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Long-term trends of water chemistry in mountain streams in Sweden – slow recovery from acidification

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Abstract

The water chemistry of streams and precipitation in the province of Jämtland, northern Sweden has been monitored since the 1980s to study long-term trends, occurrence of acid episodes, and effects of liming. The acidity and sulphur in precipitation increased in the 1970s, followed by a loss of ANC and low pH in the streams. Sulphur deposition begun to decrease in the 1980s, until approximately 2000, after which the decrease levelled out. The stream water sulphate followed the precipitation trend but decreased more slowly and since the late 1990s a subtle increase was observed. The sulphate concentrations in the snow have generally been higher than or equal to the stream sulphate levels. Since 2005, stream sulphate has sometimes exceeded snow sulphate, indicating desorption of stored soil sulphate, possibly because of climate related changes in run-off routes through the soil profiles, following shorter periods of frost.

Up to 2000, TOC increased by approximately $0.1\,\mathrm{mg\,L^{-1}\,yr^{-1}}$. The mean trends in sulphate and TOC from approximately 1990 until today are generally opposite.

Acidic episodes with pH 4.0 at flow peaks occurred frequently in the unlimed streams, despite relatively well buffered waters at base flow. To evaluate the main causes for the loss of ANC, the changes in major ions during high flow were calculated. The most important contribution resulted from dilution of base cations, with contribution from organic anions. Sulphate also had some influence, as it was somewhat enriched or only slightly diluted during high flow.

Wetland liming started in 1985 after which the earlier observed extreme peak values of Fe, Mn and Al, did not return.

The studied area is remote from emission sources in Europe, but the critical load of acidity is still exceeded. The long-term recovery observed in the unlimed streams is thus slow, and severe acidic episodes still occur.

1 Introduction

Acidic deposition has caused a widespread deterioration in the water quality of lakes, water courses, and soils in large parts of Europe, primarily Scandinavia, (Almer et al., 1974; Dickson, 1980; Henriksen, 1980; Wright et al., 1980), and North America, primarily in the NE USA (Hendrey et al., 1980), and Quebec and Ontario in Canada (Dillon et al., 1980, 1984). After several decades of increasing acidic deposition during the 1900s, the trend generally changed during the 1980s as a result of several international agreements to reduce sulphur emissions (e.g., UNEP, 1972; CLRTAP, 1979, 1985; Environment '82 Committee, 1982). The decrease of sulphur deposition has contributed to a recovery from acidification, which is currently being observed in the affected surface waters in several countries (Stoddard et al., 1999) (Wilander and Lundin, 2000; Wilander, 2001).

Sweden has been severely affected by acid rain because of the dominating igneous bedrock and relatively sparse occurrence of calcareous bedrock. Approximately 15 000 of a total number of approximately 85 000 lakes less than 1 km^2 were considered to be affected by anthropogenic acidification in 1990 (Swedish Environmental Protection Agency, 1991). Even in relatively remote areas in northern Sweden, low pH values in the snowpack were beginning to occur in the 1970s–1980s, which resulted in acidic episodes in streams (Ahlström and Isaksson, 1990; Laudon and Bishop, 1999; Edberg et al., 2001). Consequently, reproduction impairment and other negative effects on fish and benthic invertebrates have also been documented in numerous waters in northern Sweden (Ahlström et al., 1995; Andrén, 2006, 2009; Andrén and Jarlman, 2008).

The streams in this investigation were monitored from the early 1980s, and the precipitation was monitored from the 1970s to present. This study covers almost 30 yr, during a time period that has experienced dynamic changes in the deposition of acidifying substances over the area. The objectives of the present study were to follow the development of acidification and recovery, and the occurrence of acidic episodes. As a remediation, a large liming program began in the 1980s; therefore, another objective

was to study the influence of the wetlands lime treatment on the mobility of metals, primarily Fe, Mn and Al.

2   Methods

2.1   Study area

5   The streams are located in the middle region of the Swedish mountain range, in the province of Jämtland, municipality of Härjedalen. These streams drain into the impoundment Lake Lofssjön and further downstream into the Lofsån River, which is a tributary to the Ljusnan River, one of the main rivers in N Sweden draining into the Bothnian Sea (Fig. 1). The catchments are in the size range of 10–50 km^2 and are ap-

10   proximately 600–1000 m above sea level (m a.s.l.), consisting of peatbogs and mires, coniferous forests, and tundra. The catchments also include a former lake basin from the last glaciation, which contains fine grained sediments rich in Fe, Mn and Al.

As a remedy against the effects of acid precipitation, most of the streams were repeatedly treated with limestone (Table 1), which was applied by helicopter on the wet-

15   lands and primarily focused on sites with groundwater outflow (for a further description of the area and the lime treatments, see (Andersson and Nyberg, 1984; Borg, 1986; Borg et al., 1995; Nyberg et al., 1995). The river Häggingån was used as unlimed reference stream. Due to a lime treatment of a nearby catchment, also draining into the Lake Lofssjön impoundment, we moved the sampling site a few kilometers upstream

20   (site 5111). It could not be excluded that the liming possibly also influenced the lower reaches of river Häggingån, through leakage through the wetlands in between. The water chemistry at the two sites was very similar, however, and no statistically significant differences between the two could be detected for any chemical parameters (Table 1, Fig. 5).

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2.2 Sampling

During 1975–1993, snow samples were collected in Plexiglas tubes at 1000 m a.s.l. (Häggingfjället site), 800 m a.s.l. (Djursvålen site), 620 m (Djursvallen site) and 400 m (Sveg site). The sampling was performed each year in early April, before any visible snow melting had occurred (Fig. 1). The snow was transported in polyethylene bags, then melted; after melting, the pH was immediately determined. The Djursvallen site was included in a national monitoring program for precipitation chemistry in 1983; precipitation was collected monthly as total deposition in polyethylene samplers. Stream water samples were generally collected monthly, but sometimes daily and weekly; the samples were collected directly into polypropylene bottles for trace metal analysis and into polyethylene bottles for general water chemistry analysis. The bottles for trace metal determinations were cleaned by soaking in 6 M hydrochloric acid for three days at 40 °C and stored with 0.05 M nitric acid for at least one week until use. Before use, the bottles were rinsed with ultrapure deionised water (Milli-Q).

2.3 Chemical analyses

All chemical analyses were performed according to Swedish standard methods (SIS, Swedish Standards Institute), and subsequently, European standard methods (CEN, European Committee for Standardization). The pH was determined on site (snow samples) or after the samples had been transported overnight to the laboratory in Stockholm. A combined glass electrode (Radiometer analytical, Red rod, Ag/AgCl reference electrode) and liquid electrolyte (KCl) was used for all samples. Major cations were determined by air-acetylene flame AAS (Varian), and from 2008 to present by ICP-AES (Varian Vista). The anions were determined using titrimetric and spectrometric methods until 1984, and then by ion chromatography (Tecator, Dionex). The total organic carbon (TOC) was determined using TOC-instruments Carlo-Erba, Astro, and from 2006 to present, a Shimadzu TOC-V CPH. Silica, nitrogen and phosphorus were determined using spectrometry in continuous-flow autoanalysers. Trace metals were

determined using GFAAS (Perkin-Elmer Zeeman 3030), and from in 1995 to present, they were determined using ICP-MS (Sciex Elan 5000, from 2007 Thermo X-series 2). Aluminium speciation was performed by automated cation exchange and spectrometric determination of the pyrocatechol complex (Driscoll C.T., 1984), (Andrén and Rydin, 2009).

Quality assurance of all analytical results included continuous use of internal and certified reference samples, and by following further routines specified in the laboratory accreditation (Swedac accreditation no. 1295, 1993). The analytical laboratory was a part of the Swedish Environmental Protection Agency until 1 July 1992, when it was reorganised into the new Department of Applied Environmental Science (ITM), Stockholm University. The chemical analyses of the precipitations from the Djursvallen site have been included in the national precipitation monitoring network since 1984 (http://www.ivl.se/projekt/uppdrag//luftochnederbordskemiskanatet).

The fractions of sulphate, sodium, calcium and magnesium of non-marine origin, were calculated by subtracting their seawater concentration relative to chloride (e.g., non marine $SO_4^{2-} = SO_4^{2-} - 0.103 \times Cl^-$). In the following text, the ion charges are omitted for clarity.

2.4 Data analysis

Data analyses were performed using the SPSS and JMP statistical packages. The non-parametric Seasonal Kendall test was used to test the significance of trends. The method is suitable for data with strong seasonal variations and for data that are not normally distributed, such as these. For the magnitude of the trends, Theil's slope was estimated for the time series, calculated on a yearly basis, e.g. an increase or decrease by $mg\,L^{-1}\,yr^{-1}$ or $meq\,L^{-1}\,yr^{-1}$ (Helsel and Hirch, 2013).

