ACID TOXICITY AND AQUATIC ANIMALS

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Introduction

Acid rain is a short-hand term that covers a set of highly complex and controversial environmental problems. It is a subject in which emotive and political judgements tend to obscure the underlying scientific issues which are fairly easily stated but poorly understood. In this article I shall deal solely with the scientific problems involved in the acidification of surface waters, attempt to establish the facts, describe the present state of knowledge and understanding and discuss what research is needed to provide a firm basis for remedial action.

Although the term *acid rain* is commonly used to describe all acid deposition from the atmosphere that may cause damage to trees, vegetation, fisheries, buildings, etc., in fact rain (and snow) brings down only about one third of the total acids over the UK, two thirds being deposited in the dry state as gases and small particles. But wet or dry, there is little doubt that acid deposition from the atmosphere poses an ecological threat, especially to aquatic life in streams and lakes on hard rocks and thin soils in southern Scandinavia and in some parts of Scotland and North America. A great deal of research is being undertaken in these three areas but this account is based largely on work in Scandinavia and the United Kingdom where more than 30 research groups from a wide variety of disciplines and institutions are working in a closely integrated and coordinated programme under the author's direction. A complete coverage of the relevant scientific problems includes studies of the transport and chemical transformations of emitted pollutants in the atmosphere; the wet and dry deposition of the resulting acids; the acidity and chemical composition of the rain and snow; modification of the chemistry of the rainwater as it percolates through and interacts with the soil and rocks; the toxic effects of the modified water chemistry on aquatic biota in streams and lakes.

The atmospheric chemistry of acid depositions

Understanding the problem of acid deposition requires knowledge of the distribution in space and time of the major acidifying pollutants, SO_2, NO_x and HCl,

Table 1. *Annual emissions of S or N (Mt/yr)*

		1900	1950	1960	1970	1980	1984
UK	SO_2	1.4	2.3	2.8	3.0	2.33	1.77
	NO_x	0.21	0.30	0.41	0.50	0.54	0.56*
Europe SO_2 (exc. USSR)			10.0		18.4	20.0	

*recent measurements of NO_x emissions from car exhausts suggested this figure is too low by at least 10%.

their chemical transformation in the atmosphere and their removal by deposition on the Earth's surface, either directly in gaseous or particulate form (dry deposition), or after incorporation into cloud and raindrops (wet deposition). The chemical reactions involved in both the gaseous and liquid phases are complex and incompletely understood but are the subject of much active research involving the measurement of the concentrations and conversion rates of chemical species in the atmosphere, laboratory measurements of key reaction rates, and the use of complex models to simulate the many simultaneous, interactive, chemical reactions.

Emissions

The total annual emission of SO_2 and NO_x in the UK (expressed in millions of tonnes of S or N), together with the figure for Europe are shown in Table 1.

Thus the UK contributes < 2% to the total input of sulphur into the global atmosphere and < 10% of the man-made sulphur produced in western Europe. The UK emissions of SO_2, 60% of which come from power stations and about 30% from industrial plants (e.g. refineries), have fallen by 40% since 1974 and by 24% since 1980; but the emission of NO_x, about 45% of which comes from power stations and 30% from motor vehicles, continues to rise. The total deposition of sulphur on the UK in 1980 was 0.7 Mt, about 30% of the emissions, two thirds being dry deposition and one third in precipitation. About 80% of this total deposition was estimated to come from UK sources. The rain bearing westerly winds ensure that the UK emissions make a significant but not a predominant contribution to total acid deposition in Sweden and Norway, the contributions being about 8% and 16% respectively in 1980 but the latest estimates indicate lower values of about 5% and 10% respectively.

Chemical transformations

Once emitted into the atmosphere, the pollutants are carried and dispersed by atmospheric motions, the plume from a point source such as a power station spreading out into an expanding cone which meanders with fluctuations in the wind. The plume is largely confined to within the atmospheric boundary layer, in the lowest 1–2 km, unless it is carried up into cloud systems. A good deal of the acid deposition reaches the ground in dry (gaseous or particulate) form close to the source but the rest may travel for hundreds of kilometres during which time the gases SO_2 and NO_x are oxidized and converted into lowly volatile products such as sulphuric and nitric acid either in gas phase reactions or, more effectively, by becoming captured by cloud and raindrops (where the chemical transformations proceed much more rapidly in the liquid phase) and are eventually brought to the ground in rain or snow.

