ARE THE EFFECTS OF ACIDIFICATION POSTPONED AND AGGRAVATED BY LAKE LIMING?

- a laboratory study on a re-acidification of the limed Lake Gårdsjön, SW Sweden

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Department of Physical Geography
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Abstract
Several years of liming has created a large store of aluminium in the sediment of many Swedish lakes. Some scientists fear that the aluminium store is a ticking environmental bomb that will go off when the liming operations cease.

This study investigates the chemical changes occurring when limed sediment is exposed to an acid water mass, i.e. a simulated re-acidification.

The sediment cores were taken from Lake Gårdsjön, which has been limed seven times since 1982. The cores were placed in buckets leaving only the top sediment exposed. Acid water was poured into the buckets and water samples were taken during a 54-day period. The sediment content of aluminium and calcium was measured before and after the bucket experiment.

The results indicate that 51% of the added hydrogen ions were neutralised. The neutralisation was mainly accomplished through cation exchange with the topmost centimetre of sediment. It was discovered that the sediment enrichment of calcium had reached deeper than expected, possibly down to 15-20 cm depth. It is, however, unclear if the precipitated aluminium is below the active layer (~2 cm) as well. There are results presented here that suggests that most of the aluminium store may be contained in the topmost 3 cm. It is therefore accessible, but during a period of 54 days with pH around 4.5 a very small amount of aluminium was actually released. The released amount was, however, sufficient to double the water concentration.

It is concluded that a small release of sediment aluminium can yield a highly toxic water mass if the response is sudden. According to this study, the instant release was not very drastic, but further research with longer time scale is needed.

Keywords; sediment profile, Lake Gårdsjön, re-acidification, aluminium, lime dissolution, buffering
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Acknowledgements

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Foreword
This paper is a 20 p study leading to a Master degree in Physical geography. The main work was performed in the period February to June and August 1998, including one field day and several weeks of laboratory work. Bo Lind who, together with Ulf Nyström, is doing research on liming and its geochemical effects suggested the subject to me. The subject appealed to me because of its topicality and the fact that it included some hydrology, which is my main interest. Bo and Ulf have been my tutors and I wish to thank them for their enthusiastic support all through this work. This study would have been impossible to accomplish without the scholarship from Lindeqvistska donationsfonden and financial support from Bo Lind. Many thanks! Note also acknowledgements at the end of this report.

Göteborg 1998-12-14

We have found sediment! Marie Svärd on the right and the author seem very pleased with the catch. Little did they know how this would change their lives for the following months...
1 Introduction

During the end of the 1960s it was discovered that several lakes in southwestern Sweden were lacking fish. It was soon recognised that acidification was the cause. Acidification has struck hardest in Scandinavia and parts of Canada and the US where deposition of sulphur and nitrogen is high and the buffering capacity of the soils are low. Later it has been revealed that it was during the 1950s that the pH of surface waters fell drastically. The acid waters also show high levels of heavy and trace metals because of the acidification. Many of these metals are toxic to the biota.

In 1977 the Swedish government started a liming programme to counteract the damage inflicted to the biota, and bring life back to the lakes. The liming resulted in neutral pH-readings and brought acid-sensitive species back. The toxic metals were to a large extent precipitated to the sediment. In 1990 liming had been executed on more than 6000 Swedish lakes. In 1997, however, the Government proposed to perform severe cut backs on these subsidies. This awakens the question of what will happen when the liming ceases and the lakes are let to re-acidify.

1.1 Aim of this study

This study intends to clarify whether aluminium, calcium and nutrient elements are mobilised from the sediment when a limed lake is re-acidified. This is done through a simulation in the laboratory, with sediment cores from the limed Lake Gårdsjön. There are few earlier studies on the subject. Several authors have focused on effects of acidification (e.g. Dillon & Smith 1984, Renberg et al. 1993, Schindler et al. 1980) and liming (e.g. Henrikson & Brodin 1995, Sverdrup & Bjerle 1983, Yan & Dillon 1984), but there are few addressing the issue of re-acidification (e.g. Andersson & Hultberg 1997, Young et al. 1989).

Specific questions in this study concern:

- What is the buffering capacity of the sediment?
- Will the inactive lime be re-activated and dissolved at the lower pH conditions?
- How thick is the layer of residual lime that contains the great aluminium store?
- Will all aluminium precipitated during the liming period be released and thus create a toxic shock?
- How fast is the release of elements?
- How deep into the sediment will the dissolution penetrate?
- Does circulation induce additional release of elements?
2 BACKGROUND

This paragraph intends to introduce the history and chemistry of acidification, and the countermeasures applied.

2.1 Acidification

2.1.1 Natural acidification

Approximately 12,000 BP, the regressive icefront of the latest glaciation left southwestern Sweden and all present lakes were created as the land was uplifted. The water was then, in most cases, slightly alkaline. As the soil became exposed to acid precipitation there were a number of buffer systems being activated. These buffer systems work in different pH intervals according to table 1.

Table 1. The natural soil buffer systems and their dominant pH working range (Asp et al. 1986).

<table>
<thead>
<tr>
<th>pH</th>
<th>Buffer system</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.6-6.2</td>
<td>Carbonate</td>
<td>CaCO$_3$ + 2H$^+$ ⇌ H$_2$O + CO$_2$ + Ca$^{2+}$</td>
</tr>
<tr>
<td>6.2-5.0</td>
<td>Silicate</td>
<td>(Metal-SiO$_4$)$_n$ + 4nH$^+$ ⇌ (SiO$_2$)$_n$ + 2nH$_2$O + nMetal$^{2+}$</td>
</tr>
<tr>
<td>5.0-4.2</td>
<td>Cation exchange</td>
<td>colloid-Metal + nH$^+$ ⇌ colloid-nH + Metal$^{n+}$</td>
</tr>
<tr>
<td>4.2-3.0</td>
<td>Aluminium</td>
<td>Al(OH)$_3$ + 3H$^+$ ⇌ Al$^{3+}$ + 3H$_2$O</td>
</tr>
<tr>
<td>&lt; 3.0</td>
<td>Iron</td>
<td>Fe(OH)$_3$ + 3H$^+$ ⇌ Fe$^{3+}$ + 3H$_2$O</td>
</tr>
</tbody>
</table>

In addition to these buffer systems, organic acids in surface waters act as a major buffer at pH < 5 (Kullberg et al. 1993). Due to the extensive plucking and abrasion during glaciation, there was plenty of easily weathered material that acted as a buffer for the low acid load that was prevailing. Soon, however, because of the predominance of acid bedrock, the carbonate buffer was depleted, and the slow silicate weathering took over as the dominant buffer system. Charlson and Rodhe (1982) asserts that the rain in remote, unpolluted areas nowadays exhibit a pH of 5.0. This implies that the precipitation that fell 10,000 BP probably was acid as well. More acidity was successively supplied to the soil because vegetation established, and the roots released hydrogen ions as they consumed base cations. The acid load surmounted the rate of weathering and thus the ability to neutralise; a natural acidification had begun.

2.1.2 Anthropogenic acidification

The natural acidification brought the pH down to about 5.5 before humans intervened (fig. 1). The earliest signs of human influence on acidity is from the Iron age, about 2000 years ago (Renberg et al. 1993). During this period pH increased, probably because of forest burning and intensified agriculture that increased the flux of base cations and nutrient elements to the lakes.

During the last 200 years, land use practices have changed dramatically, which also leads to enhanced acidification. In the mid-19th century, much of the forest in western Sweden had been cut down and replaced by heath. Organised afforestation began at the end of the century. It was mostly spruce and pine that were planted. Coniferous forest contributes to acidification in that it produces a more acid humus layer, and filter the air of pollution more effectively than deciduous forest. Therefore, the afforestation is of importance to acidification where the deposition is high (Renberg et al. 1993).

In the beginning of the 20th century most Swedish lakes had a pH between 6 and 7 (Bernes 1991). The industrialisation has led to increased emissions of sulphur and nitrogen. When these compounds are transformed and react with atmospheric water vapour, strong acids are created. Deposition of the increasing amounts of sulphur and nitrogen led to the recent acidification (fig. 1).
Fig. 1. The acidification history of western Sweden. (I) natural acidification, (II) anthropogenic alkalisation (Iron age), (III) the recent acidification, (IV) the liming period (Renberg et al. 1993).

2.2 Liming

Liming was introduced in the 1950s as a measure to mitigate acidification. It was not until 1977, however, that liming received large-scale governmental funding. At first it was a 5-year trial programme receiving approximately 25 million SEK per year (Bernes 1991). In 1981 the programme was evaluated, indicating good results. Therefore the programme was made permanent in 1982 and the funding increased (fig. 2). The Swedish Environmental Protection Agency stated in 1988 that the aim of the programme was that “the natural flora and fauna of surface waters should be able to remain in, or re-colonise the limed waters” (Bernes 1991). This biological goal gave a chemical equivalent “to raise the pH of the water above 6 and the alkalinity above 0.1 mmol l⁻¹”.

Fig. 2. The total amount of lime spread in Swedish lakes under the governmental liming programme. In autumn 1997, the government proposed to reduce the amount by half (Svensson pers. comm.).