3   Results

3.1   pH in snow

In 1975, the pH of the snow was approximately 5.4 at all altitudes and was relatively unaffected by acidic deposition, but the pH substantially decreased during the three following years, reaching 4.0 in 1978 at an altitude of 1000 m (Fig. 2). Starting at approximately the same levels in 1975 and 1976, the pH dropped faster at the higher altitudes 800–1000 m a.s.l., while the lowest site at 400 m generally had pH values that were approximately 0.5 units higher. The emerging inverse relationship between snow pH and altitude persisted throughout the studied period. From 1978 the decrease of pH continued at a slower rate but with substantial interannual variation until 1987 when pH reached below 4.0 at 1000 m and whereafter snow pH appeared to slowly increase, at least at the highest altitudes (Fig. 2). The highest precipitation occurred at the highest altitudes, 800–1000 m a.s.l., where the snow depth generally was approximately 40–80 cm greater, than at 400 m (Fig. 3). The drastic drop in snow-pH was reflected in a decreased pH in the stream waters at spring flood, exemplified in Fig. 2 with Djursvålsbäcken brook (5006).

3.2   Deposition

The non-marine fraction (SO_4^*) of annual sulphate deposition, measured at 620 m a.s.l., substantially decreased during the 1980s, from 80 keq km^{-2} in 1985 to 25 in 1990 (Fig. 4). The decrease continued but at a slower rate during the 1990s. During the last decade, the sulphate deposition has stabilised around 5 keq km^{-2}. In contrast, the nitrate deposition shows no clear trend and has varied around approximately 10 keq km^{-2} during the entire 25 yr study period. The non-marine Ca deposition decreased during the 1980s and has then been relatively stable at approximately 5 keq km^{-2}.

3.3 Stream water chemistry

3.3.1 Long-term trends

Stream water chemistry followed the long-term trends in precipitation to some extent, but with local variation among the different streams.

The pH increased from 1994 by 0.03 units yr^{-1} in the unlimed reference stream, Övre Häggingån (5111). However, the seasonal variation was considerable, and acid episodes with pH values less than 5.0 still occurred during the most recent years (Fig. 5, Table 2).

Generally, the sulphate concentration decreased overall, but the rate of change was slower compared to the deposition trend, especially during the 1980s and 1990s. Since the late 1990s, sulphate in the streams has increased (Fig. 6). During the almost 30 yr study period, the sulphate mean level has decreased by approximately $0.03\,meq\,L^{-1}$, which corresponds to an average annual decrease of $1\,\mu eq\,L^{-1}$ (Theil's slope estimator; Helsel and Hirch, 2013) (Table 2). During the period 2000–2010, this decrease cannot be confirmed statistically, and R. Häggingån (5111) even showed an annual increase of $3\,\mu eq\,L^{-1}$ (Table 2). Similar to the observations of the deposition, no long-term trends concerning the nitrate concentration in the stream waters occurred during the study period.

The TOC concentration is relatively high in most of these streams (Table 1) because of upstream wetlands. TOC generally increased until approximately 2002 (Fig. 6), and Theil's slope estimates showed an annual increase of approximately $0.1\,mg\,L^{-1}$ in four of the streams during the study period (Table 2).

Generally, the temporal patterns of the sulphate and TOC concentrations are inversely related (Fig. 6) and there is an overall negative correlation between SO_4^* and TOC ($r^2 = 0.67$, Fig. 7).

3.3.2 Acid episodes

Some difference in seasonal variations of the major ions is evident from monthly median concentrations during unlimed conditions (Fig. 8). The concentrations of non-marine base cations (BC*) were somewhat higher during the groundwater dominated winter months and lowest during the spring flood. Silica presented the same seasonal variation but with a higher amplitude (Fig. 8). In contrast, the TOC values were highest during the summer and decreased during the winter. SO_4^{2-*} showed relatively small seasonal variations overall, with the highest median values in April, which then decreased during the spring to summer and increased again during the snow-covered period (Fig. 8). The hydrological regime of these catchments is characterised by very large seasonal variations in discharge into the streams, with a factor of more than 200 between base and high flow (Borg et al., 1995). This variation favours the occurrence of acidic episodes, when the alkalinity may be totally depleted and the pH reaches 4.0 despite the relatively high buffer capacity of the baseflow water (base flow alkalinity is often 0.5–1.0 meq L^{-1}). The unlimed reference stream Ö Häggingån (5111) had repeated episodes where the pH was approximately 5.0 or below from 1994 to 2010. Similarly, the stream Hammarbäcken (5005), where the lime treatment was terminated in 1995, had episodes with negative alkalinity and a pH less than 5.0, during 1998–2005 (Fig. 5).

To evaluate the main causes of the still frequent acid episodes, the changes in concentrations of the major ions between the base flow and high flow were calculated for three streams; Djursvasslan R (5004), Djursvålsbäcken R (5006), from the period before liming, and Övre Häggingån R (5111), the unlimed reference stream. The changes of BC*, SO$_4^*$, Cl, NO$_3$, and organic anions during high flow were calculated using sampling occasions with maximum ANC as base flow values and minimum ANC representing high flow, during the sampled years (Fig. 9). The median pH values dropped between 1.0 to 1.5 units during the high flow periods, and the loss of ANC was 0.1–0.4 meq L^{-1} (Fig. 9).

The largest change was observed for BC^* in all three streams, of -0.1 to $-0.36\,\mathrm{meq\,L^{-1}}$, which indicates a considerable dilution of the BC^* at high flow. In contrast, sulphate did not exhibit any large changes at peak flow; for most peak flow occasions, it remained unchanged or exhibited a slight dilution. In the reference stream Övre Häggingån (5111), an enrichment of sulphate was observed during the majority of high flow periods, with a median ion difference above zero. The concentration of organic anions slightly increased in stream 5004 Djursvasslan, remained unchanged in stream 5006 Djursvålsbäcken, and was diluted in stream 5111 Ö Häggingån. The chloride and nitrate ions presented only minor changes during high flow (Fig. 9).

3.3.3 Chemical effects of liming

The lime treatment of the wetlands was effective for stabilising the water chemistry and for counteracting the acid episodes during the spring flood and rainy periods. Since the beginning of the treatment, the limed streams have retained some alkalinity, even during the high flow periods, and the pH rarely reached below 5.5 for several years after treatment (Fig. 5). The former extremely high peak values of Fe, Mn and Al during high flow, e.g., in brook Djursvasslan and its tributaries, have not returned since liming began (Fig. 10) (Borg et al., 1995). Trace elements such as Cd also showed lower concentrations and less seasonal variations after liming (Fig. 10). As expected, inorganic monomeric Al (Ali) was negatively correlated to pH, and the highest Ali concentrations occurred at acid episodes, especially in the unlimed streams (Fig. 11). Some elevated concentrations also occurred in stream 5005 Hammarbäcken after the liming was terminated in 1995 along with returning acid episodes. Negative pH correlations were also observed for other typically positively charged elements such as Cd and Zn, while elements that mainly occur as oxoanions, such as Mo, showed a positive correlation with pH; the lowest concentrations were found in the unlimed streams and in the reacidifying stream 5005 (Fig. 11).

4　Discussion

4.1　Deposition

The effects of acid precipitation have been documented in Sweden since the 1960s, primarily in south-western Sweden, the area most affected by long-range airborne pollutants from the European continent (Almer et al., 1974; Odén, 1968). The more northern part of Sweden appeared to be less affected, at least until the mid-1970s, when observations of low pH values in the snow profiles followed by acid episodes in mountain streams were reported e.g. in the area studied here, and further north in Sweden, in the province of Västerbotten (Bjärnborg, 1983). The lowest pH of precipitation in our study area, Lofsdalen, Härjedalen in the province of Jämtland, was generally associated with south-easterly winds, which indicates an influence from domestic emission sources in Sweden and from long-range air pollution from central and Eastern Europe. The nearby mountain range at the Norwegian border likely somewhat protects the area from westerly winds that bring pollutants from Western Europe, e.g. the UK. During some occasions, e.g. in May 1981, pH-values as low as 3.6–3.7 were recorded in the throughfall at 800 m a.s.l. (data from E. Olofsson, Sveg, personal communication, 1995).

Similar to the general trend in many parts of Europe, sulphur deposition rapidly decreased during the 1980s from approximately 80 to 20 keq km^{-2}. The decrease continued more slowly during the 1990s to approximately 10 keq km^{-2}. During the last ten years, the sulphur deposition has been relatively unchanged and even showed a slight increase. The sulphur emission protocols agreed upon in Europe (e.g., UNECE, 1987) had a markedly positive effect, especially during the 1980s, but today's remaining emissions are likely more difficult to decrease further, which causes the earlier decreasing trend of sulphate also in the surface waters to level out or increase (Figs. 4, 6, 13).