Although acid production proceeds much more rapidly in the liquid phase, clouds and rain are present only a small fraction of the time, so gaseous transformations and deposition are important and account for about two thirds of the total acid deposition in the UK and about one third in Norway.

The rates of conversions of SO_2 and NO_x to H_2SO_4 and HNO_3 are determined by measurements from the Hercules flying laboratory of the Meteorological Office which can locate and follow a chemically marked plume from a particular power station, sample the air inside and outside the plume as it crosses the North Sea, analyse it for all the relevant chemical species, e.g. SO_2, NO, NO_2, oxidizing agents such as O_3, H_2O_2, hydrocarbons, and aerosols, collect cloud and rain water and analyse these for pH, all main ionic species, H_2O_2, etc. In order to explain the observed conversion rates of SO_2 and NO into acids it is necessary to invoke photochemical reactions involving highly reactive oxidizing agents such as O_3 and O^* leading to the formation of the important radical OH which is unreactive to oxygen and therefore relatively stable. Some of the more important chemical reactions may be summarized as follows:

Gaseous reactions in a dry atmosphere

(a) Sulphuric acid

$SO_2 + HO + M \rightarrow HSO_3 + M$ (M is a third molecule, usually N_2)

$HSO_3 + O_2 \rightarrow HSO_5$

$HSO_5 + H_20 \rightarrow H_2SO_4 + HO_2$

with HO resulting from

$O_3 + hv \rightarrow O^* + O_2$

$O^* + H_2O \rightarrow 2HO$

The aircraft measurements indicate a conversion rate of about 16% d^{-1} in summer, when solar ultraviolet radiation permits ready photolysis of ozone, but this is reduced to about 3% d^{-1} in winter.

(b) Nitric acid

$NO + O_3 \rightarrow NO_2 + O_2$ (fast)

$NO_2 + OH + M \rightarrow HNO_3 + M$

The conversion rate is about 20% per *hour* in summer and about 3% h^{-1} in winter so that conversion would be complete in a 24 h traverse of the plume across the North Sea in summer.

Liquid phase reactions in clouds and rain

$2SO_2 + 2H_2O \rightarrow SO_3^{2-} + HSO_3^- + 3H^+$

$HSO_3^- + H_2O_2 \rightarrow HSO_4^- + H_2O$

with H_2O_2 resulting from

$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$

and HO_2 from gaseous reactions such as:

$OH + CO \rightarrow CO_2 + H$

$H + O_2 + M \rightarrow HO_2 + M$

The conversion rates are very fast, almost 100% per hour in summer and 20% per hour in winter in the presence of sufficient concentrations of the oxidants O_3, OH, HO_2, H_2O_2 and hydrocarbons which may be the limiting factor.

Nitric acid

$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$

$N_2O_5 + H_2O$ (liq.) $\rightarrow 2HNO_3$

This reaction is believed to be rapid but conversion rates have not been established.

Both the aircraft measurements and the photochemical models indicate that the rates of production of acids from the precursor gases are often limited by the availability of oxidizing agents, hydrocarbons and solar ultraviolet radiation.

Acidity of precipitation

In order to assess the effects of changes in the emissions of SO_2, NO_x and hydrocarbons on the acidity of precipitation it is necessary to have long term, reliable, accurate and representative measurements of pH, alkalinity, and concentrations of the main ionic species SO_4^{2-}, NO_3^-, HCO_3^-, etc., so that one may study their variations in space and with time. Unfortunately rather few series of measurements satisfy these criteria. Accurate measurement of the pH of poorly buffered waters in the field is particularly difficult. When the same sample of rainwater was divided among 18 different reputable European laboratories, differences of one whole pH unit were obtained and the standard deviation of the 18 measurements was 0.75 unit. In addition to analysis errors, changes may occur during collection, storage and transport, resulting in contamination, evaporation and biological activity of the sample. Urgent attention is being given to the improvement of analytical techniques and to their standardization, intercomparison and intercalibration.