In the last decade nearly all liming has been performed with CaCO₃ of the fraction 0-0.2 mm. The recommended dose is 10-75 g m⁻³ depending on pH and the lake retention time (Henrikson & Brodin 1995). When calculating the dose, a slow dissolution from the bottom store is usually included in addition to the direct dissolution.
2.2.1 Dissolution efficiency

Immediately after liming the pH is increased due to primary dissolution of CaCO$_3$. The lime not dissolved, is deposited on the sediment but can, predominantly during the first year, still raise the pH through secondary dissolution. After a while, the dissolution cannot keep up with the acid input and a dilution phase commences. Dilution is, however, not complete during one turnover time. In fact, with complete mixing of chemicals, 37% of the dissolved elements are still present after one turnover time (Henrikson & Brodin 1995). In consequence, the actual re-acidification is slower than the theoretically calculated. In addition, mixing is far from complete in most lakes. Thermal stratification during winter, when ice cover drastically reduces mixing, leads to a quick dilution of the superficial water layers (0-2 m). This dilution leads to acidification of shallow zones even in newly limed lakes.

The rate of primary dissolution (during sinking) depends on technical parameters like dispersion technique, grain size, and dose. In addition, dissolution rate is influenced by physical characteristics like pH and depth. As the lime has sunk to the lake bottom, secondary dissolution takes place. This rate depends on mixing conditions and CO$_2$ partial pressure of the water. Bjerle et al. (1982) concluded that in lakes with high CO$_2$ partial pressures, secondary dissolution could be significant, but not otherwise.

Another important mechanism for the rate of secondary dissolution is precipitation of metal and humus complexes. As they precipitate on the calcite particle, due to the increase in pH, they inhibit further dissolution. Therefore, large deposits of lime can be inactive on lake bottoms, often as soon as two years after liming (Sverdrup & Bjerle 1983). There are, however, studies refuting this. The Lake Lysevatten study (Andersson & Hultberg 1997) indicated a dissolution rate keeping up with the dilution for two years (retention time=2.5 years), but even in the period 3-10 years after lime addition, considerable amounts of Ca was dissolved. Calcium content was not back to pre-liming levels until 10 years after liming.

The buffer systems, e.g. Al, utilised during acidification will act reverse at liming, i.e. they will consume substantial amounts of base cations before a storage of alkalinity can be built up. In the most acidified lakes in the experimental neutralisation in the Sudbury area, metals consumed 30-41% of the added base (Yan & Dillon 1984). Only 5-20% was utilised to raise the pH. Not only the water column is important in these calculations. A considerable amount (31-44%) of base was consumed to neutralise the sediment.

2.2.2 Effects on metals

As mentioned above, the increase in pH caused by liming makes most toxic metals precipitate to the sediment. Thus, the water column environment is improved but the sediment receives toxic metals instead. This may influence the benthic fauna, so to decrease decomposition and respiration. The reduced nitrification found by Roelofs et al. (1995) was due to decreased redox potential which also led to increase of iron in sediment pore water. Gahnström (1988) studied the microbial activity in sediment after liming. His results show an initial decrease, but the activity is recovered or even higher after 1-2 months. The initial decrease is probably due to the falling pH as Ca$^{2+}$ exchanges H$^+$ in the sediment, and perhaps also increased metal content.

Several authors have verified a decreased level of Al in the water after liming (e.g. Wright 1985, Yan & Dillon 1984, Driscoll et al. 1989a, Andersson & Hultberg 1997) (fig. 3). The reductions in the water column can, however, proceed rather slowly (a matter of months) if the lake is low in particulate matter on which the metals can precipitate (Driscoll et al. 1989a).
Fig 3. Aluminium concentration in Lake Lysevatten – one of the few re-acidified lakes that have been thoroughly investigated. Arrows mark liming operations. Note the successively higher summer concentration, and that the decrease after liming is not instantaneous (Andersson & Hultberg 1997).

2.3 Chemical considerations on re-acidification

The term re-acidification here refers to the acidification process of a lake, after a period of liming. The obvious difference between acidification and re-acidification is that the latter depends on the lake retention time and is therefore much faster. This paragraph will go deeper into the chemical aspects of acidification, especially after liming.

2.3.1 Calcium

Calcium is a rather conservative element in natural waters, i.e. it is mostly in its dissolved form and does not form precipitates. In terrestrial runoff, however, some Ca can form complexes with organic anions and humus. Calcium is supplied through weathering of soils and aerial deposition, and is thus mostly controlled by weather and hydrological load. In the Gårdsjön area, 11% was calculated to be derived from sea salts (Hultberg 1985). Some sorption to sediment occurs, but in acidified lakes, Ca content generally decreases towards the sediment surface. This is due to the mobility of the Ca$^{2+}$ ion. Already at moderately acid conditions it will exchange with H$^+$ (fig. 4, see also fig. 7).

There is dispute whether the sediment has a significant Ca exchange with the water. Wright (1985) claims that the diffusion is too slow. He concludes that large changes in Ca concentration in limed waters are due to secondary dissolution of residual limestone rather than ion exchange with the sediment.

During re-acidification, when pH falls below 6, dissolution of limestone can proceed according to reaction (1) (Asp et al. 1986).

\[
\text{CaCO}_3 (s) + H^+ \Rightarrow \text{Ca}^{2+} + \text{HCO}_3^- \quad (1)
\]

If the rate of acidification is faster than limestone dissolution, HCO$_3^-$ will be consumed according to the equilibrium reaction (2). The carbonate acid may be transformed to water and carbon dioxide, but this second step is much slower.

\[
\text{HCO}_3^- + H^+ \Leftrightarrow \text{H}_2\text{CO}_3 \Leftrightarrow \text{H}_2\text{O} + \text{CO}_2 \quad (2)
\]
Fig. 4. Metal concentration in supernatants of different pH after a few days shaking. The sediment was collected from typical headwater lakes in Canada. Aluminium show a marked increase below pH 4. Calcium is extracted in considerable amounts already at pH 6 (Oliver & Kelso 1983).

Young et al. (1989) do, however, state that the increased Ca content in bottom waters after liming will reverse the gradient, thus diffusing Ca down into the sediment (fig. 5). This diffusion will create a store for the following re-acidification. The depth of this diffusion seems to reach 4-5 cm down into the sediment.

Fig. 5. Sediment depth profiles of pH and calcium before and after calcite treatment. The treatment has created a downward flux of calcium enhancing the pH down to at least 5 cm depth. Liming was performed in June 1985 (Young et al. 1989).
2.3.2 Buffering by sediment

The sediment may buffer the water through several processes. Many of these are seasonal, such as photosynthetic activity; reduction of sulphate, iron, manganese, and nitrate; and hydrolysis of ammonia. Decomposition will lead to production of HCO$_3^-$ . These processes are predominantly active during the summer. Reduction of Fe$^{3+}$ can be the most significant source of alkalinity (Dillon et al. 1997), but it is temporary since Fe$^{2+}$ is oxidised back at autumn circulation.

The most important continuous source of alkalinity is cation exchange, but this is predominantly active during early stages of acidification. In a study where a lake was experimentally acidified from pH 6.5-6.8 to 5.0-5.2 in 6 years the sediment pore water exceeded pH 6 already 5 mm down, and seemed unaffected at greater depths (Kelly et al. 1984). After liming, alkalinity production might increase due to enhanced microbial activity, but it is exceeded by alkalinity consumption through Al hydrolysis (Driscoll et al. 1989b).

2.3.3 Aluminium

Aluminium is the most common metallic element in the lithosphere. It occurs mostly in silicates and clay minerals. In water, however, Al content is rather low because it is not leached from the soils until pH is below 4.2. Apart from the many different minerals in which Al is abundant, it also forms complexes of different kinds when in solute phase. A coarse classification of the different species of Al is presented in table 2.

<table>
<thead>
<tr>
<th>Table 2. Classification of aluminium species (Driscoll 1989).</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Soil and sediment</td>
</tr>
<tr>
<td>a) Exchangeable (acid soluble)</td>
</tr>
<tr>
<td>b) Amorphous</td>
</tr>
<tr>
<td>c) Crystalline</td>
</tr>
<tr>
<td>2. Solution</td>
</tr>
<tr>
<td>a) Free inorganic (Al$^{3+}$)</td>
</tr>
<tr>
<td>b) Inorganic complexes (OH$^-$, F$^-$, SO$_4^{2-}$, possibly Si)</td>
</tr>
<tr>
<td>c) Organic complexes</td>
</tr>
<tr>
<td>3. Living biomass</td>
</tr>
</tbody>
</table>

Here, we are most concerned with the solution forms, in which several Al species can exist synoptically. Therefore, in addition to the total content of Al, the proportion of different species is also interesting to determine. Especially since organic complexes are far less toxic than the inorganic ones. There is no specific concentration of aluminium defined as the toxic level. It is varying for different biological species. Some are harmed already at 50 µg l$^{-1}$. Such low levels are seldom reached even in the limed Lake Gårdsjön.

Generally in papers addressing acidification, aluminium is simply classified as inorganic, organic, and acid soluble. The acid soluble part is made up by the free Al$^{3+}$ ion and the Al on particulates that can be extracted by an acid (1a in table 2).