The deposition of the Ca* and SO$_4^*$ is now roughly equivalent, which provides potential possibilities for restoring water quality from the earlier excess sulphate deposition and the depletion of cations such as Ca and Mg in the soil.

Some influence of the climatic conditions on the nitrogen fractions in air during the winter (December–March) was observed, indicated by a correlation between the North Atlantic Oscillation Index (http://www.cru.uea.ac.uk/cru/data/nao) and the nitrate concentration in the precipitation ($r^2 = 0.28$, $p < 0.01$) and a weaker correlation with ammonium ($r^2 = 0.14$). There were also a general tendency towards higher pH values and lower sulphate concentrations in the precipitation during periods with a low NAO-index, which indicates that the colder winters in the area are dominated by relatively cleaner Arctic air masses.

4.2 Water chemistry: long-term trends

Like most of Sweden, the investigated area is dominated by non-calcareous bedrock, and thus its surface waters are sensitive to acid precipitation. Consequently, the increased acid deposition caused a deficiency in alkalinity of approximately $0.1\,\mathrm{meq\,L^{-1}}$ compared to the levels of BC* (Fig. 12). The increasingly acidic precipitation in 1970s in these relatively remote but acid-sensitive areas gave a fast response in the quality of the runoff surface waters (Jacks et al., 1986). Figure 2 shows an example from the unlimed Djursvålsbäcken brook (5006), with a relatively close agreement between the pH in the catchment snow and the minimum pH in the stream water during the spring floods (Degerman et al., 1992). The squared correlation coefficients (r^2) between stream water minimum pH and snow pH were 0.84 for snow at 600 m, 0.68 at 800 m, and 0.57 at 1000 m a.s.l., respectively.

The long-term trend in the precipitation chemistry is reflected in the water chemistry of the brooks (Table 1, 2). Theil's slope estimates generally show an annual decrease of sulphate with approximately $1\,\mathrm{\mu eq\,L^{-1}}$ for the study period as a whole, while no change can be detected for the years 2000–2010. In contrast, the reference stream 5111, Övre Häggingån, shows an annual increase of $3\,\mathrm{\mu eq\,L^{-1}}$ 2000–2010. The general decline of sulphate in this area is slower than the general trend found in lakes in southern Sweden and Norway and approximately the same as that in northern lakes (Skjelkvåle et al., 2007).

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The long-term winter (December–April) deposition pattern of the non-marine sulphate on the catchment of the river Djursvasslan (5004) and the concentration of sulphate in the snowpack are reflected in the concentration trend of sulphate in the stream from the 1980s until today (Fig. 13). Generally, the sulphate concentration in the catchment snow is higher than in the stream water spring flood concentration, which indicates that the precipitation-derived sulphate is the main source for the stream water sulphate. However, the sulphate concentration in this stream during high flow has occasionally exceeded the sulphate concentration in the snow. During those occasions, the formerly deposited sulphate retained in the peatlands of the catchment may contribute to the stream water sulphate. The decreasing acid deposition and the possibly increased soil water pH, may also cause a decreased sulphate absorption capacity of the soils, thereby releasing sulphate. However, at some occasions there might also be a depletion of the sulphate content in the snowpack due to selective melting during the winter, even if the samples were collected before any visible snowmelt had occur. The decreasing long-term trend of sulphate in the stream water has rather changed to an increase since the late 1990s, possibly indicating an effect of climate change that has caused changed runoff routes because of a more shallow soil layer being frozen and also shorter periods of frost (Fig. 13). Air temperature data from a monitoring site in the area actually show a statistically significant increase of annual mean temperature by 0.06 °C during the 30 yr study period (Fig. 13, temperature data from http://www.smhi.se/klimatdata/meteorologi/temperatur).

In a study of lakes in northern Sweden included in a national lake survey, the recovery from episodic acidification was also found to be related to the declining sulphate deposition during the winter (Laudon and Bishop, 2002).

The overall long-term trends in sulphate and TOC are roughly opposite to each other (Fig. 6). A significant negative correlation between non-marine sulphate and TOC in water was consequently found ($r^2 = 0.67$, Fig. 7). The increase in TOC may thus to a large extent be related to the change in sulphate concentrations in the streams. This relationship is similar to what has been reported from other areas, e.g., lakes

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and streams in the UK as well as lakes in the US and Scandinavia (Erlandsson et al., 2008; Evans et al., 2005, 2006; Monteith et al., 2007; Winterdahl et al., 2011). In those studies, it was concluded that in addition to climate-related effects (Freeman, 2004; Weyhenmeyer and Karlsson, 2009; Jennings et al., 2010), there also seems to be a connection between the decreased acid deposition and the increased run-off of organic carbon to streams and lakes in regions that were previously affected by higher load of acidifying substances. The observed trend in organic carbon in our streams may thus be a result of changed acid deposition and also of a changing climate.

4.3 Water chemistry: seasonal variations

The hydrological regime of the area favours large fluctuations in discharge in the streams (Borg et al., 1995), which cause substantial short-term variations in e.g., pH (Fig. 5). The streams are relatively well buffered during base flow but may lose all of their ANC in a few hours at rising discharge during the spring snow melt. Most of the severe episodes were associated with the spring flood following snow melt; in some years, the spring flood consisted of two or more flow peaks depending on the progress of the snow melt at lower and higher altitudes. Acid episodes caused by the rainy periods in the summer and autumn were also occasionally observed.

The seasonal variations show different patterns for different water chemistry variables. The pH and BC* are lowest during the high flow in May (Fig. 8). Silica exhibits approximately the same pattern as BC*, but with a larger amplitude. The highest concentrations were observed during the winter, which reflects a major contribution from groundwater and a dilution with runoff water during the spring flood. TOC exhibits the opposite pattern, with the highest levels during the summer-autumn months and the lowest during the periods with frozen soils, which reflects the major influence from vegetation, soil and peat, and possibly some benthic primary production in the streams. The sulphate variations were relatively small between seasons, with slightly higher values during April, decreasing May–June, and then increasing again during the autumn months. The minor dilution effect of sulphate during the spring flood, compared

to pH, ANC and BC*, indicates an influence from precipitation-derived sulphate from the snowpack and a possible contribution from older deposits of sulphur in the wetlands from previous years with higher sulphur deposition.

The general deficit of alkalinity in the streams (Fig. 12) indicates a relatively high susceptibility to acid episodes during the high flow periods, which was also observed as sharp drops in pH and ANC. At unlimed conditions in the streams, the major reason for the loss of ANC and decrease in pH at high flow was a marked dilution of BC*, decreasing with up to $0.36 \, \mathrm{meq \, L^{-1}}$ (Fig. 9). Other ions behaved slightly differently in the different streams. In river Djursvasslan (5004), which presents the largest loss of BC*, the organic anions increased slightly at high flow. This may be expected, as this stream drains large wetlands, thereby releasing organic anions that can contribute to a decreased ANC and pH. In the other two streams, the organic anions became unchanged or were diluted at flow peak, such as in the stream 5111, which was less influenced by wetlands. Sulphate was unchanged in stream 5004, somewhat diluted in 5006, and generally enriched in 5111, whereas changes in chloride and nitrate were minor and did not contribute to the loss of ANC in any substantial way (Fig. 9). Consequently, the base cation dilution was the overall most important reason for the ANC depression at acid episodes in these streams with varying contributions from the enrichment of sulphate or organic acids.

These results are in agreement with other stream water studies in northern Sweden and in the north eastern USA. Laudon and Bishop (1999), studying five streams in northern Sweden, found that dilution of base cations with some contribution from organic anions was the most important cause for ANC loss at high flow episodes. In another study, dilution at high flow was found to be the main cause for 58 % of identified acid episodes among 87 streams in Sweden, while enrichment of sulphate was found to be the main reason for 26 % of the episodes. The sulphate-related episodes were often related to preceding drought periods (Erlandsson et al., 2010).

Calculating flow related ion differences Wigington et al. (1996) found that dilution of base cations provided the most important contributions to the ANC depressions dur-

ing the episodes in streams in the north eastern USA, with some contributions from organic anions and sulphate. In an experimental study with ammonium sulphate repeatedly added to the Bear Brook Watershed in Maine, north-eastern USA, sulphate was the most important driver of the loss of ANC, and the acid episodes were mostly due to snow melt events and showed a steady increase following the beginning of the treatment (Laudon and Norton, 2010).

Using sulphur isotopes and sulphate concentrations in streams in N Sweden, Mörth et al. (2008) found that the main streamwater sulphate sources were sedimentary sulphides and anthropogenic sulphur. During snowmelt, anthropogenic sulphur from the snow and desorbing sulphate were the main sources of sulphur. A release of earlier deposited reoxidised sulphur may also contribute to streamwater sulphur during spring flood.

