

## Ecological Effects of Deposited S and N Compounds: Effects on Aquatic Biota [and Discussion]

D. J. J. Kinsman, E. D. Le Cren, James Beament and A. D. Berrie

*Phil. Trans. R. Soc. Lond. B* 1984 **305**, 479-485

doi: 10.1098/rstb.1984.0071

### Email alerting service

Receive free email alerts when new articles cite this article - sign up in the box at the top right-hand corner of the article or click [here](#)

To subscribe to *Phil. Trans. R. Soc. Lond. B* go to: <http://rstb.royalsocietypublishing.org/subscriptions>

## Ecological effects of deposited S and N compounds: effects on aquatic biota

D. J. J. KINSMAN

*Freshwater Biological Association, The Ferry House, Ambleside, Cumbria, U.K.*

Soft waters of upland streams and lakes are those most susceptible to change. Few, if any, ecological effects have been described resulting directly from enhanced S and N inputs to aquatic environments. Effects relate largely to changing levels of acidity–alkalinity; whether the stress effects relate to hydrogen alone or to related inhibition or enhancement of other ion uptake is rarely certain. Enhanced acidity also results in changing metal ion concentrations and speciation in freshwaters. The faunal and floral responses to these chemical changes are varied but in general a decrease in species diversity occurs which may lead to significant changes in community structure and in trophic relationships within the ecosystem. These latter changes may themselves play an important role in governing the presence or absence of many species.

### INTRODUCTION

The subject of anthropogenic acidification is receiving much study and various review papers and symposium volumes have appeared over the last few years. Acidification effects on the chemistry and biology of aquatic environments form chapters in a very recent (May 1983) synthesis of the literature by the United States Environmental Protection Agency, as part of its National Acid Precipitation Program (Linthurst 1983). The chapter on effects on aquatic chemistry is 162 pages in length with 25 pages of references and the chapter on effects on aquatic biology is 203 pages in length with 38 pages of references. It seems somewhat pointless to review in detail the same literature yet again and I refer readers to this publication for further detail and for the primary sources for some of the statements made in this discussion contribution.

The aquatic habitats of most interest in relation to acidification are the freshwater environments of streams, rivers and lakes, rather than estuaries or the sea, and of the freshwater environments it is those characterized by soft waters that are most susceptible to change. Freshwater environments have many of their chemical and physical characteristics constrained by reactions which take place in the terrestrial environments of their catchments. The rocks and soils, the geomorphology, the terrestrial vegetation, all play important roles in the hydrological and biogeochemical characterization of the catchment effluents that enter the streams, rivers and lakes, by more or less convoluted pathways. As the surface area ratio of stream or lake to total catchment is generally rather small ( $< 0.1$ , often  $< 0.01$ ) the chemical characteristics of freshwaters often only feebly mirror those of incoming precipitation. However, in some upland areas with high precipitation, relatively unreactive rocks and thin soils, and where catchments are small, surface water chemistry may closely resemble local precipitation.

In pre-industrial times a variety of S and N compounds was naturally involved in active cycling between the atmosphere, hydrosphere and biosphere. Some of these compounds had deep earth origins such as volcanically derived strong mineral acids; others were derived from

[ 221 ]

the surface of the earth such as mineral dust particles or marine aerosol particles. Yet others were biologically cycled as microbial decomposition processes released S and N compounds to the atmosphere or directly into surface waters. These two elements form various volatile compounds which are later washed out of the atmosphere and recycled in biological processes. Sulphur and nitrogen, also carbon and phosphorus, are critical elements for biological productivity and in some freshwater environments, such as upland oligotrophic lakes and tarns, atmospheric sources may provide a large fraction of the input of these elements. Thus one direct effect of man-made additions of S and N is to add plant and animal nutrients to ecosystems. In themselves, these additions are only likely to enhance biological productivity, as few freshwater ecosystems are either S or N limited: phosphorus is the most common limiting nutrient. However, the deleterious effects of mixtures of  $\text{SO}_2$  and  $\text{NO}_x$  will presumably affect emergent aquatic plants in a similar way to that recorded for other components of the terrestrial vegetation, but these effects are not thought to occur in the aquatic environment itself.