Liming drastically reduces the water mass content of aluminium and transports it to the sediment. If the lake is let to re-acidify, it is possible that the aluminium in the sediment will be released again. In that case, even higher concentrations than before will result since the terrestrial supply, in most cases, has not been reduced. Andersson and Hultberg (1997) found significantly higher levels of inorganic Al at the bottom than in the surface water after re-acidification of Lake Lysevatten. They suggested that this was due to re-dissolution of Al(OH)$_3$. Leaching from the sediment is probably most important at early stages of acidification. Later, when the superficial sediment have been depleted, the acid water makes it harder for the metals to precipitate which leads to reduced sedimentation (Andersson 1985b).
High concentrations of Al in land runoff usually occur during wet periods after dry spells (Driscoll 1989). During a summer dryness period, groundwater levels sink, reaching less acid and less permeable layers. This reduces the outflow and dissolution of Al. At snowmelt or rainstorms the high groundwater table reduces the soil contact time. Small amounts of Al are picked up and are instead transferred to surface waters.

In coastal areas, like Gårdsjön, storms can bring substantial amounts of sea salts to the catchment (Nyström 1996). High concentrations of Na\(^+\) compete with H\(^+\) and Al\(^{3+}\), which are expelled from the colloids. These ions are then easily transported through the soil because of the abundance of anions (Cl\(^-\) and SO\(_4^{2-}\)), also from the sea salt. Andersson and Gahnström (1985) showed that the ion exchange in the sediment also clearly was affected by increased salinity. In an exchange experiment, similar to this study, NaCl was added to one core whereby the concentrations of several metals were increased in the overlying water.

As the aluminium has reached the lake, it can be precipitated or incorporated in a complex by anions, organics or phosphorus. Since most metals increase their mobility under acid conditions, Al may again be released from the sediment during re-acidification. In general, the superficial sediment of acid lakes shows reductions in Al content towards the surface (Langelo & Steinnes 1995). This may depend on increased release because of acid conditions, or reduced sedimentation rates because of diminished supply of ligands or of the element itself.

Some studies (e.g. Renberg 1985) have indicated increased sediment accumulation of Al during acidification. This may be explained by the low pH values in the catchment yielding large quantities of dissolved Al. The lake water, and especially the hypolimnion, has higher pH, which leads to precipitation. This should occur at early stages of acidification when the lake is much less acid than its catchment.

### 2.3.4 Sediment chemistry

Acidification makes most ions more mobile and many elements are therefore released from the sediment. This can be seen in sediment depth profiles (fig. 7). Lake Lille Hovvatn is naturally acidified while Lake Store Hovvatn has been limed for several years.

![Fig. 7. Sediment depth profiles for Al, Ca and Mg in two Norwegian lakes (Langelo & Steinnes 1995).](image)
The acid lake is depleted of base cations and aluminium in the surface sediment. Note that the concentration of Mg increases towards the surface in the limed lake although no significant amount is supplied with the lime. This might depend on the high pH that reduces the mobility of Mg, and creates a downward flux to the sediment. Note also that the Mg and Al profiles diverge at 5 cm depth while Ca increase reaches deeper. This is probably an effect of undissolved CaCO$_3$ grains that have worked their way down through the lighter sediment with the aid of bioturbation and water movements.

Aluminium does not seem to be enriched very much in the limed lake, but compared to the depletion in the acid lake, the difference is substantial. Viewing these profiles it is easily understood that if a liming programme is interrupted and the re-acidification is completed in a few years instead of 30, as has been the natural case, it would be disastrous if all the precipitated aluminium was released.
3 STUDY AREA

The facts describing the study area are predominantly collected from literature written in 1985, concerning measurements done in 1979-1985. This must be kept in mind for factors like vegetation and acidification that are likely to have changed during the last 15 years.

After the governmental liming programme was initiated in 1977, it was considered that research was needed on the effects arising from liming. Lake Gårdsjön was chosen for this task. The measurements started in 1979 and were most intensive during the 1980s. Thus, the study area has a lot of background data.

3.1 General description

The area of concern, Gårdsjön, is a subcatchment to River Anråseån catchment. It is situated in Sweden, 58°04’N/12°03’E, 10 km from the west coast, 50 km north of the city of Göteborg (fig. 8a, b). This is the area of the most severe acidification in Sweden. The area of the Gårdsjön catchment is 2.1 km$^2$ and is located at the eastern water divide of the Anråseån catchment. The altitude increases successively from the coast and ranges between 113 and 170 m a.s.l. in the catchment (Olsson et al. 1985). The general geomorphology is broken into small hills and valleys. 27% of the catchment is situated above the highest coastline, which lies at 130 m a.s.l.

![Map of the study area](image)

Fig. 8. The location of the study area. The Lake Gårdsjön catchment (c) is situated at the eastern water divide of the Anråseån catchment (b). Marked in map c is the sediment sampling location (A) and the water collection site (B) (Andersson & Olsson (eds.) 1985).

3.2 Geology

3.2.1 Terrestrial features

The catchment is dominated by three similar types of bedrock; igneous granite plus old and young metamorphic granodiorite (Olsson et al. 1985). These are not easily weathered and of intermediate to acid composition.
Relatively high concentrations of Ca are found in the northern part of Lake Stora Hästevatten. The high concentrations result because a more easily weathered granodiorite is located there (Hultberg 1985). This leads to an inverse gradient of Al and H⁺, increasing in the downstream direction, contradictory to the normal case.

The ground consists of almost equal amounts of bedrock outcrop and till cover (table 3). The rest is mostly peat. The cover of till, which is thin and of local origin, accumulated in small pockets in the bedrock. The till is fine-sandy, silty with a mean clay content of 5%.

Table 3. Quaternary deposit distribution in the Lake Gårdsjön subcatchment (Olsson et al. 1985). Till cover was by Olsson et al. defined as cover >30 cm thick.

<table>
<thead>
<tr>
<th>Area (%)</th>
<th>Bedrock outcrop</th>
<th>Till cover</th>
<th>Peat</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>49</td>
<td>42</td>
<td>8</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

The shores adjoining Lake Gårdsjön are generally steep (fig. 9) and constitute 34% bare bedrock and 51% soil cover thinner than 50 cm (Johansson & Nilsson 1985). The fact that the bedrock is acid and resistant to weathering, together with the relatively sparse and thin soils, results in a very low neutralisation capacity. The pH never exceeds 5 down to a depth of 50 cm mineral soil. The cation exchange capacity is to 90% filled by Al³⁺ and H⁺ from 10 down to 50 cm depth (Olsson et al. 1985).

3.2.2 Lake sediment

The superficial sediment (0-10 mm) has a 95% water content and 40-50% organic matter (dry weight) (Gahnström & Andersson 1985). Erosional bottoms are practically absent. Bedrock and sandy bottoms constitute less than 10% of the total lake area.

Acidophilic diatoms have been increasing in abundance from 7 cm and up (Renberg & Wallin 1985). The sediment per se has, however, not been acidified more than 1 cm down (Gahnström 1985). The sedimentation rate has by Renberg (1985) been estimated to 65 g m⁻² year⁻¹. This is roughly equivalent to 1 mm year⁻¹. He discovered an increased sedimentation of Al under the acidification period (section 2.3.3). The results of Nilsson (1985) indicate a lake retention of Al, especially organic species.
Andersson (1985b) estimated the release of Ca from the sediment to 10% of the lake output. The increase with depth can result because of greater sediment-producing water column or a greater leaching in the more acid surface waters. Hultberg (1985) asserted that the sediment retention was negligible for all base cations and Cl.

Andersson (1985b) also calculated the area that theoretically should not be subjected to accumulation of organic material. The calculations indicated a depth limit of approximately 2 m, resulting in 7 ha of transport or erosional bottom. His field survey does, however, reveal a much smaller extent of erosion, and he also concludes that the massive development of benthic vegetation along with acidification has altered the depositional pattern. This means that some localities will return to a erosional bottom condition after liming, producing a re-suspension of sediment.

3.3 Vegetation

Norway spruce (Picea abies) and Scots pine (Pinus sylvestris) dominate the Gårdsjön forest. Deciduous trees are scarce (table 4), but young stands exist in the clear-felled areas. Clear-felled areas are located in the upper reaches of the catchment, resulting in relatively low dry deposition there. Soil horizons are mostly podsolic. The prevalence of coniferous trees is an exacerbating factor of acidification in the area. The area, with its broken topography, is not suited for agriculture, but was used for grazing until the 1950s. Pollen analysis shows that a shift in vegetation dominance has occurred. Coniferous forest, especially spruce, has expanded at the expance of deciduous since early 19th century.

Table 4. Forest characteristics of the Lake Gårdsjön catchment (Olsson et al. 1985).

<table>
<thead>
<tr>
<th></th>
<th>Mixed forest</th>
<th>Pine forest</th>
<th>Clear-felled area</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area (%)</td>
<td>33</td>
<td>28</td>
<td>36</td>
<td>3</td>
</tr>
</tbody>
</table>

3.4 Hydrology

3.4.1 Climate

The hydrological regime of the area is ‘Atlantic rain and snow regime’ (Olsson et al. 1985) with peak runoff at spring snowmelt, and autumn rains. The peaks are generally in the same order of magnitude. Measured annual precipitation for Lake Gårdsjön (1979-94) is 1145 mm, with maximum and minimum values of 1432 and 952 mm respectively (Andersson et al. 1998). Evaporation is only significant from April to October. Precipitation intensities are low to moderate except in the summer when heavy showers can occur. The area is normally covered with snow for 50 days per year (Dahlström 1995).