The pH of uncontaminated rainwater in equilibrium with atmospheric carbon dioxide is 5.6. Rain and snow almost everywhere, even in places as remote as Hawaii, the southern Indian Ocean and the polar regions, are more acidic than this with average pH values of 5.0 or lower. This testifies to the ubiquity of acidic pollutants, the oceans being a major source of sulphur compounds resulting from biological activity and sea spray.

In 1978/80 the annual average pH of rain falling over the UK was almost everywhere between 4.5 and 4.2, the rain being more acidic on the eastern side of the country downwind of the main industrial conurbations where the pH values are very similar to those encountered in southern Scandinavia.

Unfortunately, there are few reliable, long term records with which to assess recent trends in the acidity of precipitation. Perhaps ther best record, maintained by the Freshwater Biological Association in Cumbria, shows that the annual mean pH remained sensibly constant at 4.4 between 1955 and 1975 during which period the total sulphate deposition also remained roughly constant. This is consistent with the fact that the UK emissions of SO_2 and NO_x increased only slightly over this period and that 80% of the total sulphur deposition in the UK comes from local sources. There is now some evidence, notably from measurements made by the Freshwater Fisheries Laboratory at Pitlochry, that the acidity of rainfall has decreased (pH increased by about 0.2 unit) since 1979 in conformity with the 34% reduction in UK SO_2 emissions since then.

In Europe there is also a dearth of reliable long term measurements and some of the reported rather sharp increases in acidity of precipitation appear to have coincided with changes in measuring techniques. On balance the evidence indicates that the acidity increased gradually from 1955 to 1970 during which time European emissions of SO_2 doubled but there are indications of a slight reduction in the acidity and sulphate content of rainwater since 1980 concurrent with reduced emissions.

There is some evidence of a linear correlation between the sulphate content of rainwater and emissions of SO_2 based on average annual values but the implications of this are complicated by the fact that, in many parts of the UK and southern Scandinavia, a large fraction of the total annual acidic deposition occurs on only a few days of heavy rainfall. In order to detect these high deposition episodes, which have a major ecological impact, it is necessary to have frequent or continuous monitoring of the rainfall and its chemistry.

Moreover, the annual averages hide large seasonal variations in the acid and sulphate content of UK rainfall, with the highest values occurring in summer when the emissions are least. This is probably a consequence of the fact that the conversion of SO_2 and NO_x is limited by the availability of oxidants such as O_3, OH, H_2O_2, that are produced by photolysis more effectively in the summer time (see Figure 1).