Many of the aqueous reactions involving natural and man-made volatile S and N compounds result in production of  $\text{H}^+$ . It is this excess acid input and other reactions stemming from changed pH conditions that have a greater impact on the freshwater ecosystem than the increased input of S and N compounds themselves.

Precipitation pH has been assumed by most people to have been close to 5.6 in pre-industrial times, as a result of equilibration with atmospheric  $\text{CO}_2$  concentrations. However, this assumption has been questioned (Charlson & Rodhe 1982) and it has been suggested that a pH range of 4.5–5.6 was quite likely, with a mean of about 5; the variations being caused by temporal changes in the lower atmosphere of proton-producing volatile compounds of S and N and neutralizing compounds such as  $\text{NH}_3$  or reactive mineral dusts such as limestone. Nevertheless, except for very local environments such as *Sphagnum* bogs where organic acids largely govern the pH, the pH of natural aquatic environments would have had a lower limit of about 5.0–5.5; such waters would have been those dominated by precipitation inputs, existing typically in upland areas of high precipitation, with poor soils and relatively unreactive rocks that did not neutralize the acidity.

Today, however, precipitation in many northern temperate areas is markedly more acid, mean pH values of 4.0–4.5 being quite common, and this has come about largely as a result of industrial and domestic emissions of S and N compounds, together also with some HCl production. A recent review by Robinson & Homolya (1983) of the eastern U.S.A. has attempted to compare natural emissions with anthropogenic sources of the S,  $\text{NO}_x$ ,  $\text{NH}_3$  and Cl containing compounds which are considered to have a direct impact on precipitation pH; they concluded that for S compounds the current natural emissions comprised < 1% of the total and for  $\text{NO}_x$  less than a small percentage were derived from natural sources. However, globally, the ratio of natural to anthropogenic emission of S compounds which will affect precipitation pH is thought to be in the range 0.25–0.5 (Grant 1976). This large anthropogenic input of S and N compounds is considered to be the major reason for the drastic decrease in precipitation pH and many small streams and lakes have pH values reflecting this more acidic precipitation input.

Catchment interactions commonly buffer much of the  $\text{H}^+$  input but in more unreactive catchments little buffering may occur. Galloway (1983) has concluded that  $\text{H}^+$  derived from  $\text{H}_2\text{SO}_4$  will be responsible for long-term (over decades) acidification or alkalinity reduction; whereas  $\text{H}^+$  derived from  $\text{HNO}_3$  will cause episodic short-term (over weeks) reductions,

superimposed on the long-term sulphate reduction of alkalinity. These episodic reductions will occur predominantly during increased winter base flow periods and during spring snow melt owing to reduced residence times of  $\text{NO}_3^-$  in soil systems and reduced winter rates of biological uptake on the catchment. Thus predictable seasonal controls and unpredictable, aperiodic events (including meteorological events) will lead to pH variability in catchment effluent input into streams and lakes. It may well be that these short-term, intense spikes of acidity play a very major role in effects on aquatic organisms.

The potential sensitivity of freshwater to acidification has been well reviewed by Galloway & Dillon (1983). Biological responses to acidification have been noted at alkalinities of  $< 100 \mu\text{eq l}^{-1}$ ; the maximum input of excess acid in various areas of the U.K., U.S.A. and Scandinavia is about  $100 \mu\text{eq l}^{-1}$ , except for some short term events; thus those waters with an initial alkalinity of  $< 200 \mu\text{eq l}^{-1}$  are potentially the sensitive ones. The alkalinity is derived either from geological sources of rock weathering or may be internally produced within a lake by primary production and decomposition processes. This latter source of alkalinity may be very important and thus the nutrient status of soft water lakes is rather critical. If one uses this measure of acidification sensitivity then, for example, several of the large Lake District lakes are very poised; relatively small increases in  $\text{H}^+$  input in precipitation or decreases in the neutralization capacity of the catchments might drive them to appreciably lower pH values, at which there would be considerable biological changes (using chemical data of Carrick & Sutcliffe (1982)). Smaller lakes and tarns and especially headwater streams will, of course, be most sensitive, because they are frequently dominated by the chemistry of precipitation input; their alkalinity is derived almost solely from rock weathering and values are often relatively low.