3.4.2 Runoff

The distribution of runoff can vary substantially over the year depending primarily on winter temperatures. Mild winters, with large proportions of rain, generate high runoff during the winter, while a more severe winter delays peak runoff to spring snowmelt. The groundwater contribution is substantial in this area. During snowmelt, groundwater made up 67-80% of the total discharge, and during rainfall 81-96% (Rodhe 1985). The fraction of saturated areas generating surface runoff in the catchment is small. It amounted at the most to 0.16 at snowmelt, and 0.04 during summer rainfall events. The thin soils lead to a rapid response in runoff. Many of the tributaries, however, run dry during the summer months. In a 14-year period (1979-93), monthly runoff varied between 0 and 215 mm with an annual mean of 580 mm (Andersson et al. 1998).
3.4.3 Lake dynamics

The lake is dimictic in the southern basin where the maximum depth reaches 18 m (fig. 8c). The northern basin has a maximum depth of 10 m. The thermocline is generally at 4 m in early summer, but reaches down to 12 m in late summer (Hultberg 1985). This leaves as little as 10% of the basin as a hypolimnion. It is only in this limited volume that low oxygen levels can be encountered in late summer (Gahnström 1985). The runoff (580 mm year\(^{-1}\)) results in a theoretical turnover time for Lake Gårdsjön of 1.2 years. The lakes are usually ice-covered from December to March (Olsson et al. 1985). In the 19th century there was a regulation that raised the surface of Lake Gårdsjön with 1.5 m, increasing its area with 25%.

3.5 Acidification and liming history

3.5.1 Course of acidification

The beginning of recent acidification of Lake Gårdsjön was dated to the 1950s (Renberg & Wallin 1985). The pH dropped from around 6 to 4.5-4.8 in 30 years (fig. 10). This period is equivalent to the top 7 cm of sediment.

![Acidification history of Lake Gårdsjön as deduced from diatoms and Sphagnum leaves in the sediment (Renberg & Wallin 1985).](image)

**Fig. 10.** Acidification history of Lake Gårdsjön as deduced from diatoms and Sphagnum leaves in the sediment (Renberg & Wallin 1985).
3.5.2 Pre-liming chemical characteristics

Extensive investigations of the pre-liming conditions were conducted in the years 1979-80. Measurements of pH in sediment pore water (Andersson 1985a) show increases (5.0-6.3) down to about 6 cm. This means that even though lake water may have acidity enough to leach metals from the sediment, this acidity does not reach deep into the sediment strata. In fact, sediment pH shows a distinct acidification in the topmost 2 cm only (fig. 11). Elements are supplied through the main inlet, the seepage area, and deposition. In the case of Al, the seepage area is of great importance (fig. 12).

Persson and Broberg (1985) asserts that one third of the phosphorus input is through atmospheric deposition, suggesting that the P levels can reach approximately 2 µg l⁻¹ at the least. The main supply of nitrogen is through deposition, and the budget is very dependent on the efficiency of nitrification/denitrification. Table 5 displays some pre-liming chemical characteristics for Lake Gårdsjön.

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>Ca (µg l⁻¹)</th>
<th>Mg (µg l⁻¹)</th>
<th>K (µg l⁻¹)</th>
<th>Na (µg l⁻¹)</th>
<th>Al (µg l⁻¹)</th>
<th>Total-P (µg l⁻¹)</th>
<th>Total-N (µg l⁻¹)</th>
<th>Conductivity (mS m⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Main inlet</td>
<td>4.71</td>
<td>1880</td>
<td>1110</td>
<td>550</td>
<td>4800</td>
<td>290</td>
<td>5.6</td>
<td>385</td>
<td>6.12</td>
</tr>
<tr>
<td>Outlet</td>
<td>4.68</td>
<td>1750</td>
<td>1220</td>
<td>610</td>
<td>5550</td>
<td>290</td>
<td>4.0</td>
<td>301</td>
<td>6.74</td>
</tr>
</tbody>
</table>

3.5.3 Liming of Lake Gårdsjön

Lake Gårdsjön was first limed in 1982. 110 tonnes of CaCO₃ was dispersed. The lime was mixed with lake water into a slurry that was pumped out. The total dissolution was about 80% in 3.3 years. Of these 80%, 59% of the lime was dissolved during the first year, 14% during the second, and 6% during the third (Hultberg & Nyström 1988). Periods of high discharge flushed considerable amounts of Ca out of the lake, reducing the duration of the positive effects induced by the lime considerably. Since 1982 the lake has been limed 6 times (table 6). During this time pH has been between 6 and 7 with a few acid pulses reaching down below 6 (Nyström pers. comm.).

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Lime spread (tonnes CaCO₃)</td>
<td>110</td>
<td>37</td>
<td>104</td>
<td>56</td>
<td>56</td>
<td>31</td>
<td>31</td>
<td>74</td>
</tr>
</tbody>
</table>
Nyström (pers. comm.) has performed a budget calculation of calcium in order to get the amount of undissolved lime. These calculations are based on Ca measurements at the main inlet, outlet and a minor inlet. The value from the minor catchment has been extrapolated to the entire seepage area. The calculations yield a residual store of 26 tonnes of Ca (=74 tonnes CaCO₃). This corresponds to 85 g Ca m⁻², which with consideration to sedimentation rate is equivalent to 50-100 mg g⁻¹ (dry weight) (Andersson pers. comm.). These calculations suggest that each of the sample cores should contain a total Ca content of 129 mg.
4 Methods

4.1 Sampling
Samples were collected on March 26 1998, two days after ice break-up. The sampling site (fig. 8c) was chosen on the basis of suitable depth (3.7 m) and low organic content. A low organic content was favoured since the sediment was said to be very liquid and loose (Renberg, Gahnström, pers. comm.). The sample device was fastened to steel rods. The samples were taken in removable plexiglass tubes with an 44 mm inner diameter. Reaching the bottom, the tube was slowly driven into the sediment. A 25 cm sample needed 120 cm of depression from the bottom surface. This phenomenon is probably due to choking of the tube after some 20 cm, which then acted as a rod displacing the underlying sediment until the clay was reached. The clay offered sufficient resistance to enter the tube. Each core was enclosed with plastic foil and kept standing in its tube. A total of eight samples were taken, all from the same site. It is assumed that all cores have the same chemical composition.

In the laboratory, later the same day, six of the samples were pushed to the top of the tube, and the top 10 cm was cut off and saved. This upper part now constituted the sample. The bottom of this sample was again enclosed with plastic foil. The two remaining cores were used for examination of "pre-leaching depth characteristics".

On the same day, 100 l of acid water was collected from an unlimed upstream lake, Lake Stora Hästevatten (fig. 8c). This water was used for water exchange and reference in the experiment.

4.2 Laboratory procedures

The setting for the experimental leaching was completed on the next day, March 27. Each one of the six cores was placed on the bottom of a 10 litre polypropene bucket. The tube was stabilised with a wooden stick that was fastened to the bucket brim with adhesive tape. In three of the buckets, a so-called "filter pump" (Hydro Crystal P10II), usually used in aquariums, was installed (fig. 13). The pumps have a capacity of 30 l h⁻¹. The filter was, however, removed before installation, so the water was merely circulated. The other three buckets were kept unstirred.

Then, 5.6 l of acid lake water was carefully poured into the buckets. This volume is equivalent to the water column above the sediment in the lake. The concentrations encountered in the buckets are therefore the same that should occur in the lake.

The buckets were kept in a relatively dark room at 21-25°C. The reference water was kept in 25-litre polypropene containers with the cap removed for aeration. A water sample was taken from the reference water giving the starting value. It was then discovered that this water was not as acid as anticipated (pH=5.5).

Therefore, on day 1, HCl (0.025 M) was added to the buckets as well as the reference containers. The intention was to lower the pH of each water mass to 4.5, and the amount of acid to add was tried out on water samples from the reference container.
Since pH increased in some buckets, a second acid pulse was created on day 7, lowering the pH of the containers to 4.4. This time, a corresponding amount of acid was added to the buckets, regardless of present pH, i.e. they did not have the same target pH, as was the case at the first acid addition.

From the starting date, water samples were taken according to table 7. The water samples were taken by pipette, approximately 1 cm above the sediment.

Table 7. Schedule for sampling and management of the bucket experiment ("x" denotes operation).

<table>
<thead>
<tr>
<th>Day</th>
<th>pH</th>
<th>Alkalinity</th>
<th>Water exchange</th>
<th>Metals + Tot-P</th>
<th>Tot-N</th>
<th>Addition of HCl</th>
<th>Conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>46</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>54</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Water renewal was operated in such a manner that the turnover time of the bucket was 30 days. It was performed according to table 7. The new water was poured into the bucket. The theoretical turnover time was, however, altered by evaporation, which amounted to 0.056 l day$^{-1}$ in the unstirred buckets, and 0.130 l day$^{-1}$ in the circulated ones. To prevent this additional loss of water, the buckets were sealed with plastic foil on day 10. Despite the plastic foil, some water was lost through evaporation every day. Because the volume was held constant, this means that the circulated buckets received $7.94 \times 10^{-4}$ moles H$^+$ while the unstirred were added $7.41 \times 10^{-4}$ moles.

