Acid Groundwater

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Hans Hultberg and Sivert Johansson

Swedish Water & Air Pollution Res.Inst., Gothenburg, and
Div. of Hydrology, Uppsala University, Uppsala, Sweden

Studies of the groundwater flow and quality around the lakes Bredvatten and Lysevatten have shown, that the increased concentrations of aluminum in acid lake water is caused by acid groundwater, and hence of leaching of aluminum into the groundwater. The increased aluminum concentration was later shown to be a major factor in the widespread ecosystem changes occurring in lakes and water systems.

When a similar, but even more pronounced soil- and groundwater acidification occurred via oxidation of accumulated sulfur to sulfuric acid and thereby releasing several soil minerals to the groundwater, a number of regional investigations were carried out on wells and groundwater systems in different provinces in southern Sweden.

The widespread problem with acid groundwater and thus acid tap water, made clear in these studies, shows that several thousand individual households have already acute problems with their drinking water and corroding metal-piping.

The acidification of the groundwater has caused health problems by elevated metal concentrations and economic problems for house owners in an even more pronounced way than acidification of the surface water systems (lakes and rivers). These effects also show how severely affected the lime poor natural ecosystem has become through our own and other countries’ airborne acid pollutants.
Introduction


A study by Johansson and Hultberg (1977) showed that inflow of acid groundwater with elevated concentrations of metals was one major cause of the re-acidification of limed lakes.

In 1977 also metal precipitates (Al, Mn, Fe etc.) on bottom of a stream was shown to be caused by acid groundwater (Hultberg and Johansson 1978).

As a result of the above studies the authors initiated regional surveys of the water quality in shallow and drilled private wells during 1978-1980.

A study in 1980 of the long-term annual analyses from large municipal groundwater aquifers in the province Ålsborg was started as a result of the regional studies.

Since autumn 1979, the National Swedish Environmental Protection Board supports a joint research project titled »Acid groundwater with elevated concentrations of metals – causes, regional occurrence of the problem and future trend«. The project is cooperated between the Division of Hydrology, University of Uppsala, Swedish Water and Air Pollution Research Institute, Gothenburg and Department of Soil Science, Swedish University of Agricultural Sciences, Uppsala.

This paper is a summary report of results from this project and from other recent Swedish studies on acid groundwater.

Analyses of Groundwater Quality around the Lakes Bredvatten and Lysevatten in the Province of Bohuslän

After lime treatment of two acid lakes, a quicker re-acidification has occurred compared to the estimated duration calculated from acid deposition and the lakes' hydrology. In the lakes Bredvatten and Lysevatten with a calculated duration of ~10 years a sudden decrease of pH and alkalinity occurred in 1977 after four years. Not only the acid wet and dry deposition has had a direct effect on the lakes' buffering capacity but a further load is the inflow of acid groundwater. Groundwater was sampled at stations representing different geological environments around two lakes: bogs and fen areas, moraine and glaciofluvium.

Sampling was performed from 1977 onwards and is presented until May 1979 (Andersson and Hultberg 1979). (See Fig. 1 and Table 1). Stations with groundwater inflow from bog and fen areas around Bredvatten (B1, B2, B3 and B5) all had pH-values lower than pH = 4.0 or slightly higher during the years 1977-1979. This soil type represents a groundwater inflow of 56% of the drainage area of the lake. The groundwater from moraines, station B4, has a somewhat higher pH
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Fig. 1. Location of sampling points.

(4.3-4.6), higher concentration of aluminum (2.6-1.9 mg/l) and manganese (0.3-0.2 mg/l) and is less coloured (1-14 mg Pt/l) than the groundwater from the bog and fen areas. The aluminum concentrations are, however, high in all sampled areas and this partly explains the decreased pH and alkalinity in the lake water which appeared at high groundwater inflow to Bredvatten in 1977. The acid groundwater with increased levels of aluminum and manganese indicates that a long-term acidification of the soils has occurred in the drainage area of the lake. At the station in moraine the high aluminum content appears at low colour values, which indicates that aluminum is dominated by inorganic species, while the water from the bog and fen areas is highly coloured from humics and here aluminum probably appears more as organic complexes. (Driscoll personal communication).

