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Liming, Reacidification, and the Mobilization of Cadmium from Sediments

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Over several decades severe acidification of streams and lakes has taken place in Scandinavia and North America , with catastrophic consequences for aquatic life. In certain water systems in southern Norway fish populations have been completely eliminated by severe acidification (Henriksen et al. 1988). This fish mortality has been attributed largely to increased concentrations of toxic aluminum and, since liming counteracts acidification and reduces the aluminum levels in the water, it has become the most widespread remedy to restore fish habitats.

Cadmium (Cd) concentrations in the water are also pH-dependent and, therefore, affected by liming. According to investigations in Sweden by Dickson (1979), a decrease in pH from 7 to 4.5 gives a 10- fold increase in the Cd concentrations in the water; the increase is especially dramatic when the pH drops below 5. Elevated Cd levels in acidified waters have also been reported from Norway (Rognerud and Fjeld 1993), from Finland (Verta et al. 1990), and from Canada (Stephenson and Mackie 1988). In the late 1970s Dickson (1980) observed subsurface maxima of Cd in sediments of acid lakes in Sweden. Renberg (1985) recorded maximum concentrations about 5 cm below the surface and only negligible levels at the top. The pH was 4.5 at the top and increased downward rapidly to a maximum of about 6. Other in situ studies of acid lakes have shown the same tendency (El-Daoushy and Johannson 1983; Langelo and Steinnes 1995)

To explain the above phenomenon Nelson and Campbell (1991) have proposed different theories. Two of these are most interesting because they can be linked directly to acidification:

1) Remobilization of Cd from the sediment due to low pH in the water column,

2) Reduced sedimentation rates of Cd due to decreased metal sorption to suspended sediments in the water column, and/or decreased availability of adsorbing surfaces due to slower oxidation of Fe(II) to Fe(III.

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The significance of these factors are unclear. In a laboratory experiment Cd was released from sediments when the pH dropped below 5 (Andersson and Gahnstrom 1985). Based on Cd profiles in sediment cores from two acid lakes in Norway, Reuther et al. (1981) suggested that Cd was remobilized from the sediments when the pH declined below 5. Andersson (1985), however, suggested that Cd mobilization from sediments seems improbable due to the sharply increasing pH gradient between the overlying waters and sediment porewaters. Renberg (1985) concluded that Cd sedimentation had been reduced in recent years because water- column acidification decreased the sorption of Cd on settling sediment matter.

The present laboratory experiment was conducted to clarify the significance of liming as a factor in reducing Cd concentrations from lake water, and the behavior of Cd following reacidification. An objective was also to study the behavior of organic material under varying pH conditions. The idea was to simulate an acid - limed - reacidified development using water and sediments from natural lake systems.

MATERIALS AND METHODS

We intended to make the experiment as ecologically relevant as possible in order to maximize its transition value to natural systems. We obtained, therefore, water from the unlimed Lake Langetjønn in Bø Norway (59° 30' N 8° 47' E). It is acid (pH 4.7) with a physical and chemical composition typical for acidified lakes in southern Norway (Table1). The water samples were collected on 28 January 1995 and immediately made ready for the experiment. The sediment samples were a homogenized mixture from lakes in the area. For reacidification, we used a 1:2 mixture of HNO_3 and H_2SO_4, which is close to the acid composition of the present precipitation in Scandinavia.

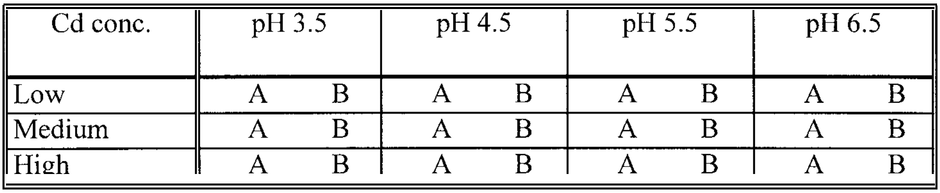
Table 1. Physical/chemical parameters of Lake Langetjønn water.