#### SUMMARY OF EFFECTS ON AQUATIC BIOTA

Studies of several kinds have been made to determine the effects or likely effects of acidification on aquatic biota (Magnuson *et al.* 1983) in (i) naturally acidic ecosystems, covering a range of pH environments; (ii) ecosystems which have become more acid in recent times; (iii) experimentally manipulated ecosystems; (iv) laboratory studies, generally of a physiological nature.

##### *Macrophytes*

There are few studies describing direct effects on macrophytes, although some studies have shown a reduction in higher plant diversity with decreasing pH. Some Swedish lakes show a development towards *Sphagnum* dominated macrophyte communities with time, but this does not appear to be a general development in acidified lakes. There is no clear effect observed on changed productivity of macrophytes. There are, however, increases recorded in the metal contents of plant tissues, especially of Al, Fe, Pb and Cu, whereas Mn, Zn and Cd are decreased. The uptake of most of these metals was by active metabolism and metals were largely derived from the sediments, but some proportion was possibly adsorbed onto external surfaces and derived from the lake water.

##### *Periphyton*

The periphyton comprises the algal community living attached to surfaces of sediments, stones and plants and it forms an important food source for larger invertebrates. Studies suggest

considerable differences in species composition between different pH environments. In lakes with pH below 5, mats of blue-green or green algae have been recorded, although there are often considerable differences between algal communities living in different lakes of the same pH. There are also marked differences in the diatom communities in response to pH; benthic diatoms begin to dominate over planktonic forms as pH decreases, and the changing diatom flora has been of value in studies of lake sediment cores, where it can be used to interpret changing pH history of a lake (Batterbee, this symposium).

#### *Phytoplankton*

Extensive studies have shown that under more acid conditions phytoplankton communities change their species composition, in particular, reducing their diversity. These effects are especially large between pH 6.0 and 5.0. Although certain species drop out from all classes as pH falls, because of disproportionate losses from certain groups the overall dominance changes. Dinoflagellates commonly dominate in acidic lakes although in some acid lakes green algae dominate but with dinoflagellates still abundant. A few acid lakes are dominated by blue-green algae, especially humic acid dominated lakes. Productivity in acid lakes is commonly as high as in neutral pH lakes and to date there is no clear indication of any direct link between low pH and primary productivity.

#### *Microbes*

There is no specific information on pH effects on benthic protozoa. There are some data on bacterial decomposition rates under different pH conditions and several studies note a general decrease in rate as pH decreases. Many studies, however, are equivocal. Some authors have proposed that under more acid conditions fungal decomposition begins to dominate but this conclusion is considered questionable by some workers.

#### *Zooplankton*

Zooplankton communities are significantly affected by pH, there being a marked decrease in diversity at around pH 5.0–5.3. In general, low pH zooplankton communities are residuals of communities typical of neutral pH lakes in the same area, the dominant species in acid lakes being important members of the communities in neutral waters. There is little or no evidence of invasion of new species into acidified lakes. Some rotifers are particularly common in acid waters. However, several species of cladocerans seem very sensitive to low pH, for example, many species of *Daphnia*. However, the cladoceran genus *Bosmina* commonly counterbalances this reduction in daphnids and certain copepods often become abundant in such waters. There is little or no information on the relation between pH and zooplankton productivity or biomass.

Some of the changes noted above in zooplankton communities may not be related simply to tolerance of low pH conditions but may reflect changing community interactions, for example changing predator–prey relationships. It has been suggested by several authors that in the absence of planktivorous fish, the zooplankton community becomes dominated by large-bodied species, those species that were earlier preyed upon preferentially by the fish. Some of these larger zooplankton feed on smaller elements of the zooplankton community and thus the complexion of the resultant community can be significantly altered.

*Zoobenthos*

Many benthic invertebrates are very sensitive to pH, those forms living on the substrate such as snails, mussels and stoneflies being more sensitive to low pH than those that live actually within the sediments. Again, there is a general observation of a decrease in diversity as pH declines, particularly at pH values below 6. At even lower pH decreases in biomass have been reported. Benthic crustaceans show a wide range of responses to pH, some being tolerant of quite acid conditions. Aquatic insects are an ecologically important group of invertebrates in lakes and streams; the mayflies (*Ephemeroptera*) are very acid sensitive, whereas the dragonflies and damselflies (*Odonata*) are much more resistant to low pH. Stoneflies (*Plecoptera*) and caddisflies (*Trichoptera*) both show a wide range of responses but many forms are affected at pH values of 4.5–5.5. Some groups of insects are, however, very tolerant of acid conditions, including midges (*Chironomidae*), and black flies (*Simuliidae*). Attempts have been made to interpret the sensitivities of insects to pH by considering taxa in functional groupings or in microhabitat communities. Such a consideration has, for example, shown that infaunal communities are less affected than epifaunal communities and that it is the epifaunal forms with filamentous gills that are most pH sensitive.