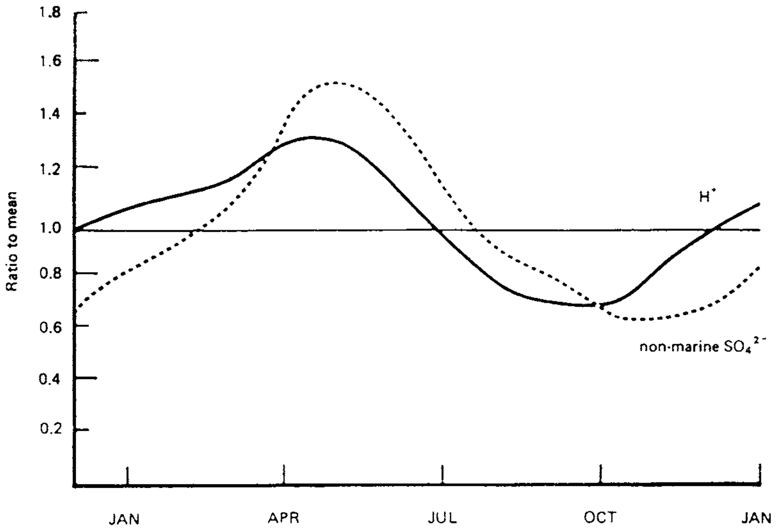
The acidification of streams and lakes

Measurements in many lakes in southern Scandinavia suggest that the pH has decreased by between 0.5 and 1.0 unit over recent decades. However there is some doubt about the reliability of the measurements and the comparability of past and recent data. A reduction of one whole pH unit is unlikely to be due solely to increases in European emissions of SO_2 and NO_x which only doubled between 1950 and 1970 and have increased only slightly since then. Part of the decrease may have resulted from additional acidification processes at work in the catchment or from the acid neutraliziang mechanisms in the soil not being able to keep pace with the acidic deposition (see next section). By contrast, biologically inactive lakes in Cumbria, subject to acidic rainfall, with hard bedrocks and thin soils very similar to those prevailing in southern Scandinavia, have shown no significant change in acidification over the last 50 years, during which period UK emissions of SO_2 doubled between 1930 and 1970 and have fallen by 40% since then. In biologically active lakes major changes of pH are caused by respiration, by photosynthesis and by decomposition of vegetation and these often show strong diurnal and seasonal variations.

A chemical survey of some hundreds of lakes in southern Norway in the early 1970s revealed that 40% of them had pH values of <5.5 and 16% with pH <5.0. It will be interesting to determine whether there have been significant changes in response to the marked reductions in emissions of SO_2 from the UK and Sweden in the meantime.

Evidence for the gradual acidification of lakes over longer periods comes from the analysis of acid-sensitive species of diatoms from radioactively dated lake sediments.

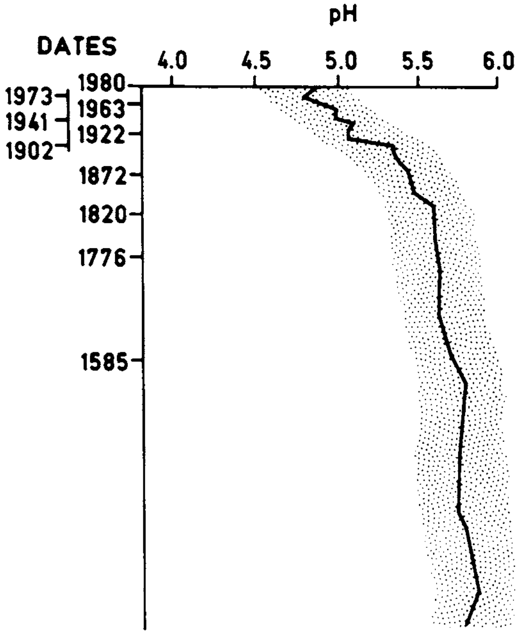
Figure 1. Seasonal variation in H^+ and non-marine SO_4^{2-}concentration in Northern Britain: average three-month running mean concentration expressed as a ratio to the annual mean. (Courtesy of Warren Spring Laboratory.)



The layers of sediment, laid down over several hundred years, are dated using radioactive lead isotopes and the diatoms found in the layers are correlated with similar populations found in the uppermost layers of lakes of known pH. It is thus possible to reconstruct a pH-age profile of the sediments. By this method it has been found that some lakes in Galloway which are situated on hard granitic bedrock and thin soil have tended to become acid in recent decades. Figure 2 shows that the pH of Round Loch remained sensibly constant at 5.5 between 1600 and 1850 but thereafter steadily declined, with fluctuations, to 4.8 in 1973, the decline being particularly rapid since 1900, but this cannot be attributed to afforestation or changes of land use. A slight recovery to pH = 4.9 is discernible between 1973 and 1980, associated perhaps with reduced emissions. Loch Grannoch showed little change in pH at 5.5 between 1840 and 1930, but in 1930/40 it apparently fell to 5.0. From 1940 to 1960 there were even larger changes in the diatom population suggesting a further fall in pH to 4.5. Again these changes could not be ascribed to afforestation or changes in land use.

A similar study on lakes near the southwestern coast of Sweden, all afforested with

Figure 2. The history of acidification of Round Loch of Glenhead, Galloway as deduced from diatom records and radioactive lead dating. (Courtesy of Dr R. Battarbee.)



hard bedrock and thin soil, also indicated a fall in pH from 6.5 to 4.5 since 1950. Diatom records from lakes in southern Norway also indicate a decrease in pH over recent decades but a lake on the west coast with pH ≈ 5 showed no significant change over 200 years.

