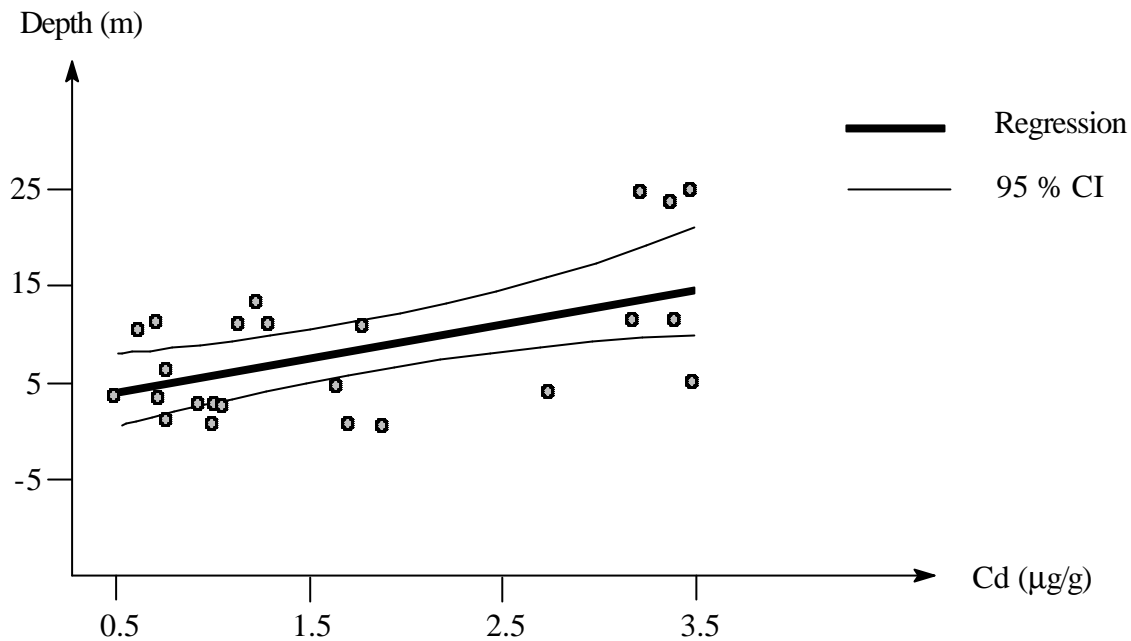


Figure 2. Relationship between Cd levels in the sediments and depth of the lakes

Organic carbon in sediments (TOC)

The two ways of determining carbon correlated significantly ($r = 0.81$). When the Fe concentrations were taken into account r was 0.82. In the following the results based on loss of ignition determinations adjusted for Fe content will be applied. The relation between Cd and carbon was not significant.

Fe in sediments

The Fe content varied among the samples (Figure 3) and therefore the impact on loss of ignition also varied considerably. Two lakes, Blakstjørn and Øytjørn, differed from the others by having very high Fe concentrations, ranging from 99 - 290 mg/g. These lakes were the deepest among the lakes. Cd and Fe concentrations were significantly correlated ($r = 0.86, p < 0.05$).