During acid episodes, extremely high concentrations of metals, especially Fe, Mn and Al, occurred in the stream waters (Borg et al., 1995). Large deposits of precipitated MnO_2 and $FeOOH$ formed in the stream beds further downstream (Erik Olofsson, personal communication, 1985). Earlier studies involving the speciation of metal forms using cation exchange and in situ dialysis have confirmed that there is a high portion of particulate and organically complexed Fe during high flow periods (Borg, 1986). Similarly, less than 20 % of Pb occurred as dissolved (dialysable), in contrast to Cd (up to 75 %) and Cu (30–100 %) The observed processes were likely caused by the following conditions. In the upper part of the catchments, there are old sediments originating from former lake basins formed by the last glaciation. These sediments consist of fine particulate silt with Fe and Mn in reduced forms bound as sulphides and carbonates. Normally, the pH of the groundwater flowing through these sediments is sufficiently high to prevent the release of Fe(II) and Mn(II). However, when the acidic deposition on the catchments increased, the groundwater pH also successively decreased, and the Mn(II), Fe(II) and Fe(III) in complexes with FeOOH were dissolved, transported to the streams and then oxidised and precipitated further downstream after contact with the oxygenated stream water. Since the wetland liming operations in the catchment of

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river Djursvasslan and its tributaries started in 1985, no high peak values of Fe, Mn or Al have been observed (Fig. 10). The application of lime on the wetlands was primarily focused on areas with groundwater discharge and apparently trapped metals successfully in the soils and peatlands.

4.4 Recovery from acidification

The streams in the study area still show frequent acid episodes, with pH-drops to 5.0 or below, with complete loss of alkalinity. Exceedance of the critical load of acidity on this region is still 200–400 keq km^{-2}, after a decrease from 400–700 keq km^{-2} during the 1980s (Sverdrup et al., 2002). Despite the large decrease in the acid deposition since the 1980s, only minor recovery of the stream waters can be observed during recent years. In general, the sulphate concentrations in the streams have only decreased by approximately 1 µeq L^{-1} yr^{-1} during the 30 yr study period, and in the latest 10 yr, the decrease has reversed. In a reference stream (5111), even an increase of sulphate by approximately 1 µeq L^{-1} yr^{-1} was measured. Simultaneously, pH showed a minor annual increase by 0.03 units (Table 2).

Consequently, in addition to natural causes, e.g. dilution of BC* at high flow, the remaining exceedance of the critical load of acidity may contribute to the acid episodes that are still occurring in the streams and to the slow recovery of water chemistry from acidification, even in these relatively remote areas in Sweden.

References

Ahlström, J. and Isaksson, K. E.: Försurningsläget i Norrlands inland och fjälltrakter, Swedish Environmental Protection Agency Report 3781, 136 pp., 1990.

Ahlström, J., Degerman, E., Lindgren, G., and Lingdell, P. E.: Försurning av små vattendrag i Norrland, Statens naturvårdsverk, report 4343, 129, 1995.

Almer, B., Dickson, W., Ekström, C., Hörnström, E., and Miller, U.: Effects of acidification on Swedish lakes, Ambio, 3, 29–36, 1974.

Andersson, P. and Nyberg, P.: Experiments with brown trout (*Salmo trutta L.*) during spring in mountain streams at low pH and elevated levels of iron, manganese and aluminium, Rep. Inst. Fresh. Research, 61, 34–47, 1984.

Andrén, C.: Acid episodes in watercourses – IKEU-programme, Special project S9, ITM-report 2006-12-15, 13 pp., 2006.

Andrén, C.: Benthic fauna and diatoms in running waters within IKEU-programme, in: Evaluation of the IKEU-programme 1990–2006, edited by: Munthe, J. and Jöborn, A., Report 6302, The Swedish Environmental Protection Agency, Stockholm, 454–472, 2009.

Andrén, C. and Jarlman, A.: Benthic diatoms as indicators of acidity in streams, Fund. Appl. Limnol., 173, 237–253, 2008.

Andrén, C. and Rydin, E.: Which aluminium fractionation method will give true inorganic monomeric Al results in fresh waters (not including colloidal Al)?, J. Environ. Monit., 11, 1639–1646, 2009.

Bjärnborg, B.: Dilution and acidification effects during spring flood of four Swedish mountain brooks, Hydrobiologia, 101, 19–26, 1983.

Borg, H.: Metal speciation in acidified mountain streams in central Sweden, Water Air Soil Pollut., 30, 1007–1014, 1986.

Borg, H., Andersson, P., Nyberg, P., and Olofsson, E.: Influence of wetland liming on water chemistry of acidified mountain streams in Lofsdalen, central Sweden, Water Air Soil Pollut., 85, 907–912, 1995.

CLRTAP: Convention of Long-Range Transboundary Air Pollution, ECE, UNEP, Geneva, 1979.

CLRTAP: Convention of Long-Range Transboundary Air Pollution, ECE, UNEP, Helsinki, 1985.

Degerman, E., Engblom, E., Lingdell, P.-E., Melin, E., and Olofsson, E.: Försurning i fjällen? Info Sötvattenslab, Fishery Board of Sweden, Drottningholm, 1, 1992.

Dickson, W.: Properties of acidified waters, in: Ecological Impact of Acid Precipitation, edited by: Drablös, D. and Tollan, A., SNSF-project, Oslo-Ås., 75–83, 1980

Dillon, P. J., Jeffries, D. S., Scheider, W. A., and Yan, N. D.: Some aspects of acidification in Southern Ontario, in: Ecological Impact of Acid Precipitation, edited by: Drablös, D. and Tollan, A., SNSF-project, Oslo-Ås., 212–213, 1980

Dillon, P. J., Yan, N. D., and Harvey, H. H.: Acidic deposition: effects on aquatic ecosystems, CRC Cr. Rev. Anal. Chem., 13, 167–194, 1984.

Driscoll, C. T.: A procedure for the fractionation of aqueous aluminium in dilute acidic waters, Int. J. Environ. Anal. Chem., 16, 267–283, 1984.

Edberg, F., Borg, H., and Åslund, J. E.: Episodic events in water chemistry and metals in streams in northern Sweden during spring flood, Water Air Soil Pollut., 130, 1697–1702, 2001.

Environment '82 Committee: Acidification Today and Tomorrow, Stockholm conference on the acidification of the environment, Swedish Ministry of Agriculture, 1982.

Erlandsson, M., Buffam, I., Fölster, J., Laudon, H., Temnerud, J., Weyhenmeyer, G. A., and Bishop, K.: Thirty-five years of synchrony in the organic matter concentrations of Swedish rivers explained by variation in flow and sulphate, Glob. Change Biol., 14, 1191–1198, 2008.

Erlandsson, M., Laudon, H., and Fölster, J.: Spatiotemporal patterns of drivers of episodic acidification in Swedish streams and their relationships to hydrometeorological factors, Sci. Total. Environ., 408, 4633–4643, 2010.

Evans, C. D., Chapman, P. J., Clark, J. M., Monteith, D. T., and Cresser, M. S.: Alternative explanations for rising dissolved organic carbon export from organic soils, Glob. Change Biol., 12, 2044–2053, 2006.

Evans, C. D., Monteith, D. T., and Cooper, D. M.: Long-term increases in surface water dissolved organic carbon: Observations, possible causes and environmental impacts, Environ. Pollut., 137, 55–71, 2005.

Freeman, C.: Export of dissolved organic carbon from peatlands under elevated carbon dioxide levels, Nature, 430, 195–198, 2004.

Helsel, D. and Hirch, R.: Statistical Methods in Water Resources, Elsevier Science B. V., Amsterdam, 2013.

Hendrey, G. R., Galloway, J. N., Norton, S. A., Schofield, C. L., Burns, D. T., and Schaffer, P. W.: Sensitivity of the eastern United States to acid precipitation impacts on surface waters, in:

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Ecological Impact of Acid Precipitation, edited by: Drablös, D. and Tollan, A., SNSF-project, Oslo-Ås., 216–217, 1980.

Henriksen, A.: Acidification of fresh waters – a large scale titration, in: Ecological Impact of Acid Precipitation, edited by: Drablös, D. and Tollan, A., SNSF-project, Oslo-Ås., 68–74, 1980.

Jacks, G., Olofsson, E., and Werme, G.: An acid surge in a well-buffered stream, Ambio, 15, 282–285, 1986.

Jennings, E., Järvinen, M., Allot, N., Arvola, L., Moore, K., Naden, P., Aonghusa, C. N., Noges, T., and Weyhenmeyer, G. A.: The impact of the changing climate on the flux of dissolved organic carbon from catchments, in: The Impact of Climate Change on European Lakes, edited by: George, D. G., Aquatic Ecology Series, Springer, 199–220, 2010.