Depth m	pH	Conduct. uS/cm	Color mgPt/L	Alkalinity mmol/L	Ca mg/L	P µg/L
0	4.7	18	40	0.006	0.07	8
1	4.8	14	35	0.014	0.07	5
2	4.7	18	39	0.009	0.15	44

To study the development of the Cd concentrations with a high degree of certainty, three concentration levels were used. Cadmium was added to the water with the aim to reach the concentrations of 0.2, 0.5, and 1.0 µg Cd/L, respectively. However, the water contained such high amounts of humic matter (color factor 40) that some Cd was adsorbed to particles and deposited. Therefore, and possibly for other reasons, the three Cd concentration levels were reduced under the experiment and they will hereafter be referred to as high, medium, and low. Instead of the intended 0.2, 0.5, and 1.0 µg Cd/L, the blind samples showed 0.11, 0.14 and 0.26 µg Cd/L, respectively, and the control 0.03 µg Cd/L. This should not have caused any consequences for the experiment except that we were operating at a lower concentration level (but probably a more realistic one) than originally intended. The lime we used in the experiment contained 98 per cent $CaCO_3$.

The experiment was set up with 12 different combinations of pH levels and Cd concentrations, each with two replicates (Table 2).

Table 2. Experimental design showing the 12 combinations of three different Cd concentrations and four pH levels in water samples from Lake Langetjønn, each with two replicates, indicated as A and B.



Cd conc.	pH 3.5		pH 4.5		pH 5.5		pH 6.5	
Low	A	B	A	B	A	B	A	B
Medium	A	B	A	B	A	B	A	B
High	A	B	A	B	A	B	A	B

Three-hundred mL of water (pH 4.7) and 5.00 g homogenized dried sediments were put into each testbeaker. The pH was adjusted with strongly diluted acids ($HNO_3 + H_2SO_4$) and NaOH to reach the desired values and followed by exact pH control. Lime was added in appropriate quantities to reach pH 6.5. The system was then allowed to stabilize for one week in darkness at 20°C. Compensation for evaporation was done with distilled water. Water samples, each 4 ml, were collected and acid-preserved for Cd analysis. Then we added strongly diluted solutions of $HNO_3 + H_2SO_4$ in proportion 1:2. This was done gradually until pH stabilized at 3.5, 4.5, and 5.5, respectively; thereafter the system was allowed to stabilize for 24 hr. Samples were then collected and acid-preserved for analysis (4 mL for Cd analysis and 25 mL for TOC analysis). The Cd concentrations were determined by atomic absorption spectrophotometry using the graphite furnace technique. Total organic carbon was determined using a TOC analyzer (Carlo Erba -Total Carbon Monitor mod. 400/P).

For statistical correlation and regression analysis we followed Sokal and Rohlf (1969).

RESULTS AND DISCUSSION

Since the samples were all collected at pH 6.5 the differences among the samples constituted only the amounts of lime added, due to the fact that the initial pH was

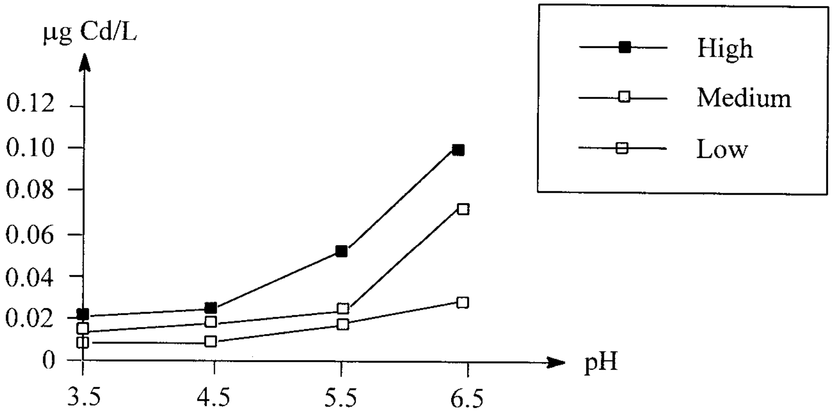


Figure 1. Cadmium levels in the water after addition of lime as a function of starting pH (pH prior to lime addition). High , medium, and low Cd initial levels are shown.