The decreases in pH since the industrial revolution are likely to be due mainly to increased acidic deposition from the atmosphere but more extensive measurements involving a wider variety of acid-sensitive species are required to establish the historical trends and help resolve the apparent differences between the results for different locations.

Apart from the effects of man-made depositions, there appears to be a natural tendency for lakes to become more acidic with time due to the natural acid-producing mechanisms in the soil (see next section) and a gradual decline of their neutralizing capacity. These natural acidification processes are normally slow but may be accelerated by changes in land use.

The importance of hydrogeology and soil chemistry

There is undoubtedly a correlation between rainfall acidity and the occurrence of acid streams and lakes in susceptible areas. However, little of the water feeding streams and lakes arrives directly from the atmosphere; most does so only after flowing over the land surface or through the soil. The details of the flow pathways and of the soil–water interactions are not well known. Hydrological conditions and water flow pathways through the soil and rock determine the contact time of the acidified water with neutralizing substances and thus the ultimate degree of water and soil acidification.

When the acidified rainwater reaches the ground some seeps through the soil but some, especially during continuous heavy rain, runs over the surface or through macro-pores and may enter the nearest stream with its chemical composition little changed. If, however, the rainwater penetrates the soil its chemistry may be profoundly modified as the result of complex reactions with the underlying rocks, soil and vegetation involving many processes such as dissolution and weathering of minerals, cation exchange, accumulation and release of contaminants including humic and other organic acids.

If the rain or melt water of low pH passes through sandy soils poor in base minerals (e.g. Ca/Mg carbonates and bicarbonates) or passes over hard granitic rocks then the rain/melt water will be only partially neutralized by cation exchange or weathering. The H^+ in the percolate will tend to be associated with SO_4^{2-}. In most catchments any NO_3^- ions which are present in the rain are largely taken up by the roots of growing plants and trees, thus immobilising the associated H^+. (This may change if the increasing trend in NO_x emissions continues). The acidified water therefore passes through the soil with only a moderate pH change and the soil itself undergoes little acidification.

In base-rich soils, H^+ in the acid water are either neutralized by bicarbonate ions during the dissolution of limestone or removed by exchange with cations such as Mg^{2+}, K^+, Na^+, Al^{3+} on the surfaces of mineral particles or with cations on organic macromolecules in humus. H^+ may also be consumed in the soil by the reduction of nitrates and sulphates.

Chemical weathering of primary and secondary minerals is the ultimate means by which inputs of acids are counteracted. Chemical weathering transfers basic cations from primary minerals to the pool of exchangeable cations. A fraction of these are retained on the surfaces of soil particles and the remainder are lost in the runoff or percolate. Hydrogen ions from the acidic inputs are exchanged for the basic cations on the surfaces of the soil so that the acidity of the percolate decreases and that of the soil tends to increase. If the release of base cations by weathering keeps pace with the rate of increase of acid input, no soil acidification occurs. However, if the rate of chemical weathering is not increased sufficiently, soil acidification and subsequently water acidification results. Soil acidification partly caused by acid deposition seems to have occurred both in Central Europe and Scandinavia.