Laudon, H. and Bishop, K.: Quantifying sources of acid neutralisation capacity depression during spring flood episodes in Northern Sweden, Environ. Pollut., 105, 427–435, 1999.

Laudon, H. and Bishop, K.: The rapid and extensive recovery from episodic acidification in northern Sweden due to declines in SO_4^{2-} deposition, Geophys. Res. Lett., 29, 1594, doi:10.1029/2001GL014211, 2002.

Laudon, H. and Norton, S. A.: Drivers and evolution of episodic acidification at the Bear Brook Watershed in Maine, USA, Environ. Monit. Assess., 171, 59–69, 2010.

Monteith, D. T., Stoddard, J. L., Evans, C. D., de Wit, H. A., Forsius, M., Högåsen, T., Wilander, A., Skjelkvåle, B. L., Jeffries, D. S., Vuorenmaa, J., Keller, B., Kopacek, J., and Vesely, J.: Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry, Nature, 450, 537–540, 2007.

Mörth, C. M., Laudon, H., Mellqvist, E., Torssander, P., and Giesler, R.: Sources of stream water sulphate during the spring snowmelt in boreal streams: Evidence from δ^{34}S isotope measurements, J. Geophys. Res., 113, G01005, doi:10.1029/2007JG000457, 2008.

Nyberg, P., Andersson, P., Degerman, E., Borg, H., and Olofsson, E.: Labile inorganic manganese – an overlooked reason for fish mortality in acidified streams?, Water Air Soil Pollut., 85, 333–340, 1995.

Odén, S.: The acidification of air and precipitation and its consequences on the natural environment, Swed. Nat. Sci. Res. Council, Ecol. Comm. Bull., 1, 1–68, 1968.

Skjelkvåle, B. L., Borg, H., Hindar, A., and Wilander, A.: Large scale patterns of chemical recovery in lakes in Norway and Sweden: Importance of seasalt episodes and changes in dissolved organic carbon, Appl. Geochem., 22, 1174–1180, 2007.

Long-term trends of water chemistry in mountain streams

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Stoddard, J. L., Jeffries, D. S., Lükewille, A., Clair, T. A., Dillon, P. J., Driscoll, C. T., Forsius, M., Johannessen, M., Kahl, J. S., Kellogg, J. H., Kemp, A., Mannio, J., Monteith, D. T., Murdoch, P. S., Patrick, S., Rebsdorf, A., Skjelkvåle, B. L., Stainton, M. P., Traaen, T., van Dam, H., Webster, K. E., and Wilander, A.: Regional trends in aquatic recovery from acidification in North America and Europe, Nature, 401, 575–578, 1999.

Sverdrup, H., Staaf, H., and Rapp, L. A. M.: Kritisk belastning för svavel och kväve, in: Kritisk Belastning för Svavel och Kväve, edited by: Bertills, U. and Lövblad, G., Swedish Environmental Protection Agency, 52–80, 2002.

Swedish Environmental Protection Agency: Acidification and liming of Swedish freshwaters, Monitor, 12, 144 pp., 1991.

UNECE: The 1985 Helsinki Protocol on the Reduction of Sulphur Emissions or their Transboundary Fluxes by at least 30 per cent, Protocol to the 1979 convention on long-range transboundary air pollution on further reduction of sulphur emissions, The Economic Commission for Europe, Helsinki, 1987.

UNEP: Declaration of the United Nations Conference of the Human Environment, 1972, United Nations Environment Programme, 21st plenary meeting, 1972-06-16, Stockholm, 1972.

Weyhenmeyer, G. A. and Karlsson, J.: Nonlinear response of dissolved organic carbon concentrations in boreal lakes to increasing temperatures, Limnol. Oceanogr., 54, 2513–2519, 2009.

Wigington, P. J., DeWalle, D. R., Murdoch, P. S., Kretser, W. A., Simonin, H. A., VanSickle, J., and Baker, J. P.: Episodic acidification of small streams in the northeastern United States: Ionic controls of episodes, Ecol. Appl., 6, 389–407, 1996.

Wilander, A. and Lundin, L.: Recovery of surface waters and forest soils in Sweden, in: Recovery from Acidification in the Natural Environment: Present Knowledge and Future Scenarios, edited by: Warfvinge, P. and Bertills, U., Swedish Environmental Protection Agency, Report 5034, 53–64, 2000.

Wilander, A.: Effects of reduced S deposition on large-scale transport of sulphur in Swedish rivers, Water Air Soil Pollut., 130, 1421–1426, 2001.

Winterdahl, M., Temnerud, J., Futter, M. N., Löfgren, S., Moldan, F., and Bishop, K.: Riparian zone influence on stream water dissolved organic carbon concentrations at the Swedish integrated monitoring sites, Ambio, 40, 920–930, 2011.

Long-term trends of water chemistry in mountain streams

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Wright, R. F., Harriman, R., Henriksen, A., Morrison, B., and Caines, L. A.: Acid lakes and streams in the Galloway area, southwestern Scotland, in: Ecological Impact of Acid Precipitation, edited by: Drablös, D. and Tollan, A., SNSF-project, Oslo-Ås., 248–249, 1980.

Long-term trends of water chemistry in mountain streams

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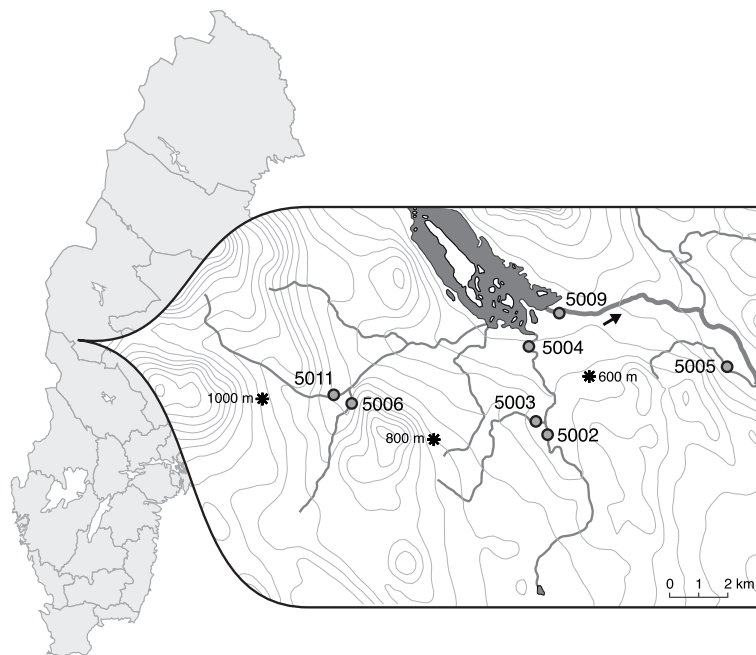Full Screen / Esc

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Table 1. Water chemical data from streams in the Lofsdalen area, Härjedalen, province of Jämtland (Mean, 5- and 95-percentiles).

|	Liming		pH	Alk meq L^{-1}	ANC meq L^{-1}	BC* meq L^{-1}	SO$_4^*$ meq L^{-1}	TOC mg L^{-1}	Fe µg L^{-1}	Mn µg L^{-1}	Al µg L^{-1}
5004 R. Djursvasslan 1981–2010	Unlimed 1981– 1985	Mean 5 perc 95 perc	6.05 4.68 7.46	0.186 −0.010 0.840	0.331 0.055 0.820	0.374 0.095 0.867	0.043 0.019 0.079	9.0 2.1 16.0	3256 390 10 300	482 10 960	124 20 442
Lat 62.0285° N Long 13.4885° E	Limed 1985–	Mean 5 perc 95 perc	6.93 6.10 7.55	0.351 0.050 0.810	0.456 0.135 0.890	0.476 0.149 0.927	0.020 < 0.010 0.048	10.2 3.3 19.0	603 250 1290	66 11 230	59 16 116
5005 R. Hammarbäcken 1983–2010	Unlimed 1983– 1984	Mean 5 perc 95 perc	5.68 4.47 7.05	0.051 −0.010 0.180	0.119 0.045 0.205	0.176 0.075 0.238	0.056 0.018 0.098	13.5 8.9 18.0	3090 210 47 000	302 11 1390	151 35 400
Lat 62.0402° N Long 13.5670° E	Limed 1985– 1995	Mean 5 perc 95 perc	6.41 5.47 6.97	0.125 0.020 0.270	0.216 0.090 0.354	0.245 0.125 0.382	0.029 0.009 0.048	10.6 4.8 20.0	750 160 1800	81 8 166	89 39 191
	After terminated liming 1996–	Mean 5 perc 95 perc	6.37 5.18 7.10	0.119 −0.003 0.270	0.214 0.100 0.304	0.231 0.125 0.338	0.017 < 0.010 0.035	13.0 4.8 26.4	793 295 1390	62 11 178	106 39 191
5006 R. Djursvålsbäcken 1982–2010	Unlimed 1982– 1992	Mean 5 perc 95 perc	5.67 4.21 7.10	0.073 −0.010 0.330	0.104 0.015 0.370	0.140 0.053 0.408	0.036 0.009 0.059	9.1 1.0 24.0	448 48 1470	33 1 140	97 19 197
Lat 62.0063° N Long 13.3709° E	Limed 1992–	Mean 5 perc 95 perc	6.63 5.60 7.20	0.153 0.020 0.390	0.229 0.099 0.503	0.251 0.129 0.525	0.022 < 0.010 0.048	9.5 1.7 24.0	345 105 1010	31 2 132	82 21 148
5009 R. Lofsån 1981–2010 (outlet river)	Unlimed 1981– 1985	Mean 5 perc 95 perc	6.17 5.17 6.91	0.092 −0.005 0.235	0.149 0.070 0.270	0.196 0.108 0.329	0.046 0.009 0.068	10.4 7.7 14.0	574 140 2080	114 13 490	101 59 196
Lat 62.0379° N Long 13.5127° E	Limed 1985–	Mean 5 perc 95 perc	6.63 6.13 7.00	0.170 0.060 0.330	0.237 0.140 0.389	0.268 0.172 0.410	0.031 0.009 0.048	8.1 5.5 11.5	375 130 766	66 13 195	71 42 108
5110/5111 R. Häggingån 1984–2010 Lat 62.0116° N Long 13.3666° E	Unlimed reference	Mean 5 perc 95 perc	6.06 4.50 7.03	0.060 −0.023 0.230	0.114 0.020 0.291	0.155 0.062 0.318	0.036 < 0.010 0.059	8.4 1.0 28.0	212 33 680	17 1 50	89 23 177