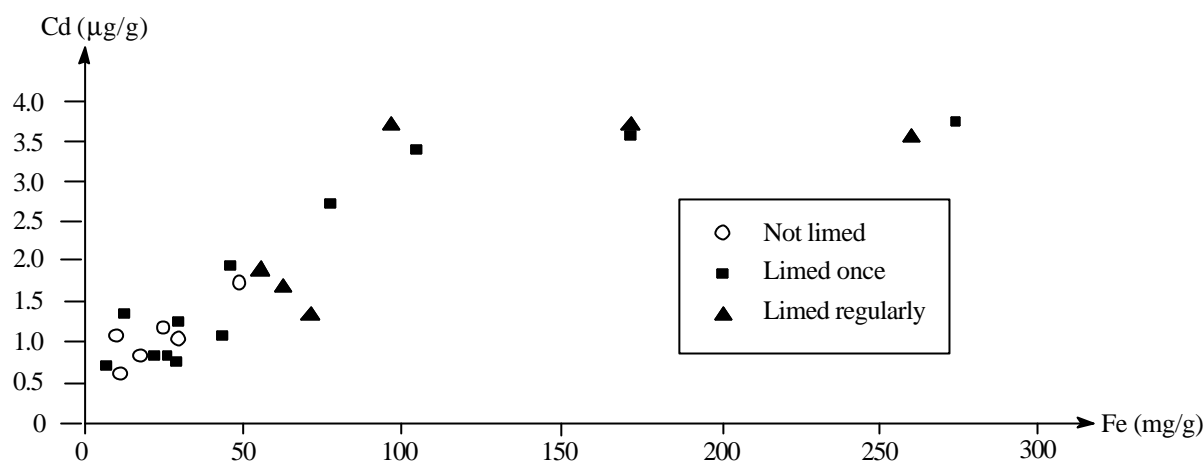


Figure 3. Relationship between Cd and Fe levels in sediments

Discussion

Since our sediments were collected using a grab sampler and not a corer we can not distinguish between upper and lower layers. In non or little acid stressed lakes a decline of Cd levels towards surface of the sediments is common (Nriagu et al. 1982). In lakes that have been acidified for more than 30 years no such decline has been documented (Rognerud and Fjeld 1993). In lake Hovatrn (pH = 4.4) in southern Norway Reuther et al. (1981) measured the highest Cd concentrations 4-5 cm below surface and lowest at the uppermost sediment while in the nearby Lake Langetjønn (pH = 4.9) Cd concentrations increased towards the surface. We feel that our results therefore are comparable with those reported from other acidified lakes in southern Norway when taking into account the above variations where pH apparently is a significant factor.

In general, we found concentration differences among the lakes as expected. The limed lakes contained the least Cd in the water column and the most Cd in sediment, as found in previous studies (Dickson 1980, Borg 1983, Borg and Andersson 1984). Such differences, however, were less pronounced in the present study, what is not surprising as the unlimed lakes held a pH of 5.0 while the effect of acidification manifests itself most clearly when pH declines below 5.0 (Reuther et al. 1981, Fimreite et al. 1996). The lakes that had been limed only once had been slightly reacidified after two years in spite of a very short turnover time in these lakes of approximately 0.5 years. The

liming effects are somewhat more persistent than expected as the duration of liming effects in lakes with turnover time less than 1 year according to Sverdrup et al. (1986) and SEPA (1988) is 2- 3 years. The partial reacidification effects were reflected in Cd levels in those lakes which in general held an intermediate rank in the water Cd as well as in the sediments Cd.

However, some of the results diverged from this general picture. Physical factors, especially depth, had a substantial effect on Cd levels in the sediments. Thus Blakstjørn, limed only once (1992) and with pH 5.3 contained as much Cd as those limed regularly since 1982 and with water pH above 6. The samples from this lake were collected from 22-23 m depths versus 2 - 13 m for all other localities. The relationship between Fe levels and depth from which the sediment samples was collected, was clear. We found an even stronger relationship between Fe and Cd levels ($r = 0.86$, $p < 0.05$) while we found no significant relationship between sediment Cd levels and TOC. The latter indicates that Fe hydroxides have had a significant effect on sedimentation of Cd in contrast to what has been suggested by Rognerud and Fjeld (1993) who maintained that such sedimentation in acidified lakes in southern Norway probably is bound in organic components that are not associated to Fe/Mn hydroxides. Based on the solubility product for $\text{Fe}(\text{OH})_3$ we calculated that when Fe^{3+} reach a concentration of $100 \mu\text{g/l}$ precipitation of $\text{Fe}(\text{OH})_3$ starts already at pH 3.5, and it increases with increasing pH. It is possible that we have a precipitation effect of $\text{Fe}(\text{OH})_3$ on Cd.

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