The water samples were transferred to polyetene bottles or test tubes which had been rinsed with 3 M HCl. Bottles for metal analysis were refrigerated while the water for total-N analysis were filtered, transferred to test tubes, and stored in the freezer. The analysis was performed on an ANTEK 7000 element analyser. Metals and phosphorus were, however, analysed by the method ICP200. Any speciation of aluminium could unfortunately not be fitted into the budget of this study.

The two remaining cores were divided into eight slices on March 31 in order to get depth profiles. The uppermost 2 cm were divided into three parts, then 1 cm slices down to 5 cm, and finally section 6-7 and 8-9 cm. After drying in room temperature, the slices were weighed. Then the samples were boiled in 40 ml of HNO$_3$ (2M) at 85° C for 2 h. The supernatant was decanted and centrifuged at 4000 rpm for 15 minutes. This method is developed at the Earth Sciences Centre.
In order to see how much aluminium that could not be extracted by acid, the residual from the boiling was filtered, dried, weighed, and then put into the oven at 600° C for 1 h. After weighing, these burnt residuals were again boiled in HNO₃. The supernatants from the boiling were analysed for aluminium, calcium, and magnesium by an ICP.

After the leaching experiment two of the bucket cores, one from each type of bucket, were treated in the same manner as the pre-leaching ones.

4.3 Sources of error
The choking of the sample tubes described in section 4.1 is likely to has occurred at different sediment depths. Some cores may have been split in the top 10 cm.

As the sediment was very loose, it was probably compacted by the sampling and some of the surface sediment may have escaped out the top of the sample tube.

The rapid increase in temperature as the water was brought indoors (0-20° C in one day) is highly unnatural.

The two “pre-leaching cores” were standing for five days before they were sliced. During this time they were of course aerated to some extent and the interstitial water was drained down the cores. This might have caused chemical transformation and migration.

Although the water renewal was performed very carefully it still gave rise to some unwanted circulation in the unstirred buckets. This circulation was probably enough to mix the water completely, but should not affect the diffusion rate significantly.

The experimental setting can, of course, not be similar to in-lake conditions. The most important discrepancies should be different temperature, pressure, light conditions, biotic interactions, water exchange rate, advection and supply of elements.

The pH measurements were not fully reliable because of an old electrode. There was a drop on day 22 which is hard to explain. Similar drops have been recognised in other studies (Wällstedt 1998) and the cause has been ascribed to sulphide oxidising bacteria. In this study, however, the drop cannot be verified in any other measurements and it is highly unlikely that the sediment should have been anoxic (section 3.4.3). To check the electrode, all samples were measured with two different electrodes from day 12 and onwards. The result is reported in section 5.1.2. Both electrodes actually mark a drastic fall of 0.4 pH-units on day 22. pH was, however, continuously rising during the actual measurements. It seems that pH actually was very low, but there was some kind of transformation in the water as it was taken from the buckets. At the next measurement, on day 25, pH was still low according to the old instrument while it was back to “normal” with the new one. No explanation has been found for this behaviour. The old electrode values were corrected in the period 22-35. For validation and further discussion, see section 5.1.2.

The water analyses were divided into two series; the first 30 days and the rest. This could have significance, e.g. if the storage time was different.

The reference water made up a very small volume from the last water exchange on day 50 to the last sampling on day 54. This is probably the reason for some strange values from this day.

Only one reference sample was taken each day, which makes those results vulnerable for measuring errors.
5 RESULTS

5.1 Leaching experiment

5.1.1 Chemical characteristics of the reference water

Some chemical parameters measured on day 0, before it was added to the buckets, are compared to one year weighted means (table 8) calculated by Hultberg (1985). All parameters are somewhat lower now than in 1980, except Na and pH.

Table 8. Some chemical parameters of the reference water compared to measurements from 1980 from the same sample location (Hultberg 1985). The values from 1980 are weighted means for one hydrological year.

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>Ca (µg l(^{-1}))</th>
<th>Mg (µg l(^{-1}))</th>
<th>K (µg l(^{-1}))</th>
<th>Na (µg l(^{-1}))</th>
<th>Al (µg l(^{-1}))</th>
<th>Mn (µg l(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>L. Stora Hästevatten N (1980)</td>
<td>5.28</td>
<td>2270</td>
<td>1160</td>
<td>610</td>
<td>4560</td>
<td>130</td>
<td>40</td>
</tr>
<tr>
<td>Reference container (1998)</td>
<td>5.47</td>
<td>1960</td>
<td>1070</td>
<td>560</td>
<td>6420</td>
<td>85</td>
<td>27</td>
</tr>
</tbody>
</table>

5.1.2 pH

The pH in the reference container was 5.5 at the start of the experiment (fig. 14). This level was sustained until day 1 when HCl was added, and the pH fell to 4.7. During the rest of the first week the pH was stable.

The bucket water exhibited a different outcome during the first days. The circulated ones exhibited a raised pH and the acid pulse could not reduce the acid level to lower than pH 5.1. Obviously there was significant buffering taking place. The pH was again raised after the first acid pulse, and the buffer store had apparently not been exhausted. The buffering was lower in the unstirred buckets which stabilised at pH 4.9.

![Development of measured pH during the leaching experiment](image)

**Fig. 14.** Development of measured pH during the leaching experiment (old electrode, see section 4.3). Arrows indicate time for addition of HCl (day 1 and 7). Note the small difference between buckets with one exception.
The second acid pulse, performed on day 7, was gentler and reduced the pH in the reference container and the unstirred buckets to 4.4. The unstirred buckets did not offer any resistance to this addition of acidity and the buffer store seems depleted. The circulated buckets experienced a fall to pH 5.0 but did not recover.

It should be noted that measurements were not made every day (table 7). A gradual decrease in pH from day 7 to 10 results since no measurements were made in this period. The actual development was probably an instantaneous fall, followed by a relatively stable phase.

In the experiment there are three circulated buckets, three unstirred, and one reference without sediment (section 4.2). The similarity between buckets (as in fig. 14) goes for all measured parameters and results are therefore presented as means in the following figures.

There is a drop in pH from day 20 to 22, which probably is due to some instrumental malfunction (section 4.3). This suspicion is strengthened when viewing figure 15 where the cumulative change in conductivity is compared with the cumulative change in the proportion of conductivity that can be explained by changes in pH (H⁺).

This proportion is unexpectedly large but this is not the main issue. During the first 20 days the graphs follow each other well. At day 20, however, the H⁺ curve is rising rapidly and this is not accompanied with a rise in conductivity. This verifies the assumption of pH instrument malfunctioning. It is, however, hard to assess when the values are normal again.

Fig. 15. Comparison of the cumulative change of conductivity and conductivity caused by change in hydrogen ion concentration during the leaching experiment. On day 20 the graphs diverge in an unnatural manner, probably because of pH instrument malfunctioning (old electrode, see section 4.3). Calculations presented here are for unstirred buckets only.

The control measurements mentioned in section 4.3 are presented in figure 16. The old and the new electrode readings are relatively well correlated in day 12-20. On day 22 the mysterious drop occurs according to both electrodes. In days 25-40 the new electrode is back to “pre-drop values” and is stable there. In the same period, the old electrode seems to be catching up. In days 40-54 the difference between the two series is of the same magnitude and they are again well correlated.
Fig. 16. *Comparison of pH measurements with two different electrodes in circulated (broken lines) and unstirred buckets (solid lines).* The poor correlation in the “bad period” is taken as an indication that the old electrode is malfunctioning.

The two series lie at different levels because the new instrument gives a reading automatically after approximately 1 minute while the old is read manually when the drifting stops (approximately 8 min.). Thus the old level is considered more accurate. Since both instruments indicate a drop on day 22 this must be accepted and the old reading is used. In the period of day 25-35, however, the old readings are corrected. The difference between the two electrodes from the “good period” (days 12-20 and 40-54) is subtracted from the new electrode readings in the “bad period” (days 25-35).

The justification of the pH correction is as follows:

- There are three readings at every measurement with the new electrode instead of one with the old one.
- There are no changes in conductivity or ion concentration that could suggest a lowered pH in this period.
- The two electrodes are well correlated except in this period.
- The new electrode is more sensitive to waters of weak ion strength.

To investigate the buffering further the calculated pH expected by dilution from the water exchange was compared to the observed (fig. 17). It can be seen that the buffering was rather effective during the first acid pulse, but not at the second. The dilution curve displays an increase after the first acid pulse, which is impossible without buffering. This is explained by the fact that the reference water also offered some resistance to the acid addition (table 9). Thereby the observed pH in the reference container was higher than the calculated value for the buckets. The unstirred buckets suffered hard at the acid pulses but kept up relatively well with the circulated buckets as long as water exchange was the only acid addition (table 9).
Fig. 17. Comparison of the observed pH value (corrected, see section 4.3) in the buckets with the expected through dilution and no buffering. The acid additions on day 1 and 7 are included in the dilution series. It can be seen that the circulated buckets offered a more effective buffering.

Table 9. The proportion of hydrogen ions that were neutralised at the acid additions. A proportion over 100% means that the pH was higher than before even though acid was added. Note that even the reference water offered buffering. This is why the dilution curve in figure 17 is not planar.