Table 2. Long term changes of SO_4^*, TOC and pH in the streams during the whole period and the last 10 yr, respectively. Seasonal Kendall–Theil's slope estimates, significant changes in bold ($p < 0.05$ at least).

Stream	Period	SO_4^{2-} Theils slope ($\mathrm{meq\,L^{-1}\,yr^{-1}}$)	Sign.	TOC Theils slope ($\mathrm{mg\,L^{-1}\,yr^{-1}}$)	Sign.	pH Theils slope ($\mathrm{pH\,units\,yr^{-1}}$)	Sign.
5004	1982–2010	**-0.001**	< 0.001	**+0.10**	< 0.01	(limed)	
R. Djursvasslan	2000–2010	−0.0002	–	+0.045	–		
5005	1982–2010	**-0.001**	< 0.0005	**-0.13**	< 0.04	(limed)	
R. Hammarbäcken	2000–2010	−0.0005	–	0	–		–
5006	1982–2010	**-0.001**	< 0.001	+0.08	–	(limed)	
R. Djursvålsbäcken	2000–2010	+0.0004	–	−0.16	–		–
5009	1982–2010	**-0.001**	< 0.0001	**+0.06**	< 0.004	(limed)	
R. Lofsån (outlet stream)	2000–2010	+0.0002	–	+0.1	–		
5111	1994–2010	+0.001	–	−0.23	–	**+0.031**	< 0.07
R. Övre Häggingån (referens)	2000–2010	**+0.003**	< 0.03	**-0.45**	< 0.05	+0.044	–

Fig. 1. Map of the study area, with water and snow (*) sampling sites and the location in Sweden.
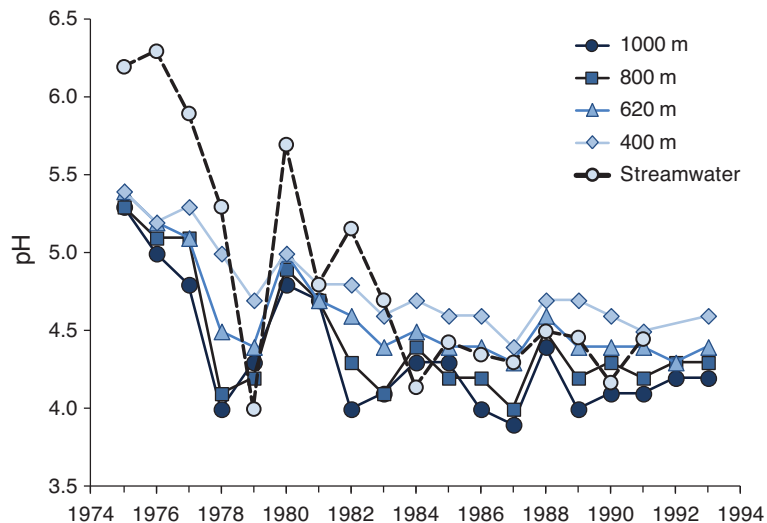
Fig. 2. pH of the snowpack at different altitudes a.s.l., and springflood minimum-pH in brook Djursvålsbäcken (5006). Snow samples was collected in April 1975–1993 (data from Erik Olofsson, Sveg, municipality of Härjedalen).
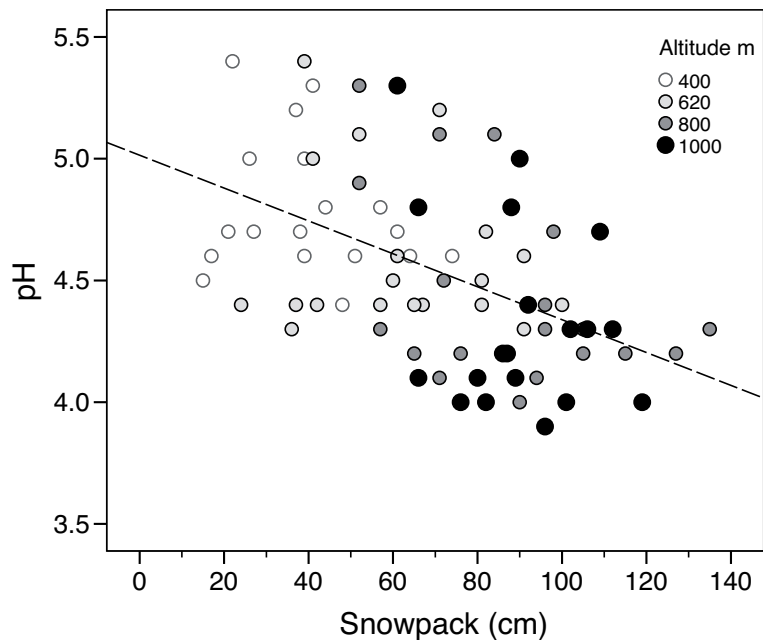
Fig. 3. Correlation between snow depth and snow pH at different altitudes a.s.l. (data from Erik Olofsson, Sveg, municipality of Härjedalen).
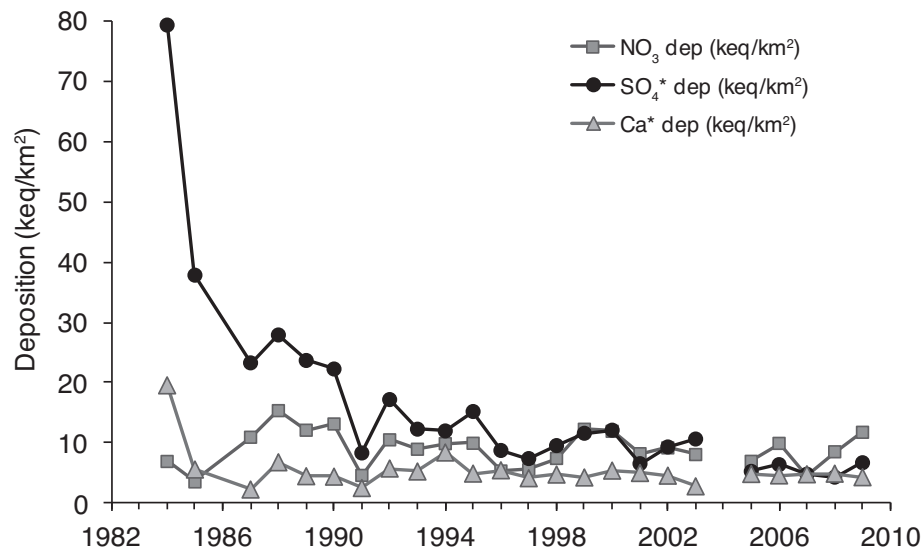
Fig. 4. SO_4^*-, NO_3^--, and Ca^*-deposition at the precipitation monitoring site Djursvallen, close to stream 5004, R. Djursvasslan in Lofsdalen, 1984–2009 ("*" indicates the non marine fractions).

