Palaeoecology Surface water acidification

from Hans M. Seip

Few topics have been the subject of so much recent debate as acid precipitation. Are there other causes for the surface water acidification and the dramatic loss of fish populations observed particularly in Scandinavia, but also in other parts of Europe and in North America? Palaeoecological studies, such as the one described on page 157 of this issue', support deposition of compounds of anthropogenic origin as the primary cause.

It is now generally accepted that the recent increase in acidity (H⁺ concentration) of precipitation is caused by anthropogenic emissions of sulphur and nitrogen oxides. Recent surface-water acidification is also well documented. Although there is a reasonably good correlation in space and time between acid precipitation and water acidification, it is difficult to prove a causal relationship.

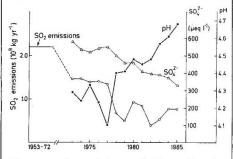
The main alternative hypothesis was originally forwarded by Rosenqvist², who believes that soil acidification caused by changes in land use is the most important cause of the recent water acidification. Although this view is not generally accepted, it has some support³ and there is a consensus on which processes to consider; the differences arise in their relative importance⁴.

Because most of the precipitation will come into close contact with the terrestrial part of most catchments, acid soil is a prerequisite for acid water. Changes in the chemical properties of the soil, as well as changes in the hydrology⁵, affect the water chemistry. Several studies demonstrate soil acidification in Scandinavia and in Central Europe, which at least partly seems to be caused by acid deposition. Except for agricultural areas, estimation of H⁺ fluxes to the soils supports the importance of acid deposition in acidification.

Water acidification depends not only on soil properties, but also critically on the concentration of 'mobile' anions, particularly sulphate, nitrate and chloride, that move easily through the terrestrial part of the system. Because a charge balance must exist in any solution, increased anion concentration will lead to increased cation concentration, including increases in H⁺ and aluminium in runoff from acid soils. In most areas, the most important mobile anion seems to be sulphate; nitrate is mainly taken up by the vegetation but may affect water acidity, particularly during snow melt.

It is difficult to quantify the relative importance of acid deposition and other causes of water acidification. Simulation models indicate that increased sulphur deposition may cause a considerable decrease in the pH of surface water while deposition may cause similar increases^{6.7}. These theoretical calculations are supported by observations around Sudbury (see figure), where the emissions have been dramatically reduced since 1972 and surface water quality is improving. Conversely, a historical approach used in three Norwegian studies did not reveal a relationship between land-use changes and loss of fish populations8.

Jones et al. combine a detailed palaeoecological study of vegetation changes from the last glaciation until the present day around a lake in Galloway, Scotland,



The decreasing emissions at Sudbury, Ontario, have resulted in decreasing sulphate concentrations and acidity in the Clearwater lake14.

with estimates of historical pH values using the diatoms in the lake sediments. Despite the rather dramatic changes in vegetation from a forest to an acid peatland, the pH of the lake remained surprisingly stable between 5.4 and 6.0 until the recent acidification started in about 1850. Although this study considers vegetation changes in particular detail, other palaeoecological results support the conclusion that acid deposition is a necessary condition for the recent acidification⁴⁻ . For example, the pH of a lake in the Adirondack Mountains, United States, was about 5.7 during the period 1800-1950 despite major logging operations in the catchment. From about 1950 the inferred pH dropped to about 4.7 (ref. 12).

How reliable are these results? One complication is that the distribution of diatoms depends not only on pH, but also on other factors, such as the concentrations of humic substances and major ions in the water. The dependence on the content of humic substances has been used to infer changes from moderately acid humic water to more acid clear water in two Norwegian lakes, presumably because of acid deposition¹³. Seasonal variations in water acidity are often important and it is not clear how acid episodes are reflected in the diatom record. Despite some uncertainties in interpretation, palaeoecological methods may be the best way to determine the importance of acid deposition.

Can we draw the general conclusion that water acidification does not occur in an area without acid deposition? The diatom studies usually give inferred pH values of more than 5 in pre-industrial times for lakes that are now acidified. This agrees with the observation that fresh water in 'clean' areas seldom has a pH less than 5.0. There are simply not enough anions to balance the charge of high concentrations of H⁺ and aluminium ions. There are exceptions - highly coloured water may contain enough organic anions to make it more acid. But the recent acidification is not caused by increased concentration of organic compounds.

Sea-spray deposition with high concentrations of Cl⁻ and Na⁺ may also cause acidification if sodium is retained and H* ions are released from the soil. But in a stable terrestrial system there will be no long-term accumulation of Na⁺ and therefore only episodic acidification from sea-spray; in an aggrading system sodium may accumulate for longer periods.

Afforestation causes important changes in hydrology and soils, and several studies in the United Kingdom show more acid and aluminium-rich waters in afforested compared with non-forested areas in exposed regions. It is not clear whether a similar acidification would occur in areas with natural precipitation. The forest 'filters' the air and thus increases the deposition of both anthropogenic and natural compounds. Increased sulphate concentration in runoff may therefore be the main cause of acidification here.

In conclusion, there is at present little solid evidence for recent water acidification in areas not exposed to acid deposition. If occurring, it is likely to be found in areas with high sea-salt influence and recent vegetation changes such as afforestation, but the primary cause is evidently anthropogenic emissions of sulphur compounds.

- 1. Jones, V.J., Stevenson, A.C. & Battarbee, R.W. Nature 322, 157 (1986). Rosengvist, I.Th. Sci. Total Environ. 10, 39 (1978).
- Krug, E.C. & Frink, C.R. Science 221, 520 (1983).
- Rosenqvist, I.Th. & Seip, H.M. Kjemi 46, 13 (1986).
 Whitehead, P.G., Neal, C. & Neale R. J. Hydrol. (in the
- press). 6. Reuss. J.O. & Johnson, D.W. J. environ. Qual. 14, 26 (1985)
- Rustad, S., Christophersen, N., Seip, H.M. & Dillon, P.J. Can. J. Fish. Aquat. Sci. 43, 625 (1986).
 Drabløs, D. Sevaldrud, I. & Timberlid, J.A. in Ecological
- Impact of Acid Precipitation (eds Drabløs, D. & Tollan, A.) 367 (SNSF, Oslo, 1980).
- Battarbee, R.W., Flower, R.J., Stevenson, A.C. & Rippey, B. *Nature* 314, 350 (1985).
 Battarbee, R.W. *Phil. Trans. R. Soc.* B305, 451 (1984).
- Renberg, I. & Hellberg, T. Ambio 11, 30 (1982)
- 12. Charles, D.F. Verh. Internat. Verein. Limnol. 22, 559
- (1984) 13. Davis, R.B., Anderson, D.S. & Berge, F. Nature 316, 436 (1985).
- 14. Dillion, P.J., Reid, R.A. & Girard, R. Water Air Soil Pollut. (in the press).

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