Molluscs are very sensitive to low pH, with few species tolerating pH below 6, although Ca<sup>2+</sup> concentrations seem particularly important for these animals.

*Fish*

Loss of fish populations from acidified streams and lakes has been widely reported although many of the earlier data are questionable, detailed studies rarely having been made. A variety of causes has been suggested: (i) low pH, particularly very acid, short term events; (ii) decreased food availability in acidified environments; or (iii) recruitment failure. There is much debate about the relative importance of these three causes, some aspects of which are discussed by Dr Howells at this meeting.

## CONCLUDING REMARKS

The accurate measurement of pH in poorly buffered waters is difficult and uncertainties between operators and between electrodes can be relatively large. However, the range of pH in the environments under consideration and the pH changes recorded in some locations are certainly much larger than these inaccuracies. We need to develop instrumentation and methods that will provide more accurate measures of pH. This need will become pressing when we try to determine changes in pH which might follow from any emissions control programme. In streams, in particular, we need ideally to monitor pH continuously because pH spikes of minutes duration may be the critical events for some components of the biota. The biota in the stream is responding continuously to the variations in the environmental conditions, whereas our most frequent measurements rarely describe the stream environment for more than 1 in 10<sup>3</sup> or 1 in 10<sup>4</sup> of the time (daily or weekly measurement frequencies respectively).

The onset of enhanced acid inputs to surface environments occurred presumably in the mid-19th century when industrialization got underway in Europe and North America. There are no records of water chemistry or detailed descriptions of aquatic communities predating this onset. The assumption that pristine aquatic environments, unaffected by enhanced acid

precipitation, can be found today is surely questionable and thus we have no firm base-lines to work from. Past pH measurements generally post-date the 1920s, are often only spot or short series measurements, are commonly for surface waters in summer at which time annual pH values are at their maximum, and the methods themselves were not very precise. Diatom stratigraphy may offer the promise of more precise determination of both the onset of pH change for any specific lake and the actual extent of the pH change. Superimposed on the acid precipitation effects on surface water environments are alkalinity changes brought about by changing levels of eutrophication; these changes have been mostly in the direction of increasing eutrophication, the effect of which will counter acidification.

To date, most changes in aquatic biota have been considered to result from increasing  $H^+$  concentration alone, although fish studies in particular have more recently emphasized the effects of Al and of physiologically important cations such as  $Ca^{2+}$  and  $Na^+$ . These studies apart (for example, Brown (1982)), there has been little attempt to grapple seriously with the real causative factors controlling absence of particular faunal or floral elements from particular aquatic environments. Until the causative factors are better understood the application of control, preventive or ameliorative measures will be a high-risk activity. Many past studies have produced correlations that have been presented or interpreted as cause-effect relationships, yet it is questionable whether this is true. The interactive, dynamic nature of aquatic communities makes the interpretation of changes affecting one component very difficult.

The sensitive water bodies can be fairly readily identified, and these have alkalinities today below  $\approx 100 \mu\text{eq l}^{-1}$ ; those with values  $\approx 50 \mu\text{eq l}^{-1}$  are particularly precariously poised and their pH could change quite drastically in response to seemingly small additional inputs of acidity. Those waters whose pH drops below about 6, even for only limited periods, are likely to show the most severely affected plant and animal communities.