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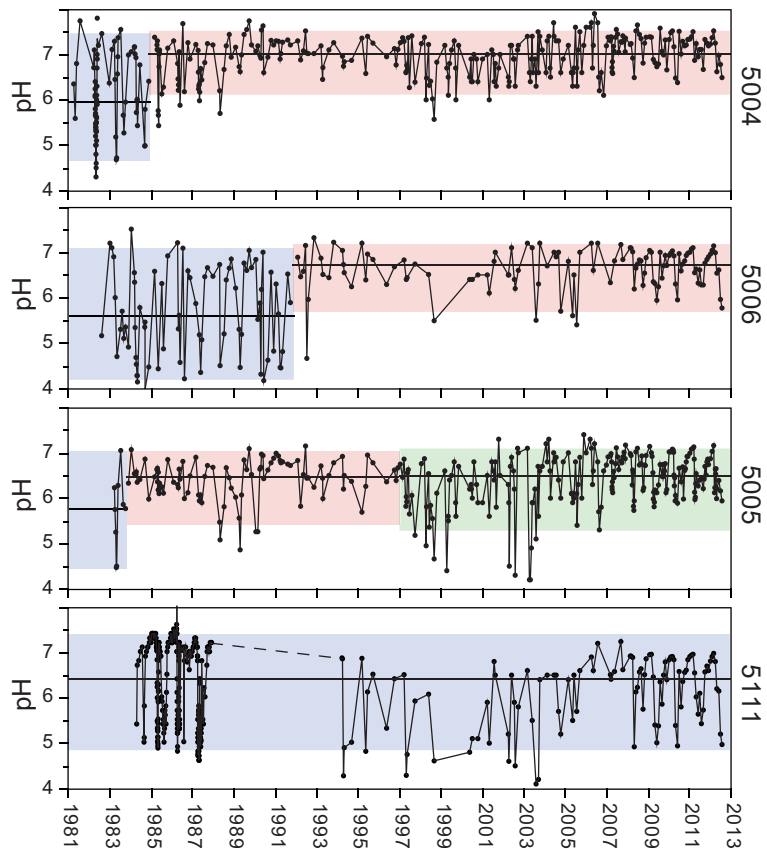
Fig. 5. Fluctuations of pH in the streams 5004, 5005, 5006, and 5111. Blue areas mark the unlimed periods, red areas the limed periods, and green area the period after terminated liming. Stream 5111 is an unlimed reference stream. The horizontal lines represent median pH for the respective periods.