different. From Fig. 1 we see that the more lime we added the more Cd was sedimented. In fact, the amount of lime had a very significant influence on the precipitation of Cd as the reduction in the Cd content in the water varied from 93 % when the initial pH was 3.5 to 52 % (initial pH 5.5). The most probable explanation is that Cd was adsorbed on the lime particles. Kinniburgh and Jackson 1981) found the pH 50 value (pH at which 50 % of the initial concentration is adsorbed) for Cd to be 5.9 on $Fe(OH)_3$ gel. The latter experiment was of short duration and we must assume that equilibrium conditions were rapidly established and, thus, comparable to the present study except for the amount of lime added. This strengthens the theory that the higher sedimentation rate recorded in our study was due to liming. The lime particles obviously play the same role as has been shown for organic particles in other studies. Stephenson and Mackie (1988) found that Cd concentration in surficial littoral sediments covaried with the sediment organic matter(r = 0.74) and was not correlated with either lake pH or aqueous Cd concentration.

The analyses were carried out on samples collected a day after the pH had stabilized at the original level. The Cd levels in the water phase increased with decreasing pH, and especially when the pH dropped below 4.5 (Fig. 2). Such remobilization was not surprising as pH-dependent Cd mobilization has been documented in field studies (Dickson 1980), and in a laboratory experiment with sediment-water microcosms Anderson and Gahnstrom (1985) found that Cd was released from sediments below pH 5. The latter, as well as the present study, indicated that Cd mobilization occurs only at extreme conditions (pH below 4.5 - 5) or such as those connected with snow melting in the spring when such pH values are quite often recorded. Stephenson and Mackie (1988) concluded that

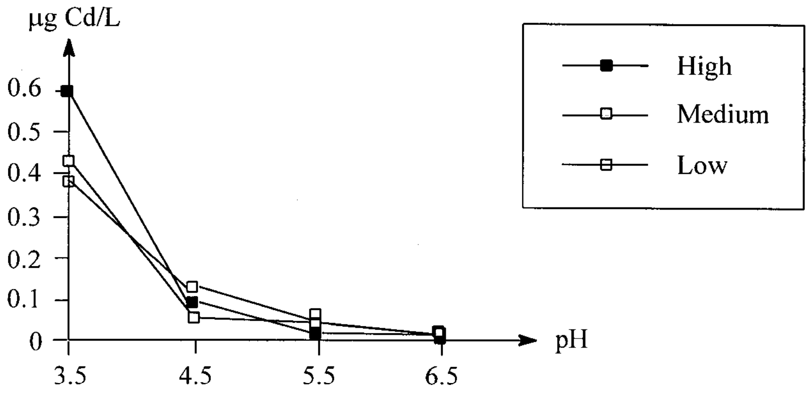


Figure 2. Cadmium levels in the water after reacidification as a function of pH. High, medium, and low Cd initial levels are shown.

reduced Cd burdens in the acidified lakes were the result of a reduction of Cd sedimentation rather than Cd leakage from the sediments. The present findings, however, indicated that remobilization also is a significant factor as the increased Cd levels following acidification in this experiment had to have sedimented Cd as the source.

Water samples collected when pH had stabilized at the respective pH categories contained TOC that were clearly related to pH. The organic content at pH 4.5 constituted only half of that at pH 6.5 (Fig. 3). Similar findings were registered in the field by Wright (1985). When pH decreases fewer organic molecules will be available as adsorption surfaces for Cd and, consequently, less Cd is sedimented. It is, however, important to evaluate how central this mechanism is to govern the Cd-distribution pattern. We have also to consider the properties of the humus particles to retain metals in a solution (*E. G. Gjessing, unpublished data*).

From Fig. 4 we see that there was a clear negative correlation (r = - 0.72) between TOC and Cd in the water phase, but this does not necessarly mean that there was a causal relationship. In this case with the experiment conducted in a closed system the Cd had to occur either in the water phase or precipitated/adsorbed to the sediment. When Cd, prior to addition of acids, occurred only to a very limited extent in the water, the strong increase after reacidification had to have been caused by remobilization from the sediment. This indicates that in this experiment remobilization of Cd from the sediment rather than reduced sedimentation was the dominating mechanism. Since the Cd content prior to addition of acid was very low, it is difficult to say how extensive the reduced sedimentation can be.