#### REFERENCES

- Brown, D. J. A. 1982 The effect of pH and calcium on fish and fisheries. *Wat. Air Soil Pollut.* **18**, 343–351.
- Carrick, T. R. & Sutcliffe, D. W. 1982 Concentrations of major ions in lakes and tarns of the English Lake District (1953–1978). *Occ. Pubs. Freshw. Biol. Ass.* no. 16, pp. 1–168.
- Charlson, R. J. & Rodhe, H. 1982 Factors controlling the acidity of natural rainwater. *Nature, Lond.* **295**, 683–685.
- Galloway, J. N. 1983 Effects on aquatic chemistry. In *The acidic deposition phenomenon and its effects*, chapter E4, Critical Assessment Review Papers, vol. II (ed. R. H. Linthurst). U.S. Environmental Protection Agency.
- Galloway, J. N. & Dillon, P. J. 1983 Effects on aquatic chemistry. In *The acidic deposition phenomenon and its effects*, chapter E4, Critical Assessment Review Papers, vol. II (ed. R. H. Linthurst). U.S. Environmental Protection Agency.
- Grant, L. 1976 Nitrogen, phosphorus and sulphur – global cycles. S.C.O.P.E. report 7 (ed. B. H. Svensson & R. Söderlund), pp. 102–122.
- Linthurst, R. H. 1983 *The acidic deposition phenomenon and its effects*. Critical Assessment Review Papers, vol. II, U.S. Environmental Protection Agency.
- Magnuson, J. J. 1983 Effects on aquatic biology. In *The acidic deposition phenomenon and its effects*, chapter E5, Critical Assessment Review Papers, vol. II (ed. R. H. Linthurst). U.S. Environmental Protection Agency.
- Robinson, E. & Homolya, J. B. 1983 Natural and anthropogenic emission sources. In *The acidic deposition phenomenon and its effects*, chapter A2, Critical Assessment Review Papers, vol. I (ed. A. P. Althshuller). U.S. Environmental Protection Agency.

#### Discussion

E. D. LE CREN (*Freshwater Biological Association, Ambleside, Cumbria, U.K.*). As well as the actual measurement of pH we have to realise the practical problems of taking continuous or frequent measurements of pH or other variables (and biological samples) in many of the remote and

difficult environments that we have been discussing. For example there are problems of access over difficult terrain and putting instruments in streams in ways that will protect them from vandals and floods. New small instruments will need to be developed and money spent on manpower.

D. J. J. KINSMAN. The accurate measurement of pH is fundamental to all 'acid rain' and related studies. Available electrode systems do not enable this to be achieved; accuracy is commonly  $\pm 0.2$  pH units (roughly a factor of  $\times 2$  uncertainty in the determination of  $H^+$ ; no other major determinant has this uncertainty associated with it). One study concerning problems with reference electrodes has been completed at the F.B.A. (Whalley 1982).

Currently available electrode systems are designed for work with laboratory solutions whereas the need is to design systems for field use. We need to expose electrode systems to natural samples of a wide range of compositions (varying humic concentrations, etc.) and assess performance under realistic working conditions. In addition, there is a need to develop a protocol for measurement procedures.

#### Reference

Whalley, P. 1982 Factors affecting the precision of pH measurements in freshwaters. Ph.D. thesis, University of Newcastle.

SIR JAMES BEAMENT, F.R.S. (*Department of Applied Biology, Cambridge University, Pembroke Street, Cambridge, U.K.*). Reference has been made to a large named lake with a pH of, for example, 5. Since the pH measured in a lake can be quite different depending on the depth of the measurement, the time of day, season of the year, as well as differing in one part of a lake from another, is it meaningful to categorize a lake in this way?

A. D. BERRIE (*Freshwater Biological Association, River Laboratory, East Stoke, Wareham, Dorset BH20 6BB, U.K.*). The point raised by Professor Beament can also cause difficulty in comparing recent observations with earlier measurements from the same lake which have been recorded without adequate information about exactly where and when they were made. Discrepancies may also arise owing to different methods being used to measure pH and modern instruments cannot be relied upon under all conditions unless they have been carefully checked and calibrated.

D. J. J. KINSMAN. The accurate measurement of pH is fundamental to all 'acid rain' and related studies. Available electrode systems do not enable this to be achieved; accuracy is commonly  $\pm 0.2$  pH units (roughly a factor of  $\times 2$  uncertainty in the determination of  $H^+$ ; no other major determinant has this uncertainty associated with it). One study concerning problems with reference electrodes has been completed at the F.B.A. (P. Whalley (1982) Ph.D. thesis, University of Newcastle).

Currently available electrode systems are designed for work with laboratory solutions whereas the need is to design systems for field use. We need to expose electrode systems to natural samples of a wide range of compositions (varying humic concentrations, etc.) and assess performance under realistic working conditions. In addition, there is a need to develop a protocol for measurement procedures.