<table>
<thead>
<tr>
<th></th>
<th>Acid pulse 1</th>
<th>Days 2-7</th>
<th>Acid pulse 2</th>
<th>Days 10-20</th>
<th>Days 20-30</th>
<th>Days 30-40</th>
<th>Days 40-54</th>
<th>TOTAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>53</td>
<td>-</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>34</td>
</tr>
<tr>
<td>Unstirred</td>
<td>67</td>
<td>137</td>
<td>-21</td>
<td>76</td>
<td>36</td>
<td>65</td>
<td>68</td>
<td>51</td>
</tr>
<tr>
<td>Circulated</td>
<td>84</td>
<td>154</td>
<td>68</td>
<td>78</td>
<td>67</td>
<td>76</td>
<td>86</td>
<td>80</td>
</tr>
</tbody>
</table>

5.1.3 Water concentrations

In figure 18 it can be seen that the development for most elements are the same. A rapid increase in concentration the first 10 days followed by a slow decline. This development is verified by the conductivity with one exception. The conductivity peaks at day 15 instead of day 10. Because no data are available on anions, the plausibility cannot be analysed.

Total nitrogen concentration experienced a drastic fall from 1600 to 400 µg l\(^{-1}\) during the first day (fig. 18). This was probably due to enhanced biologic uptake triggered by the increase in water temperature (0-20\(^{\circ}\) C). Later the nitrogen remained stable around 500 µg l\(^{-1}\) and there was no difference between the buckets. There may actually have been an increase the first 10 days, possibly because some species could not stand the rapid change in environment and died, thereby reducing uptake and releasing nitrogen. The rise on day 30 is probably an effect of two different analysis series (section 4.3). The starting value was very high (cf. table 5), even when considering that the water was collected in the spring. There is no obvious connection between pH and concentration of Total-N.

The phosphorus level was below detection limit (50 µg l\(^{-1}\)) during the entire series and can therefore not be analysed. The expected concentration should be approximately 5 µg l\(^{-1}\) (table 5).

Alkalinity was 0 on day 0, but fell to negative values after the first acid pulse. The method used does not allow titration with a base. Therefore, the negative alkalinity (acidity) could not be quantified.
Figure 19 displays the water concentrations of metals during the leaching experiment. Aluminium exhibits the highest concentrations in the reference water. This result, and especially the fact that the content in the reference container has doubled, is somewhat surprising. The aluminium concentration increased 33% during the first day, i.e. without any acidification. In the same period no major changes occurred in the buckets.

The metals zinc and manganese behave differently than the base cations and Al (fig. 18, 19). Zinc and manganese exhibit a relatively fast increase for the first 20-30 days instead of 10, as is the case for the base cations. A possible explanation is that the base cations are merely adsorbed to colloids and are therefore relatively mobile while Zn and Mn probably are bound in complexes. This may take some time to dissolve.

Manganese does, however, show some similarities to aluminium in that it is sensitive to pH change. It has the greatest concentration in the unstirred buckets where the pH is low. One important difference is that the reference water has low and relatively constant Mn values. This may indicate that the reference container was contaminated with aluminium.
The barium diagram (fig. 19) is included as an example of contamination from the pumps. Barium is a rather rare element, and the concentration is low and comparable to the reference in the unstirred buckets. The concentration graph for the circulated buckets, on the other hand, displays a dramatic increase that levels off smoothly. There is no correlation with pH.

It seems like the concentration of Al is governed by pH to a large extent. The circulated buckets, which have higher content of all base cations, are lower in aluminium. This ought to be an effect of their higher pH. To further investigate the relationship between pH and aluminium, a simple regression analysis was performed (fig. 20).

**Fig. 19.** Water concentration of Al, Mn, Zn and Ba during the leaching experiment. The thick line represents the concentration in the reference water, the thin solid line unstirred buckets, while the broken line displays the circulated buckets. Note the different scales on the y-axis.

The barium diagram (fig. 19) is included as an example of contamination from the pumps. Barium is a rather rare element, and the concentration is low and comparable to the reference in the unstirred buckets. The concentration graph for the circulated buckets, on the other hand, displays a dramatic increase that levels off smoothly. There is no correlation with pH.

It seems like the concentration of Al is governed by pH to a large extent. The circulated buckets, which have higher content of all base cations, are lower in aluminium. This ought to be an effect of their higher pH. To further investigate the relationship between pH and aluminium, a simple regression analysis was performed (fig. 20).

**Fig. 20.** Linear regression on the relationship between pH and Al for one circulated and one unstirred bucket. Both of the buckets exhibit a linear relationship as the best fit.
A line could explain most of the data ($r^2 = 0.69-0.78$). This is in contrast to the observations of Oliver and Kelso (1983) who found an exponential relationship (cf. fig. 4). One must, however, consider that the measuring range is rather narrow ($4.34 < \text{pH} < 5.84$), and the extraction method utilised by Oliver and Kelso was more effective (shaking with strong acid).

5.1.4 Sediment net release

Base cations were released from the sediment immediately (fig. 21). The fast release was sustained after the first addition of acid but declined somewhat after the second day. After the second acid pulse the release rate was increased and it is obviously sensitive to changes in pH. From day 10 and onwards the rate levels out. During this period pH was relatively stable, but some acidity was constantly supplied through water exchange.

Fig. 21. Sediment net release of Ca, Mg, Na and K in unstirred (solid line) and circulated buckets (broken line). Note the different scales on the y axis. The arrows in the Ca diagram indicate the times for acid addition.

From figure 22 it can be concluded that it is not only the addition of H$^+$ that makes the base cations to be released. The Gårdsjön sediment has established equilibrium with the calcium-rich water and when the core encounters the poor Lake Stora Hästevatten water, the sediment moves towards a new equilibrium. In this way, more equivalents of base cations can be released in the buckets than hydrogen ions have been supplied. It is obvious though, that the release is governed by H$^+$ addition all through the experiment since the graphs follow each other well. Figure 22 also features the greater addition of H$^+$ to the circulated buckets caused by the greater evaporation there (section 4.2).

The release of Ca is very similar to the other base cations. With dissolution of residual lime, the Ca release should be significantly greater. This might indicate that the release is chiefly through cation exchange.

The faster release in the circulated buckets is probably because of greater addition of H$^+$, but this might not explain all the difference. It could also be the circulation that initiates the faster dissolution since it creates a sharper gradient at the water/sediment interface.
Fig. 22. The amount of supplied hydrogen ions (broken lines) compared with the release of base cations for unstirred (thick lines) and circulated buckets (thin lines). The release is to a great extent governed by the addition of $H^+$, but also circulation.

In an attempt to quantify the influence of circulation, the release ratio for circulated over unstirred buckets was calculated. This ratio was divided by the corresponding $H^+$ ratio to compensate for the greater acid addition to the circulated buckets. Assuming that the release rate is linear with respect to $H^+$ addition (cf. fig. 4), this would give the percent of excess release in the circulated buckets that cannot be explained by acidification. According to these definitions magnesium is not greatly benefited from a circulated environment (table 10). The other elements show greater circulation dependence, especially calcium.

Table 10. The excessive release of some elements in the circulated buckets compared to the unstirred. This percent is interpreted as induced by circulation.

<table>
<thead>
<tr>
<th>Circulation induced release (%)</th>
<th>Calcium</th>
<th>Magnesium</th>
<th>Sodium</th>
<th>Potassium</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>91</td>
<td>5</td>
<td>48</td>
<td>40</td>
</tr>
</tbody>
</table>

The net release of aluminium in the buckets shows a marked increase at the first acid pulse (fig. 23). The release is greatest in the unstirred buckets because they have a lower pH. This is verified by the precipitation of Al after the first acid pulse in the circulated buckets, when the pH was rising (cf. fig. 14).

Fig. 23. Sediment net release of Al, Mn and Zn during the leaching experiment in unstirred (solid line) and circulated buckets (broken line). Note the different scales on the y axis. The arrows in the Al diagram indicate the times for acid addition.
Apart from the acid pulses, there is actually a net precipitation of aluminium. As the reference water has the highest concentration, a net addition of Al occurs at each water exchange. The concentration in the buckets is, however, kept relatively constant (fig. 19) which means that Al is lost from the water mass. Note, however, that the concentration, after a four-week decline, begins to increase after day 40.

5.2 Sediment profiles

5.2.1 General core description

The cores exhibit rather different stratification, although they were all sampled within a few square meters. From the surface down to 3-4 cm the sediment is dark brown organic material as well defined spherical grains. Beneath this upper layer lies a paler brown, more homogenous, decomposed strata down to 10-15 cm. Below 15 cm, down to 20-30 cm there is clay with some organic material, and below 30 cm there is pure glacial clay. As explained in section 4.1, this does probably not represent the complete stratigraphy. The sediment depth above the glacial clay should amount to 1.1 m and there is a hiatus in the sample from 0.2-1.0 m. It is feasible that the strata with clay content lies below the hiatus and that the cores have been split at 10-15 cm depth.

The organic content in the sediment cores is between 30-45%, slowly declining downwards (fig. 24). This is in accordance with Andersson (1985b) who found an organic content around 30% at the sampling location. The fact that the pre-leaching cores seem to have a lower content of organic material is most certainly an example of the spatial variance at the sampling location.

