

Introduction

The water chemistry of precipitation and streams in Härjedalen (Fig.1) was monitored since the 1980s in order to study long-term trends, occurrence of acid episodes, and the effects of wetland liming. The acidity of precipitation increased in the 1970s, reflected in a drastic decrease of snow pH, also followed by a decreased pH in affected streams (Fig.2). The sulphur deposition decreased in the 1980s, until approximately 2000, after which the decrease levelled out and stabilised. NO_3^- and Ca^{2+} did not show any long term trend during the 30 year period (Fig. 3).

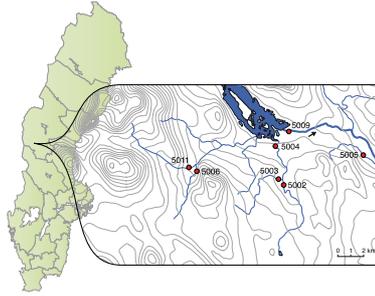


Fig.1. The study area and long-term monitoring stations in Lofsдалen, Härjedalen.

Conclusions

- The studied area is remote from emission sources in Sweden and Europe, and the deposition of sulphur has decreased since the 1980's. The critical load of acidity is however still exceeded, and the long-term recovery of the streams is slow; during the 30 year study period, the SO_4^{2-} concentration has decreased with approximately $1 \mu\text{eq/l/year}$, primarily in the 1980's and 1990's.

- The general decrease of SO_4^{2-} in the stream occurred simultaneously with an increase of organic carbon (TOC) in the waters, indicating an influence on TOC of decreasing acid deposition, besides a possible climate effect.

- Severe acidic episodes are still occurring at high flow periods, and besides natural causes such as dilution of base cations and enrichment of organic anions, some influence of sulphate derived from the catchment snow or the catchment soil could be detected.

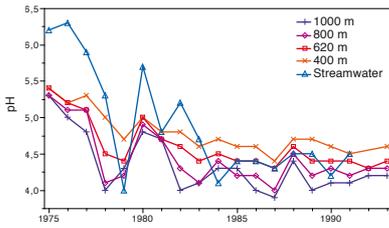


Fig. 2. pH in catchment snow and springflood of brook 5006 Djursvålsbäcken (Data from Erik Olofsson, Sveg, municipality of Härjedalen).

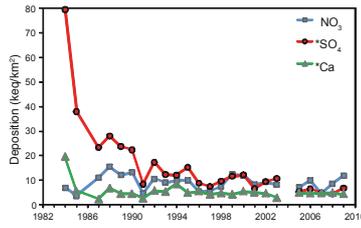


Fig. 3. SO_4^{2-} , NO_3^- , and Ca^{2+} -deposition at the precipitation monitoring site Djursvallen in Lofsдалen, 1984 to 2009 (** indicates the non-marine fractions).

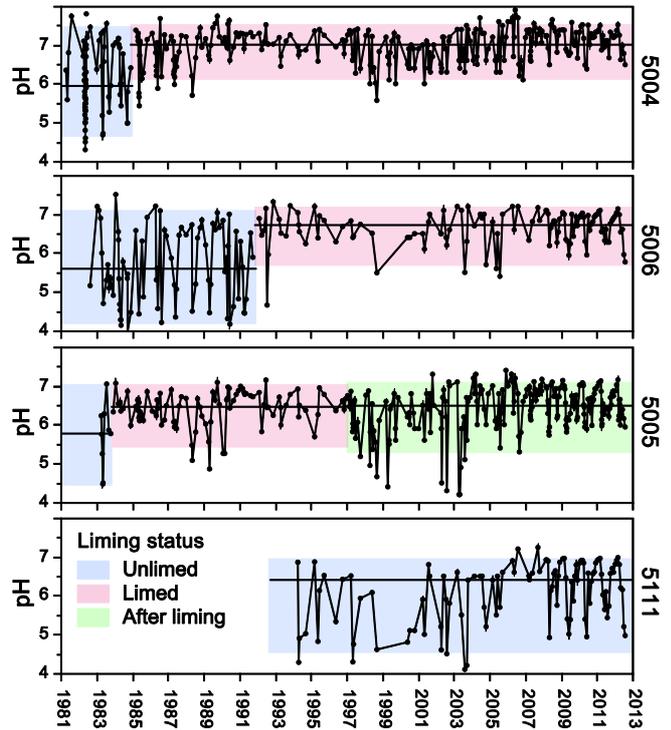


Fig. 6. Variations of pH in the streams. Limed periods (red), unlimed (blue), reacidified, liming terminated in 1995 (green).