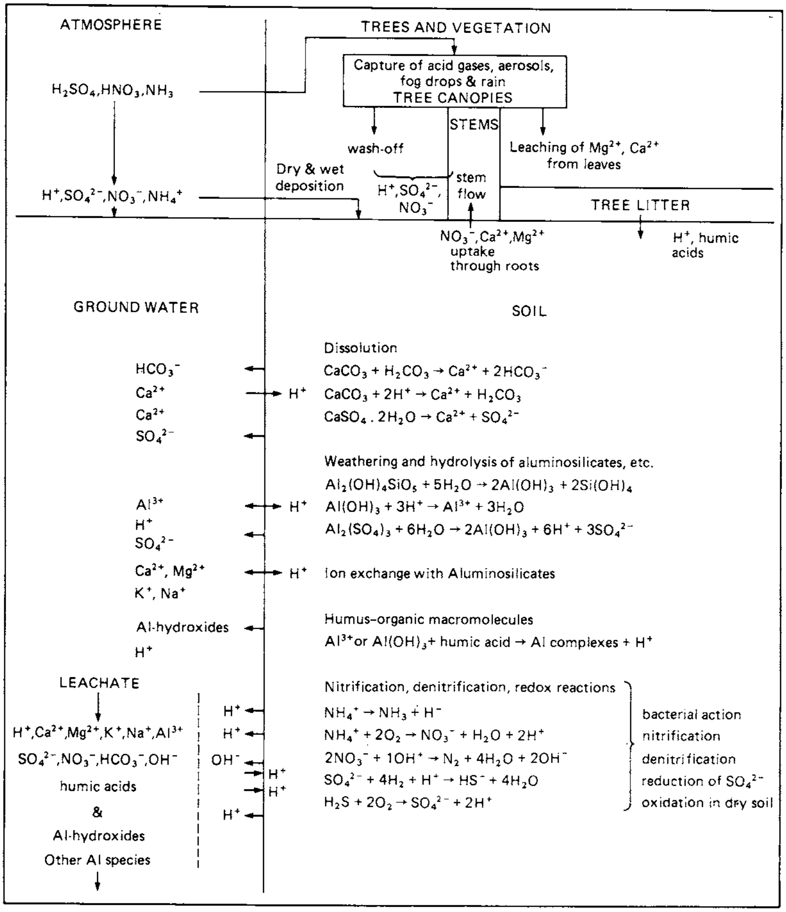
However, besides the deposition of acid substances from the atmosphere, several natural processes produce H^+ in the soil and reduce the pH of the percolating water – see Figure 3. These include the production of carbonic acid by CO_2, the hydrolysis of minerals, the decomposition and nitrification of ammonium produced by bacterial decomposition of vegetation and by fertilisers, the oxidation of sulphur in dry soil, the action of organic acids from decaying humus, and the release of H^+ from the roots of plants and trees to compensate for the take up of Mg^{2+} and Ca^{2+}.

The acidity/alkalinity of the percolate is the net result of all these processes which act at different rates depending, in many cases, on the pH. In general, base-rich, weatherable soils tend to reduce the acidity of the percolate whilst growing plants and trees, aided by fertilisers, tend to acidify both the soil and soil water. The deposition of acidifying components is also in general larger in a coniferous forest than in an unforested area. The rate of water acidification and the time lags involved probably depend very much on the amount of sulphate accumulated in the soil and the rate at which the SO_4^{2-} are released to accompany the H^+ in the percolate. After a long dry spell followed by heavy rain, or during snow melt, there is often a heavy transient release of mobile anions including NO_3^- which cannot all be taken up by plants and so is available for mobilizing the H^+, thereby increasing the acidity of the soil water.

Studies are underway in Scandinavia and Scotland to investigate the above mentioned processes: chemical, biological, and hydrogeological, that determine the quality of the surface waters and therefore the populations of fish and the organisms that provide their food. Each experimental catchment will require detailed surveys of the geology, soils and vegetation and the mapping of the hydrogeological pathways of the water over and through the ground on its way to the streams and lakes. Of key importance is the modification of the chemistry of the water as it percolates through the soil by a variety of acidifying and neutralizing processes. This will be studied by extraction and detailed chemical analysis of the percolate from different levels in the soil profile and relating these changes to the physical and chemical properties of the soils, measured weathering rates of the minerals, the rates of water flow (residence times) and the measured input/output budgets of the whole system. By making parallel studies in highly acidified, 'clean' and intermediate catchments, it should be possible to deduce how the contributions and balance of the various processes and agencies are affected by changes in acid deposition.

Considerable effort is also being devoted to the development of hydrochemical models to help identify the key processes, design the field experiments and interpret the results.