![Fig. 24. Sediment depth profiles of organic content before and after the leaching experiment. The organic content should not differ before and after the leaching experiment and is therefore an indication of the spatial variance at the sampling location.](image)

5.2.2 Comparison between pre- and post-leaching cores

The pre-leaching depth profiles of calcium (fig. 25) exhibit high concentrations (4-5 mg g$^{-1}$) compared to the measurements performed by Andersson (1985b) who found concentrations of 1-2 mg g$^{-1}$ before the liming operations. The enhanced values are expected since there has been seven liming operations since 1982. In fact, they are a little low. The budget calculations (Nyström & Andersson, pers. comm.) suggest that the cores should have a calcium content of 50-100 mg g$^{-1}$ from the liming operations alone. The concentration is well below that. Another deviation from expectation is the even distribution without any large peaks. In addition, the concentration never reaches the background level of 1-2 mg g$^{-1}$. From these profiles it is difficult to assess the depth that corresponds to the first liming.
Fig. 25. Sediment depth profiles of calcium concentration before and after the leaching experiment. The post-leaching cores have been depleted in the topmost centimetre, but the variance is large even at greater depths.

The pre-leaching cores had a total Ca content of 74 mg of which 17 mg (23%) was contained in the upper 2 cm. The budget calculation figure 129 mg (section 3.5.3) is clearly an overestimate, at least for this location. There is of course a possibility that the lime is unevenly spread.

The profiles of post-leaching calcium are depleted in the topmost centimetre, but not to an extent that should be expected from the leaching results (fig. 25). The post-leaching cores now contain 70 and 58 mg respectively. Of these amounts approximately 20% is in the topmost two centimetres. A comparison of the amount of Ca in the surface sediment (0-2 cm) pre- and post-leaching indicates that the unstirred and circulated core have been depleted by 16 and 33% respectively (2.7 and 5.7 mg). One must of course bear in mind the scarcity of data.

According to the leaching results, 7.3 mg has been released from the unstirred core and 16.6 mg from the circulated. Thus the leaching results indicate a three times greater release than the sediment profiles. The circulated core has the same graph shape as the unstirred, but the general concentration is significantly lower in the circulated one.

The change in sediment calcium content at each depth can be seen in figure 26. The surface layers are indeed depleted to some extent but there is obviously great uncertainty in the results since large differences can be seen at greater depths. The content below 5 cm should be unchanged to be satisfactory.
The release efficiency illustrated as the post-leaching sediment content in each core divided by the pre-leaching mean concentration. The cores seem depleted at the top, but the great variance at depth reduces the reliability.

The profiles of another important base cation, magnesium, present lower concentrations towards the surface (fig. 27). Andersson (1985b) found concentrations between 1.0 to 1.5 mg g\(^{-1}\) in superficial sediment. The depletion of magnesium in the pre-leaching cores seems to have come to a halt at 2.5 cm depth. This ion has not been supplied through liming, but this could still represent the time for the first liming in 1982. The stabilisation then results from a decreased sediment release of Mg because of the increase in pH (cf. fig. 7).

**Fig. 26.** The release efficiency illustrated as the post-leaching sediment content in each core divided by the pre-leaching mean concentration. The cores seem depleted at the top, but the great variance at depth reduces the reliability.

**Fig. 27.** Sediment depth profiles of magnesium concentration before and after the leaching experiment. The sediment content is increased post-leaching. This result contradicts the leaching results, but confirms the great uncertainty in sediment measurements (cf. fig. 26), or perhaps the spatial variance described in figure 24.
The post-leaching profiles exhibit a totally different picture. Just as for Ca the pattern with the entire circulated core dislocated from the unstirred is the same (fig. 27). In this case, however, it is the unstirred core that exhibits unexpectedly high concentrations; higher than the pre-leaching conditions. This is, on the other hand, the core that displays the anticipated shape of the profile with depletion at the surface and increasing concentrations with depth. The profiles are therefore hard to analyse and any calculations are meaningless.

The actual release in the leaching experiment was 1.7 mg in the unstirred bucket and 2.7 mg in the circulated. This implies a great uncertainty in the sediment measurements.

The pre-leaching profiles of aluminium display a decrease from 8.5 to 4.5 cm, a stable period from 4.5 to 2.5 cm and then a sudden increase up to the surface (fig. 28). In general, the values are low compared to the study of Andersson (1985b), which gave 20-30 mg g\(^{-1}\), but those measurements also included mineral Al content. The result of burning the residual sample after the acid boiling indicated that approximately 20% of the total aluminium content were left.

The upper 2 cm contains 71 mg of aluminium while the maximum release was 0.4 mg. The seemingly drastic increase in Al concentration (fig. 19) thus only involved a fraction (0.6%) of the available amount.

The post-leaching depth profiles of aluminium are quite similar (fig. 28). The small release indicated by the leaching experiment is too small to be noticed in the depth profiles.

The correlation between the Ca, Mg and Al profiles is rather low. The low connection makes it hard to assess the depth of the first liming event in 1982.
6 DISCUSSION

6.1 The distribution of calcium

According to the budget calculations (Nyström, pers. comm.) as much as 22% of the net sedimentation during the last 16 years might have been CaCO$_3$. This should result in a reduction in organic content of 5 percentage points, with the decline towards the surface. This cannot be verified in the organic content profiles (fig. 24).

The budget calculations also suggest that each core should contain 129 mg of Ca ($85 \text{ g m}^{-2} \times 1.52 \times 10^{-3} \text{ m}^2$). With a concentration of 75 mg g$^{-1}$, only the topmost 1.7 cm should be affected by the liming operations. This is of course theoretically. The residual lime can reach deeper through bioturbation and sinking of the grains down through the lighter sediment if there are bottom currents (cf. fig. 7). This could explain why the concentration does not reach the anticipated level. The entire core contains 74 mg, which then would suggest a very deep migration to accommodate the 129 mg proposed to have been received from the limings.

A comparison with two Norwegian studies (table 11) gives some insight of what sediment profiles usually look like after liming. Lake Store Hovvatn had four large limings in the period 1987-93 and some minor events as well. From cores taken in 1994, calcium concentration is greatest at the surface (fig. 7). The maximum to background level ratio is 5, and the first increase can be seen at 8 cm depth. Thus 8 cm corresponded to 7 years although general sedimentation rates seldom exceed a few millimetres per year. In this perspective, it is not strange if the 16 liming years of Lake Gårdsjön should be accommodated in more than 9 cm.

In the Terjevann project (Andersen 1995), on the other hand, where liming was performed in small doses every year for an 8-year period, a large peak is seen at 7 cm depth. This peak exhibits 8 times higher concentrations than the background level. Andersen’s conclusion was that the peak originates from the greatest liming in 1984 and that the following lime additions have been consumed. Thus 7 cm correspond to 10 years and the first increase seen at 11 cm has perhaps arisen from migration of lime grains. These comparisons suggest that the first liming of Lake Gårdsjön is not to be seen until 15-20 cm depth.

<table>
<thead>
<tr>
<th></th>
<th>Lake Gårdsjön</th>
<th>Lake Store Hovvatn</th>
<th>Lake Terjevann</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turnover time (years)</td>
<td>1.2</td>
<td>0.9</td>
<td>0.7</td>
</tr>
<tr>
<td>Number of operations</td>
<td>7</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>Doses (g m$^{-3}$)</td>
<td>21-73</td>
<td>13-32</td>
<td>8-26</td>
</tr>
<tr>
<td>Background level (mg Ca (g sed.)$^{-1}$)</td>
<td>1.5</td>
<td>1.4</td>
<td>5.5</td>
</tr>
<tr>
<td>Max conc. (mg g$^{-1}$): Max at depth (cm)</td>
<td>5.0 : 2</td>
<td>5.3 : 1</td>
<td>42.5 : 7</td>
</tr>
<tr>
<td>First major increase at depth (cm)</td>
<td>?</td>
<td>8</td>
<td>11</td>
</tr>
</tbody>
</table>

The magnesium profiles (fig. 27) does not fit into the calcium sedimentation history described above. It was assumed in section 5.2.2 that the upper 2.5 cm should correspond to the liming period. On the other hand, it seems peculiar that Mg should have been released during the later part of the liming period (cf. fig. 7).
It has been very difficult to obtain any working plan for the liming operations. After the sampling, a map of the 1992 liming has been found. This map indicates that the sampling location is on the border to a no-liming bay. If this is the case for all liming events, it may well be that unfortunate that the sampling location has never received any undissolved lime. The enhanced values are then merely a result of 16 years of calcium-rich water that has created a downward flux into the sediment (cf. fig. 5). Svärd (pers. comm.) who sampled at the same location examined the mineral composition of the sediment. She found no crystals that resembled calcite. It is, however, hard to see how the Ca could have penetrated to 15 cm or more, as suggested earlier, merely through ion diffusion.

6.2 Release mechanisms

The sediment offered considerable buffering to the first acid pulse (fig. 14, table 9). This did not only depend on an eventual dissolution of residual limestone. All base cations were released in substantial amounts, and especially in the circulated buckets. These buckets can be said to represent a beach environment where the wave action constantly reworks the sediment. Because Lake Gårdsjön is a small lake with short fetch and steep shores, this condition does not represent a large area.

The fact that the release development of Ca is very similar to the other base cations (fig. 22) might indeed suggest that the calcium ions are derived from cation exchange rather than limestone dissolution. There are at least three theories that can explain the disruption of ion release after day 10:

1. It is during the first 10 days that the bulk of $H^+$ is added. Acidity is the most important factor for ion release.
2. It may be that the active layer, i.e. the layer from which elements can be released under the prevailing circumstances, was depleted in 10 days.
3. It might be that the Ca release during the first 10 days is from the lime of the latest liming event in 1996 that have not been deactivated by metals yet. There is still some lime present in the sediment after day 10, but it is old and covered by precipitated metals. If these metals are released, the lime can possibly be dissolved. This will, however, take place at very low pH values.