This study has shown that in experimentally acidified water reduced Cd levels can be caused by liming and that sedimentation due to adsorption to the lime particles probably is the most significant factor. It has also shown that when the water is reacidified the Cd levels increase with decreasing pH, indicating that the acidity

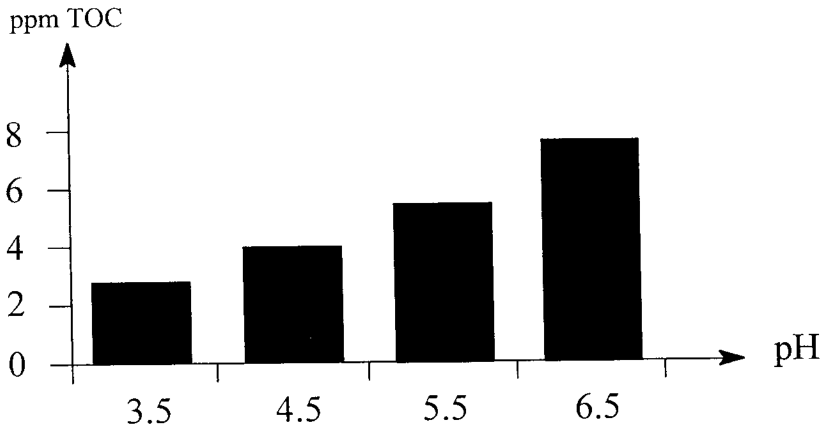


Figure 3. The relation between TOC and pH in the water.

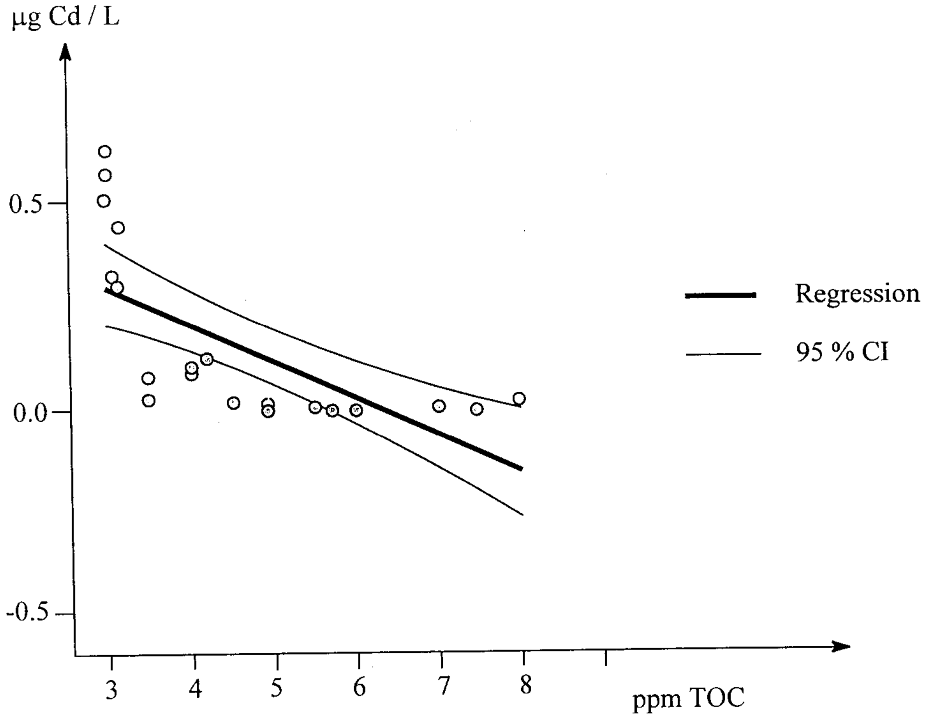


Figure 4. The relation between TOC and Cd levels in the water phase (r=0.72).

itself causes remobilization of Cd. The latter seems to be the dominant mechanism. Furthermore, we found that TOC increased with increasing pH, while the relation between TOC and Cd content was clearly negative.

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