The elevated concentrations also indicate that the store of aluminum in the podzol profile has decreased and that a generally increased mobility is caused by the low pH in the soil water. The high aluminum concentration also shows that the moraine around lake Bredvatten are thinner than the glaciofluvial deposits at Lysevatten, where aluminum still is retained in the soil profile (L1, Table 2). The groundwater around lake Lysevatten has generally higher pH than around lake Bredvatten, and the re-acidification also is slower compared to lake Bredvatten. The amount of inflow from bog and fen areas (L4) to lake Lysevatten is one half (27%) of that to lake Bredvatten (56%) and here the pH is 4.17-4.36 compared to <4.0 at Bredvatten. The inflow from moraine (L2, L3) is less acid and pH is 4.29-4.84, but, as at the station B4 (moraine, at Bredvatten) there are high aluminum concentrations (1.3-0.74 mg/l). The groundwater inflow from glaciofluvium (station L1) has a totally different chemical nature with higher pH (5.2-5.95) and low
### Table 1 – Lake Bredvatten. Quality of inflowing groundwater.

<table>
<thead>
<tr>
<th></th>
<th>B1</th>
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<th>B3</th>
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<tr>
<td>Mg²⁺</td>
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<td>17.4</td>
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<tr>
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### Table 2 – Lake Lysevatten. Quality of inflowing groundwater.

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<td>Mg²⁺</td>
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<td>2.0</td>
<td>2.5</td>
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<td>Alkalin</td>
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### Notes
- pH values range from 7.71 to 4.06.
- H₂S and CO₂ concentrations vary widely.
- Ca²⁺ and Mg²⁺ levels are generally high.
- SO₄²⁻ concentrations are relatively low.
- Chloride (Cl⁻) and Total-P (Tot-P) levels are within normal ranges.

References:
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concentrations of aluminum. The soil is here much thicker than at any of the other sampling stations and the groundwater table is here at a depth of >5 m compared to <1 m at the other stations and is therefore less sensitive to the acid deposition.

The above results explain the general appearance of increased aluminum concentrations in acid lakes and streams. Elevated aluminum concentrations in acid surface water have been documented from several other countries (Norway, USA, Canada, Belgium, Scotland) and it appears to be one of the major factors of the ecosystem changes that occurs with acidification.

Hydrochemical Effects of Acid Groundwater in the Drainage Area of Stenunge Stream

The investigated part of the drainage area to Stenunge stream is a small farmed valley at 85 to 95 m above the sea level, surrounded by a bedrock-ridge of gneiss with an elevation of at the most 115-135 m above sea level, with softwoods on a thin soil cover. After the last glaciation the sea reached a height corresponding to 110-120 m above the present sea level in this area which caused heavy wave action which resulted in the rock outcrops and thin soil cover on the ridge. In the valley the soil within a boundary along the bedrock ridge and the centre of the valley is sand or sandy silt which covers (with a 1.2 m thick layer) the top of the marine clay in the centre of the valley. Groundwater and soil samples were collected after drilling both in the sandy areas surrounding the central clay area, and underneath the clay in a sandy/gravelly layer onto the bedrock, as well as in dug pits in the shallow aquifer on top of the clay. Groundwater pH from the sandy areas (data from 3 drilled holes) varied between 5.1-5.7 at depths of 5.0-8.5 m in April 1978 and increased to 5.8-6.2 in May 1978.

Groundwater pH from the aquifer underneath the clay layer was 7.0 and the alkalinity 0.54 mekv/l and tritium analyses showed that this water was 20 years old compared to <2 years in the shallow aquifer on top of the clay where pH was very low (3.2-4.8) and high in aluminum, manganese, etc.

Further downstreams in the valley low pH and high metal content was found in two main areas both with shallow aquifers. Inflow from a farmed area (not limetreated) had pH 3.6-4.6 and an aluminum content of 7.6-1.6 mg/l and groundwater analysis from an alder marsh had pH of 3.6-5.4 and an aluminum content <1.6-0.2 mg/l.