The fact that the release after day 10 was disrupted for all other base cations as well strengthens theory 1 and 2.

The dilemma with the deep penetration versus cation exchange (section 6.1) can be hypothesised as follows:

There is actually residual lime in the sediment samples that have penetrated to depths greater than 10 cm. This lime is, however, inactive and does not contribute to the Ca release. The release is accomplished by cations in the surface layer. In other words, we do have residual lime, but it does not dissolve at re-acidification.

6.3 Release efficiency

All base cations were favoured by circulation, but to a different extent in the sequence Ca > Na > K > Mg. The order of the sequence does not seem to be determined by charge or size of the atom. The accessibility may be of importance since figure 27 revealed that the content of magnesium was unexpectedly low.

The total amount of released calcium indicates that the sediment must have contained considerable amounts of calcium. Andersson and Gahnström (1985) conducted a similar leaching experiment. The duration of their experiment was 251 days. They had eight Lake Gårdsjön cores that were exposed to different pH, but the reference core (no acid addition) is most interesting for this study. The water above this core had a starting pH of 5.4, which declined to 4.4 because of supply of CO₂ and NH₃ through air bubbling. This development is similar to this study.
During that experiment the Ca concentration in the supernatant increased from 1560 to 6200 µg l$^{-1}$, and this was under pre-liming conditions. As they had no water exchange this means that the release was 4.6 mg (Andersson & Gahnström, 1985) which is equivalent to 014 mg cm$^{-2}$. The flux in this study was 0.48-1.09 mg cm$^{-2}$, which means that the flux ratio is larger than the concentration ratio. In other words, the difference in flux was greater than the sediment concentration difference between the studies, and the release of Ca went easier in this study. The two studies have similar reductions in pH but the release of Ca differs. It is possible that this is only an indication that the flux does not describe a linear relationship with calcium availability. It may also be a result of the calcium deficit in the Lake Stora Hästevatten water.

6.4 Aluminium dynamics

Monthly measurements of pH and major ions have been conducted since 1979 to 1993 in Lake Stora Hästevatten and even longer in Lake Gårdsjön (Nyström pers. comm.). These measurements indicate a pH interval of 4.6-5.7 in Lake Stora Hästevatten. The reference pH of this study (5.5) is thus rather high. The lake had probably been subjected to spring circulation the days preceding the sampling. Even more interesting is the Al measurements. The reference value of 85 µg l$^{-1}$ can be compared with the interval 50-540 µg l$^{-1}$. This is therefore a very low value. With a newly circulated lake and reduced deposition of SO$_2$, decreasing the weathering and leaching, it might be possible with such a low value. There is, however, a risk that the reference value on day 0 is underestimated (measuring error) which of course influences the calculations of net release substantially.

The rapid increase in Al in the reference water during the first days is hard to explain. The only difference between the reference and the buckets during the first day is the release of base cations. These ions cannot precipitate or adsorb Al since this is a cation too. One explanation would be that the release of base cations increased pH which in turn made it harder for Al to stay in solution. According to measurements, however, pH was stable during this period. Another alternative is that the value on day 0 is wrong. It would be reasonable to assume that the Al concentration should decrease in the buckets since pH was rising and cations were released during the first day. The reference, on the other hand, should remain stable from day 0 to 1. These assumptions suggest an initial reference concentration of ca. 115 µg l$^{-1}$. This concentration was then sustained during the first day while the buckets fell to ca. 80 µg l$^{-1}$.

The fact that the regression lines are so similar for an unstirred and circulated bucket suggests that the circulation is unimportant for the release of aluminium. The circulation has an indirect influence in that it causes a higher pH, which immobilises the aluminium.

As the water was very high in aluminium before the first liming event, this operation should result in a sharp increase in sediment Al content. According to the discussion above, this increase is perhaps seen at greater depths than those sampled here. Just as for Mg, there is a change at 2.5 cm depth. These elements are therefore, at least weakly, correlated; but not with calcium. It has been implied that much of the deposited lime will never be dissolved. The important question is then how well correlated aluminium is with calcium distribution. Is the aluminium store also to a great part below the active layer and therefore out of question of re-dissolution? This cannot be verified from figure 28. Unfortunately, most of the aluminium store seems to be accommodated in the upper 3 cm.

6.5 Nutrient dynamics and other questions

The level of Total-N shows no correlation to pH in this study. There is a possibility that the acid effect on biota displays a time lag, but this is too difficult to analyse with the present data.

When discussing results from the circulated buckets, one must consider the possibility that the pumps can contaminate the water in some way. For example, is the strong increase in barium (from 11 to 600 µg l$^{-1}$) thought to have originated from the pumps (fig. 19).
The circulated post-leaching core displays a significantly lower content of calcium, magnesium and aluminium all through the core. This might suggest that leaching has occurred from the entire core. Even so, the topmost layers should be most depleted since the flux is governed by the gradient at the sediment/water interface. Such great release of elements can, however, not be verified by the leaching results. This is probably an indication that this core had significantly lower values even before the experiment, i.e. it is not a result from the leaching experiment.

The leaching results suggest a three times greater release of calcium than the sediment profiles do. This is a large discrepancy, which might depend on measuring errors or additional release from pumps and tubes in the buckets.

No major changes are apparent for aluminium, neither from leaching experiment, nor the sediment profiles.

The sediment measurements seem to have a low accuracy, but the active layer is 2 cm at the most. Longer exposing would perhaps deepen this layer, but the diffusion is then of course very slow and not of great significance. A total depletion of the topmost 2 cm would, however, be more than enough to eradicate most of the organisms now present in the lake. “Total depletion” here refers to the acid soluble part, which in this study was determined to 80% of total content (section 5.2.2). Other studies have indicated much lower values (15-20%) according to Lind (pers. comm.).

6.6 Application of the laboratory results

The intention with the experiment was that the bucket concentration should reflect the actual concentration in the lake. The experiment water exchange was, however, much faster (17-21 times) than the actual Lake Gårdsjön turnover time. The real lake concentrations would therefore be somewhat higher. The low bucket concentrations probably induced a faster release though. It should not differ by much, however, since a near equilibrium situation established after 10 days. Concentrations were slowly reduced, probably by a combination of sediment depletion and too fast water renewal.

The unstirred buckets, rather than the circulated, are probably closest to the actual development in the lake. In fact, the simulation is far from realistic and the actual possibility to apply the results to Lake Gårdsjön is perhaps low. Bearing this in mind, the amount of hydrogen ions supplied after 10 days is equivalent to nearly 2.5 years in Lake Gårdsjön, assuming an inlet pH of 4.5 and an inflow of 39 l s⁻¹. After that, the Al concentration would, according to results presented here, lie around 160 µg l⁻¹. This can be compared to an approximate mean value of 110 µg l⁻¹ during the 1990s (Nyström pers. comm.). This is a high value but not as bad as one could anticipate. Before the limings, concentrations were around 350 µg l⁻¹.

The dissolution is only a fraction of the sediment content. One must, however, consider the possibility that 54 days is too short a period for the Al to dissolve in considerable amounts. Remember that the net precipitation trend was broken on day 40 (fig. 23). If this indeed should be a new release phase it must concern a different Al species than at the first increases. The response at liming has in earlier studies also been proven to be slow (cf. fig. 3). The aspect of time is therefore very important.
7 CONCLUDING REMARKS

There has been speculation on the severity of the re-acidification effects. The results of this study, where pH was lowered to 4.5, indicates the following:

- The limed sediment offers some buffering during re-acidification (51% of added hydrogen ions in a calm environment).
- The buffering is mainly through cation exchange rather than dissolution of residual limestone.
- The layer containing residual limestone is thicker than the expected ~2 cm. It is probably as thick as 15-20 cm.
- Very small amounts of aluminium are released at pH=4.5 but the concentrations may still reach high levels.
- Base cations reacted immediately on pH reductions while the metals Mn and Zn reacted somewhat slower.
- Only the topmost centimetre of sediment was active in the cation exchange.
- A continuously circulated water mass increased the leaching for Ca, Na and K with 40-91% compared with unstirred water, while Mg release was almost the same in both environments.
- Aluminium was not directly affected by water circulation, but indirectly through pH change.
- As only the topmost centimetre of sediment is active in element exchange, all aluminium precipitated during the liming period cannot be released since it is incorporated to greater depths.
- It is unclear whether the aluminium store has the same distribution as calcium (down to 15-20 cm depth). It is possibly contained in more superficial layers. In that case, it is still relatively accessible for a re-acidification.

These results suggest that the feared environmental bomb is more of a firecracker. It must, however, be emphasised that the measuring period of 54 days is very short in the time scale of eco-cycling. The conclusion is that most of the precipitated aluminium is still accessible, but all precipitated aluminium will not be released again. In the perspective of years, however, considerable release of aluminium may still take place, even if the active layer is thin. The question is then if the active layer contains enough exchangeable aluminium to create toxic effects. That depends on the time scale. This calls for further research with longer measuring periods.
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