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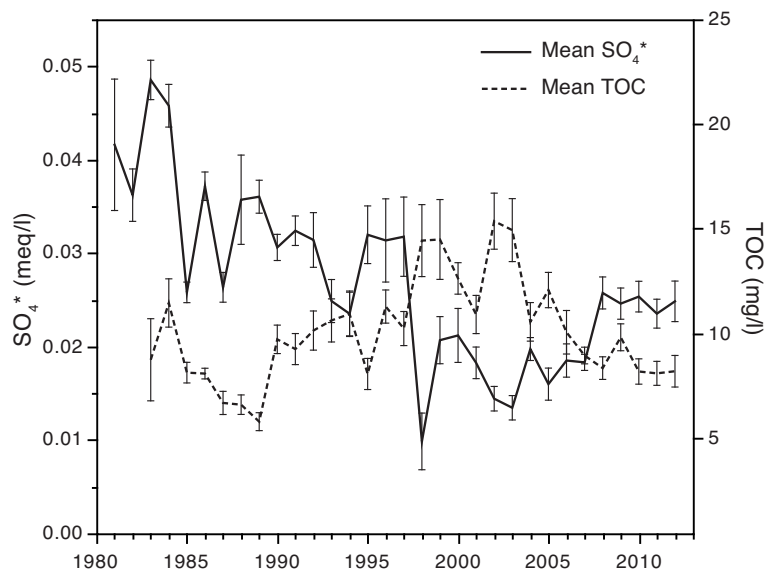
Fig. 6. Trends in SO_4^* (straight line) and TOC (dashed line) in the streams during the study period (annual mean, standard error). Data include the streams 5004 (with the two tributaries 5002, 5003), 5005, 5006, 5009, and 5111.
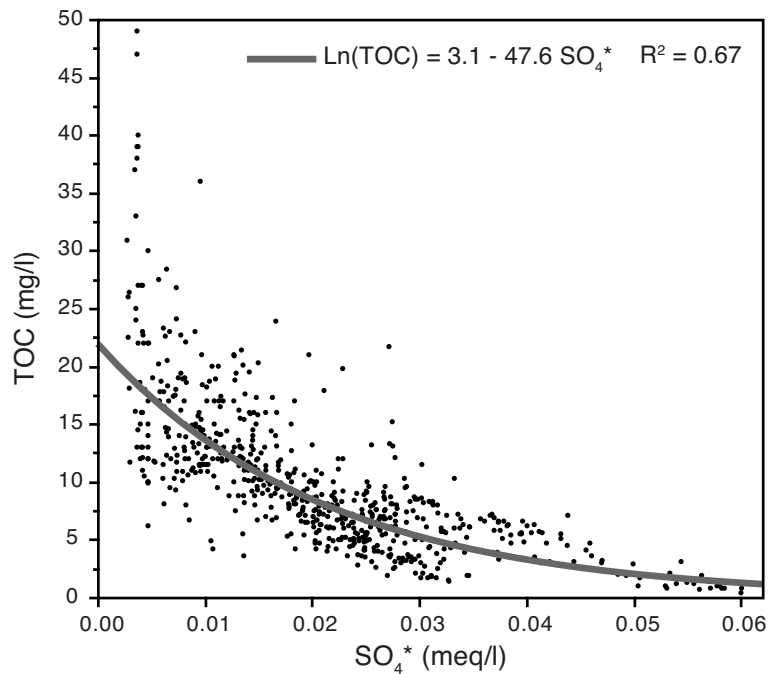
Fig. 7. Correlation between TOC- and SO$_4^*$-concentrations in the streams waters.
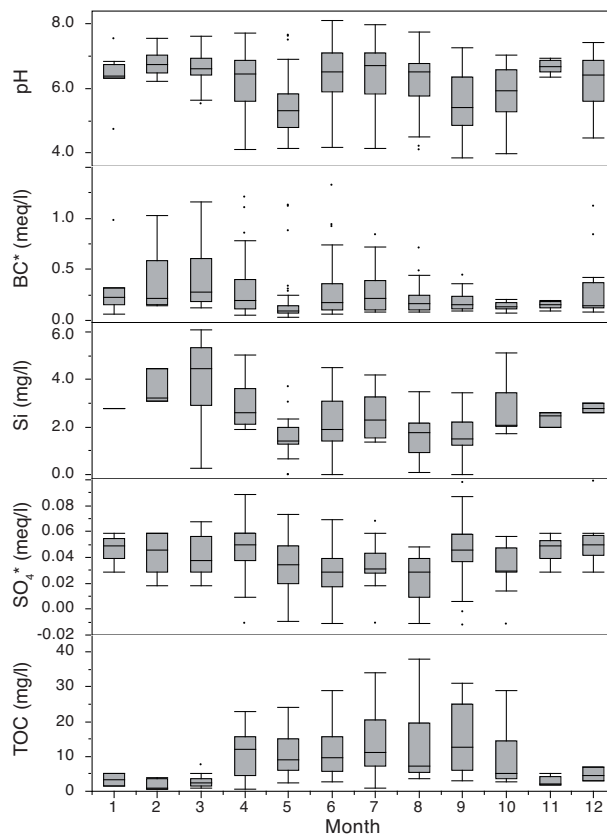
Fig. 8. Seasonal variations in water chemical parameters at unlimed conditions. Boxes represent 25- 50- and 75-percentiles and whiskers represent 10- and 90-percentiles.
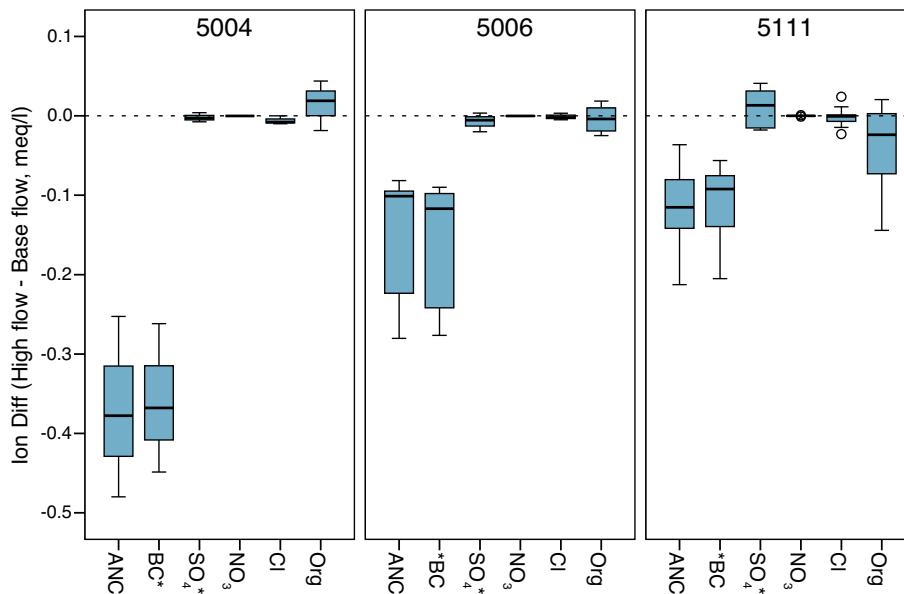
Fig. 9. Loss of ANC and the resulting changes in major ions in unlimed streams at high flow compared to base flow (high flow – base flow, i.e. negative numbers indicate dilution at high flow).
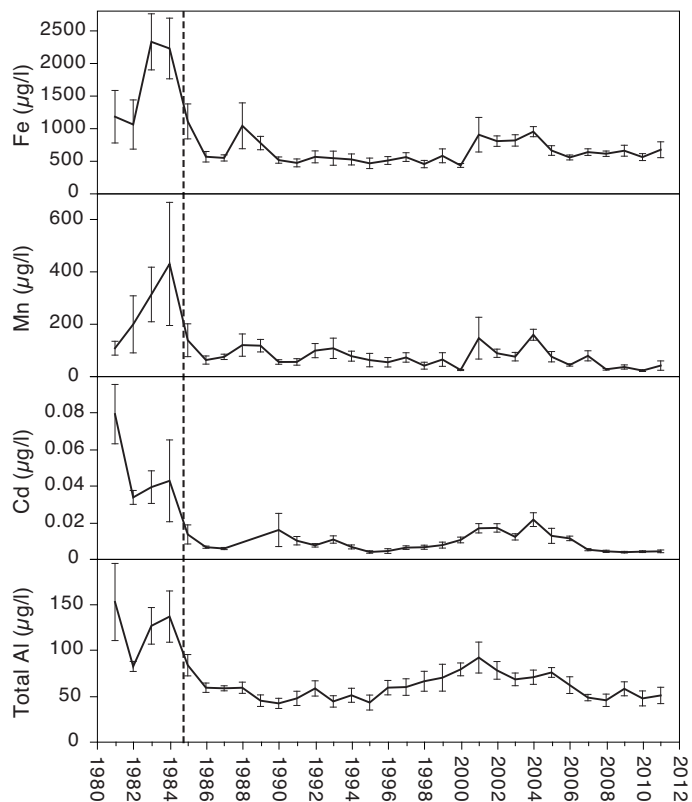
Fig. 10. Concentrations of Fe, Mn, Cd, and Al in R. Djursvasslan (5004) and its two tributaries (5002,5003) before and after the start of liming (annual means, ± SD).
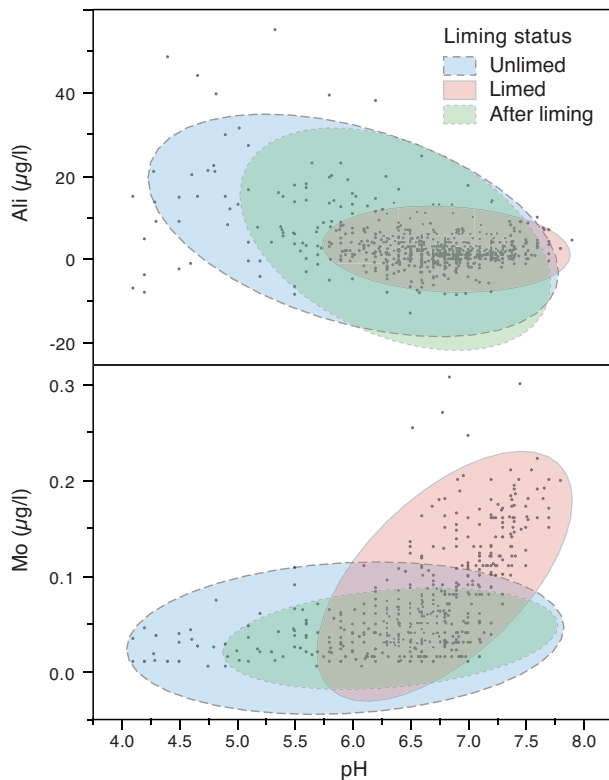
Fig. 11. Correlations between pH and inorganic Al (Ali, upper panel) and Mo (lower panel), respectively. Unlimed conditions (blue areas); limed conditions (red areas); liming terminated in 1995 (green areas). The ellipses are density contours and confidence curves for 90 % of the observations.
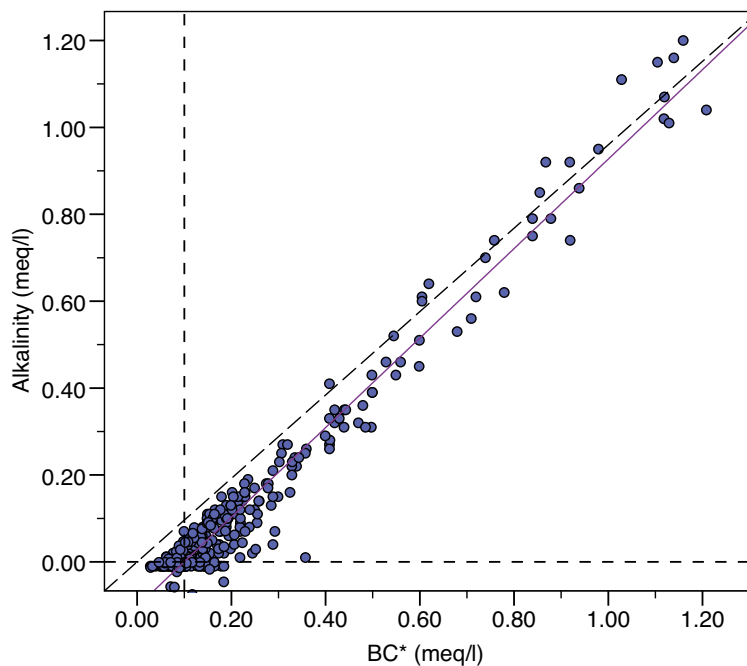
Fig. 12. An average deficit of alkalinity of approximately $0.1\,\mathrm{meq\,L^{-1}}$ was found before liming of the stream waters.
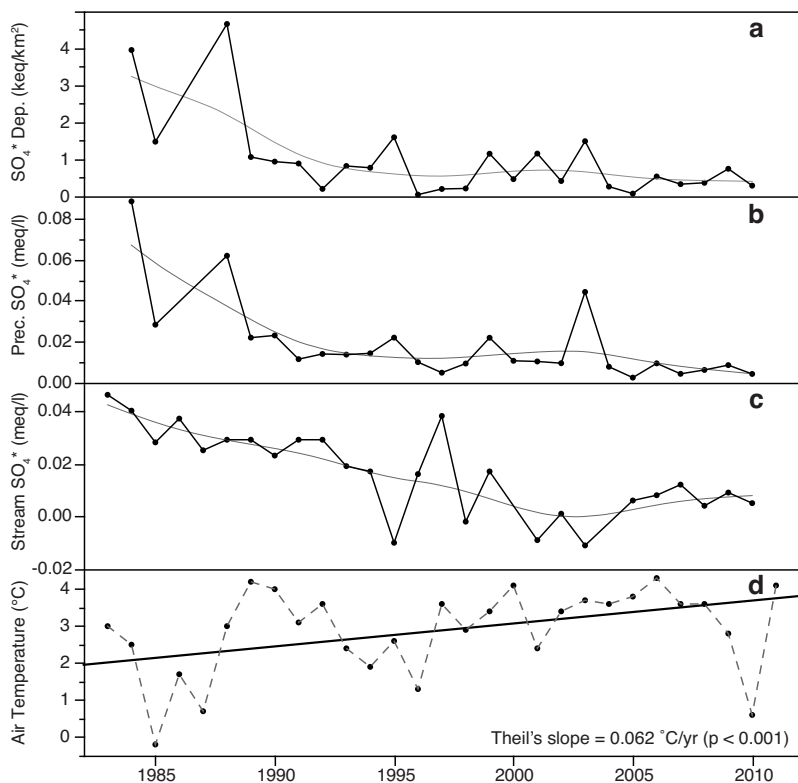
Fig. 13. (a) Trends in winter (November–April) SO_4^*-deposition (keq km^{-2}); **(b)** SO_4^*- concentration in snow (precipitation weighted mean, meq L^{-1}); **(c)** SO_4^*-concentration in R. Djursvasslan (5004) streamwater during springflood (May, meq L^{-1}); **(d)** annual mean air temperature. The thin lines represent a spline function fitted to the data.