The inflow of the acid groundwater with elevated concentrations of metals caused a metal precipitation on the bottom of the stream. The metal precipitate contained Al, Mn, Fe, Ca, Mg and to some extent Zn, Cu, Cr and Cd.

The sudden appearance of metals in the stream water and metal precipitates has severely affected the sea trout reproduction (one and two summer old fry) along >2 km of the stream. Downstreams, inflow of groundwater with higher pH (>6.0)
from deeper aquifers, continuously increased the pH of the stream water and caused the precipitation of the metals.

At low water temperatures in April – early May 1978, however, the precipitation of aluminium was retarded and the relative amount of aluminium increased in the precipitates the further downstreams the samples were taken. Aluminum precipitates were observed >2 km downstream of the nearest area with very acid groundwater (the alder marsh).

The elevated metal content in Stenunge stream occurred after two dry years (1975 and 1976) which resulted in a general decrease of the groundwater level of >1.5 m in the area (Fig. 2). All thin aquifers in the area were dried out resulting in total oxidation on the soil profiles in the shallow aquifers.

pH versus metal content of all analysed groundwater samples from different aquifers and sampling depths are summarized in Figs. 3 and 4. The graphs show that while pH decreases to about 5 other elements increase exponentially with further reduction of the pH. This is particularly relevant for calcium, magnesium and is indicated for silica while aluminum and manganese increase strongly when pH is lower than 4.5. Potassium shows a different picture with a minimum at pH = 5.5 and an increase with lower and higher pH values, respectively.

Theoretical calculations of aluminum dissolution from gibbsite with decreasing pH (Erik Eriksson »The effect of acid precipitation on aluminum compounds in soil« 1978-10-31) agree with these data, summarized in Fig. 3 from the field samples.

The cause of the severely acid groundwater and resulting leaching of metals from the soil is the formation of the strong acid H₂SO₄ during the dry years 1975 and 1976.

Long distance transported sulfur and input from a nearby oil fired power plant gave a total non-marine deposition of about 4g S/m²-year = 12g SO₄/m²-year during
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Fig. 3. Concentrations of sulphate, aluminium and manganese in relation to pH in acidified groundwater.

Fig. 4. Concentrations of calcium, magnesium, silica and potassium in relation to pH in acidified groundwater.

the last 15 years (Granat and Söderlund 1975). During these years the thin aquifers <1.5 m in depth have received ~1.8 tons of sulfate per hectare. The total sulfate deposition to the whole investigated part of the drainage area to Stenunge stream (7.0 km²) has been 1260 tons during the last 15 years. This has resulted in generally elevated concentrations of sulfates in both ground and surface water.

The sulfate concentration ranged 15-27 mg/l in groundwater in the sandy soils surrounding the clay area in centre of the valley, and the sulfate content of the
stream water upstreams the three areas with very acid groundwater was 24-38 mg/l, which is >2 times the sulfate concentration found in acid surface water in southwestern Sweden. Downstream the uppermost situated aquifer with very acid groundwater the sulfate concentration of the stream water increased to 108-210 mg/l.

The inflow average sulfate concentration from the three shallow aquifers was about 150 mg/l. In 1977, the amount of precipitation was 910 mm. After evapotranspiration (~450 mm) and a groundwater accumulation in the dried out thin aquifers an estimated inflow of about 300 mm as groundwater to Stenunge stream with a sulfate concentration of 150 mg/l, results in a total transport of 300 l/m² × 150 mg × 10000 m² = 450 kg SO₄/ha from these shallow aquifers. This is 25% of the total deposition of sulfur in the form of sulfates (1800 kg/ha) during the last 15 years. The thin aquifers normally have a high groundwater table and the soil has a high organic content rich in iron. The properties of the soil cause reducing conditions and formation of sulfides, which can accumulate in the soil profile.

During extreme climatic conditions like the dry years 1975 and -76 or as a result of ditching an oxidation of the soil profile results in formation of sulfate corresponding two moles of H⁺ mole of SO₄²⁻. The investigations at the Stenunge stream area strongly indicate that the above explanation is of major importance to the sudden appearance of an inflow of very acid groundwater with high concentrations of several »soil-metals« to the stream. Sulfate retention in catchment areas are earlier described by e.g. Shriner and Hendersson (1978), Dahl et al. (1979) Andersson and Eriksson (1979), while others have shown a balanced input-output budget for sulfate over several years. Obviously, there are differences in sulfur retention from one catchment area to another, caused by differences in soil type and hydrological regime.