Results

The stream water sulphate followed the precipitation trend (Fig. 4a) but decreased more slowly ($1 \mu\text{eq/l/yr}$, Theil slope estimate). The sulphate concentrations in the catchment snow was generally higher than or equal to the stream sulphate level (Fig. 4b,c). However, the stream sulphate has sometimes exceeded the snow sulphate, indicating a release of soil sulphate, possibly because of a temperature induced change in the run-off routes in the soil profiles, following shorter periods of frost during the latest years.

Up to around year 2000, TOC increased by approximately 0.1 mg/l/yr , and the mean trends in SO_4^{2-} and TOC are generally opposite, indicated by a strong negative correlation between sulphate and TOC in the stream waters (Fig 5).

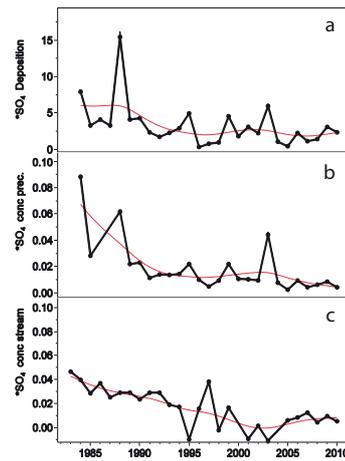


Fig. 4. Trends in (a) winter SO_4 deposition (keq/km²), (b) SO_4 concentration in snow (precipitation weighted mean, meq/l), and (c) SO_4 concentration in River Djursvassian (5004) during springflood.

Acidic episodes with pH reaching 4.0 at flow peaks, occurred frequently in the unlimed streams, despite relatively well buffered waters at base flow (Fig. 6). Wetland liming stabilized the water chemistry for several years after treatment, with less fluctuations in pH and mostly with some alkalinity retained even at high-flow periods.

To evaluate the main causes for the loss of ANC during high flow in the unlimed streams, the concentration differences between high flow and base flow were calculated for major ions. Dilution of base cations contributed the most to the ANC loss. Organic anions increased somewhat in one of streams, causing a further decrease in ANC. Sulphate also contributed to the loss of ANC as it was slightly enriched or unchanged during high flow (Fig. 7).

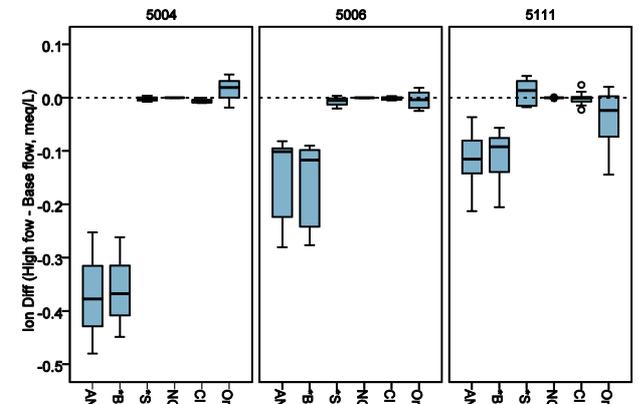


Fig. 7. Loss of ANC and the changes in major ions in three unlimed streams during spring flood. Negative numbers indicate dilution at high flow whereas positive numbers indicate enrichment.

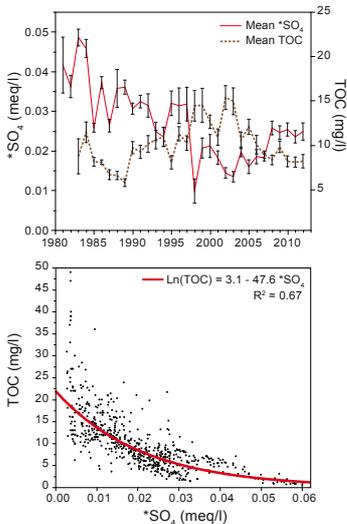


Fig. 5. Opposite time trends in annual TOC and SO_4 mean concentrations in stream water (top) and a negative correlation between TOC and SO_4 (bottom).

Acknowledgements

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