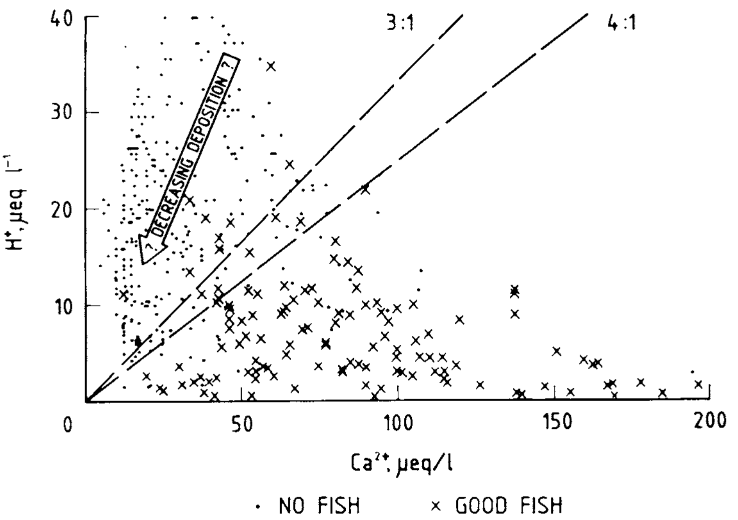
Figure 3. Examples of ion transfer processes involved in the acidification/alkalization of soil and soil water.



Effects of acidity and aluminium toxicity on fishes

A decline in fisheries, or loss of certain species since the 1930s has been reported for many lakes in S. Norway, S. Sweden, parts of UK, Ontario and NE USA. In view of the (not entirely convincing) evidence that the pH of some lakes has declined by as much as 1 whole unit and that low pH (<4.5) is known to be lethal to some fish, especially in early life stages, it is reasonable to attribute decline in fish populations to an increase in acidity of surface waters. Unfortunately, well documented, long term records of fishery status and of water quality exist for only a relatively few lakes in Scandinavia and NE America. For a sample of lakes in S. Norway over half of those with pH <5 were found to be fishless compared with about one in seven of those with pH >5. This is illustrated in Figure 4 which also shows the importance of calcium in the water, higher concentrations of which tend to compensate for lower pH (higher acidity). An extensive survey of fishery status and water quality for some 700 lakes in S.Norway failed to establish a direct relationship between fishery status and sulphate concentration because the calcium concentration and pH of the lakes, which are correlated with their altitude and distance from the coast, are dominant factors. More recently the toxic effects of aluminium leached from the soil and lake sediments have become firmly established. The toxicity of aluminium is a function of pH and is greatly moderated by the presence of calcium in solution (see Brown & Sadler, this volume).

Figure 4. The fishery status of a large number of Norwegian lakes in relation to their acidity (H^+ concentration) and the calcium content.



In the pH range below 4.5, acidity *per se* may be a direct cause of mortality in fish depending on the species, (salmon and trout are especially vulnerable), the age, size and genetic origin of the fish and the degree of acclimatization. Acidity may also affect growth, fertility, egg mortality and recruitment of fry to the population.

Attempts to establish clear cut relationships between water acidity and fishery status have been hampered by conflicting evidence between field observations, which are usually concerned with long term and fluctuating acid exposures, and laboratory studies which almost always involve short term, constant exposures. It is important to investigate the response to both types of exposure, long term and episodic, since it is not clear which is the more important in the depletion of fish stocks. However there is increasing evidence that large kills are produced by short episodes of high acidity, lasting only a few hours and associated with snow melt or rain after a long dry spell. It appears that these occasional or seasonal pulses of acidity, often accompanied by high concentrations of aluminium, are more lethal than sustained exposure to which the fish may adjust more easily. (See Reader & Dempsey, this volume).

The toxic effects of aluminium on fish are complex. Certain inorganic aluminium ions appears to be particularly potent whereas organic complexes of aluminium formed by interaction with organic acids derived from humus in the soil appear relatively innocuous. The detailed mechanisms controlling the salt balance of fish and involving ion exchange across the gill membranes will have to be further elucidated before the relative toxicity of the various aluminium species and their moderation by calcium and organic complexation can be assessed. These matters are discussed in much greater detail in later chapters.

Concluding remarks

I have attempted, in this paper, to demonstrate that the acidification of surface waters is a complex problem spanning a wide range of disciplines and that there are considerable gaps in our present understanding of all the contributory mechanisms and their interactions. I hope that our rather comprehensive, strongly coordinated and focused research programme will, over the next few years, do much to increase our knowledge of recent changes in the chemistry and biology of surface waters, elucidate the underlying mechanisms, establish more accurately the contribution made by man-made emissions relative to natural acidification processes, and provide a firm scientific basis for effective remedial action.