Regional Occurrence of Acid Water in Shallow and Drilled Wells and Larger Municipal Aquifers

The first large scale well survey was made in an area poor in lime and with acidified lakes within the area. The study was undertaken by the Province Health Organization together with the authors in the southern part of the province of Bohuslän (Länsläkarorganisationen 1980).

Within the project »Acid groundwater with elevated concentrations of metals« studies have now been completed in the provinces of Halland, Älvsborg, Örebro and Blekinge. The district of Laholm has recently completed a study of shallow and drilled wells (Nilsson 1980). The occurrence of acid wells in the province of Värmland have been completed by Swedish Water and Air Pollution Research Institute in Fryksta, Värmland (Grahn 1980). In all the provinces where well surveys have been completed, acidification of lakes and streams is a widespread
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Fig. 5. Regional groundwater surveys in south- and southwestern Sweden.

In the provinces of Halland, Bohuslän, Älvsborg, Värmland, Örebro and Blekinge the proportion of shallow wells with pH <6.0 is 66%, 76%, 41%, 43%, 39% and 31%, respectively (see Fig. 5). In Laholm district of Halland 58% of the shallow wells had pH <6.0.

The drilled wells were generally less acid. The proportion of drilled wells with pH <6.0 were 35%, 10%, 5%, 13% and 26% in the four provinces Bohuslän, Värmland, Örebro, Blekinge and the district of Laholm, respectively (see Fig. 5).

In the province of Bohuslän where the most widespread problem with acid
groundwater was observed, some 49% of the households with shallow wells had a pH <5.5, while only 13% of the drilled wells have such a low pH. In this study pH in shallow wells was shown to decrease the higher the well was situated above sea level. This is earlier shown for acid lakes in the same area. pH of the well water also was shown to decrease with decreasing depth (1-10 m) of the well. Wells in highly permeable ground, such as sand and gravel, generally have the lowest pH value (in Bohuslän, an average of 5.10), moraine with varying permeability generally had low but more varying pH (in Bohuslän, average = 5.45). Shallow wells in clayey (marine) soil often had high pH-values but still the average pH is just over 6.0 in Bohuslän (see Fig. 6).

The aluminum content in shallow well water increased sharply from pH 5.5 and downwards, and about 10% of the households with dug wells had an aluminum concentration of >0.5 mg/l (see Fig. 7).

The copper concentrations were only analyzed in a few samples: copper values of >1.0 mg/l were found in 6 of 10 sampled households with pH 5.50-5.95 in cold tap water faucet in the morning prior to use. 13% of 279 house owners complained
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of corrosion to cold and warm water copper piping and in several houses the copper piping had corroded through in 10-15 years.

In a recent study the district health authorities of Lilla Edet found 1-14 mg copper /l in cold morning tap water in houses with a tap water pH of 5.0-6.2.

In some cases copper concentrations of >1 mg/l have been shown to cause diarrhoea to young children and bad taste of the water. In several cases women's hair have become green coloured after washing in tap water with elevated copper concentrations.

Some hen-farmers with acid groundwater and elevated concentrations of aluminum have suggested that the water causes an increased problem with thin-shelled eggs. Accumulation of aluminum as aluminumphosphates replacing the calcium in pied flycatchers have earlier been shown to cause thin egg-shells and death of the adult female after egg laying (Nyholm 1979).

It is of concern that the mechanism of action of several of the metals which are moderately elevated in drinking water (Cu, Al, Mn, Zn, Pb) is not yet sufficiently understood to rule out synergistic action after long-term consumption.

Besides, the health concern from acid tap water, the corrosion effects on copper piping, eternite piping (contains asbestos) and galvanized iron piping cause economic problems due to replacement costs and damage to floors and walls in the houses by leaking water.

An estimation of the total number of households in the whole of the surveyed provinces that have acid tap water problems, is not presently possible, but of the 1,190 shallow wells investigated 31% - 76% and 5% - 26% of the 190 drilled wells, had severely aggressive water which is why several thousands of households probably are affected.

To investigate if large municipal groundwater aquifers are undergoing a long-term acidification, annual analyses from 7-23 years were compiled from nine municipal supplies in high permeable (sand, gravel) soils (Märtensson 1979, Hultberg and Wenblad 1980). With few exceptions, the pH were >6.0 and no significant changes were indicated.

However, the alkalinity had decreased in seven of the nine aquifers. In five of them the decrease was statistically significant during a 10-15 year period. In some cases the bicarbonate concentration were halved during this period. Similarly a significant increase of the calcium concentration was shown in aquifers which had decreasing alkalinity.

Compared to the studies from shallow wells it is seen that even deep large groundwater aquifers have gradually been acidified.

The groundwater acidification, however, is in many cases a slow process, but nevertheless, some 20,000 lakes with inflow of both surface and groundwater are already affected in Sweden.

The acidification of lakes has continued for several years and this is now visible in the groundwater aquifers.
Conclusion

Recently acid groundwater was documented as a widespread problem causing increased metal content in acid lake and stream water, problems with drinking water quality and corrosion of metal piping in southern Sweden.

In 1977, acid groundwater with elevated levels of aluminum was found to be one major cause of re-acidification of two limed lakes. During 1977-79 ten sampled groundwater areas around the lakes had a pH-range of 3.8-5.7 and an aluminum content of 2.6-0.1 mg/l.

Metal precipitation appeared on bottom along >2 km of a sea trout stream in 1977. Acid groundwater (pH <6.0) was found in the lime poor sandy soils in all the investigated areas of the upper part of the drainage area to the stream. Very acid groundwater (pH <4.5) with elevated metal content originated from three shallow aquifers. Deep groundwater >12 m still had high pH and alkalinity. The relations: pH/metals from all sampled stations plotted in the same figure showed a general increase of aluminum and manganese at pH <4.5 of the groundwater and an increase of calcium, magnesium and silica at pH <5.0. The Al-concentration of the groundwater conformed well with theoretically calculated concentrations based on solution equilibria of pH and gibbsite.

As a result of these observations water samples from private shallow (1,190) and drilled wells (190) were selected from houses in areas with soils and bedrock poor in lime.

Shallow wells with pH <6.0 accounted for 66%, 76%, 41%, 43%, 39%, 31% and 54% in six provinces and one district, respectively.

The drilled wells were generally less acid. Drilled wells with pH <6.0 were 35%, 10%, 5%, 13% and 26% in four provinces and the district above, respectively.

In the southern part of the province of Bohuslän pH in shallow wells was shown to decrease the higher the well was situated above sea level – the same effect is earlier described for acid lakes in the same area. pH of the shallow wells was also shown to decrease with decreased depth of the well.

pH of the wells also varied due to different soil types around the well: sandy soil pH median = 5.10, moraine pH median = 5.45 and clay (marine) pH median = 6.10. In all shallow wells with pH <5.5 (49% of the totally 225 investigated in the province of Bohuslän) increased aluminum concentrations were correlated to decreased pH. Corrosion to copper piping causing leaking and elevated copper concentrations in both warm and cold tap water were common in all the provinces investigated.

Long term chemical change in groundwater from large municipal aquifers in sandy soils, with annual analyses, were evaluated in the province of Älvsborg. Alkalinity was shown to have decreased and in some cases calcium was showed to have increased during the last 10-15 years. pH showed no significant change, however, due to alkalinity still remaining in the well water.
Acknowledgements

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References


Granat, L. and Söderlund, R. (1975) Atmospheric deposition due to long and short distance sources with special reference to wet and dry deposition of sulfur compounds around an oil-fired power plant. Report AC 32, University of Stockholm, Department of Meteorology, International Meteorological Institute.


H. Hultberg and S. Johansson


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**Address:**
Hans Hultberg,
Swedish Water & Air Pollution Research Institute,
P. O. Box 5207,
S-402 24 Gothenburg, Sweden.

Sivert Johansson,
Division of Hydrology,
Uppsala University,
Box 554,
S-751 22 Uppsala, Sweden.