REVIEW ARTICLES

ACID PRECIPITATION AND ITS EFFECTS ON AQUATIC SYSTEMS IN THE ENGLISH LAKE DISTRICT (CUMBRIA)

D. W. SUTCLIFFE

Introduction

In view of recent publicity on acid rainfall and its effects on freshwater bodies in northern Europe and America, it is timely to review work done on this topic in the English Lake District. To do this I have drawn on data obtained mainly by myself and others working at the Windermere Laboratory of the Freshwater Biological Association. Older work will be familiar to some readers but is included here because it is essential for placing the so-called 'acid rain problem' into a scientific perspective. A paper by Sutcliffe et al. (1982) gives references to work on 'acidification' done outside the FBA.

I thank my colleagues for their interest and help over the years, especially T. R. Carrick who has done much of the work with me for the past 12 years. I also thank him and J. M. Elliott, D. J. J. Kinsman, E. D. Le Cren and J. F. Talling for helpful and critical comments on an earlier draft of this review. The text-figures were drawn by T. I. Furnass and I. Naylor.

Sampling atmospheric precipitation in Cumbria

Atmospheric precipitation occurs by (i) wet deposition of gases and ionized particles (ions) in rainfall and snow, and (ii) dry deposition of large particles (dust) and impaction of ions and gases on vegetation and other obstacles. Studies on the chemical composition of precipitation, including those done by the FBA, are mostly based on catching rainfall, snow and dry deposits, in a plastic funnel connected to a collecting bottle. The standard metal meteorological rain gauge cannot be used for measuring the acidity of rainfall because strong acids react with copper in the metal and are thereby largely neutralized (Crowther & Steuart 1913). It is difficult to prevent small insects from entering a sampler but this is minimized by fixing fine nylon or plastic gauze over the top of the funnel. A gauze cover increases the catch of some substances by impaction, e.g. potassium and calcium, but fortunately it does not markedly affect pH of the collected precipitation (Sutcliffe et al. 1982). The resultant mix of wet and dry deposition is termed *bulk precipitation* and results discussed below refer to this mixture.

Bulk precipitation contains ten *major ions* or electrolytes whose concentrations are best expressed as microequivalents per litre of water ($\mu E\ l^{-1}$). For monovalent ions, $1\ \mu E\ l^{-1} = 1\ \mu mol\ l^{-1}$; for divalent ions, $1\ \mu E\ l^{-1} = \frac{1}{2}\ \mu mol\ l^{-1}$. There are six cations (positively charged) – ammonia and ammonium (NH_3 + NH_4^+), hydrogen (H^+, measured as pH), sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), and four anions (negatively charged) – chloride (Cl^-), nitrate (NO_3^-), bicarbonate (HCO_3^-), sulphate (SO_4^{2-}). Numerous other ions or trace elements occur in very small quantities. These are normally determined only in special studies on the composition of atmospheric precipitation, but phosphorus is usually determined with the major ions for studies on inputs of plant nutrients.

Major ions were studied at the FBA by E. Gorham in 1954 (Wraymires) and 1955 (Grizedale), and by D. W. Sutcliffe, T. R. Carrick and others in 1971-72 (Duddon), 1973-74 (Windermere Laboratory), 1975-76 (Wraymires), 1976 (Grasmere and Kirkstone Pass), all at sites in south Cumbria. In addition, Mr Carrick has set up a series of samplers to study major ions in 1983-84 at a wider range of sites although the north-western part of Cumbria is not included. In the 1960s, researchers at Merlewood Research Station (Nature Conservancy; now part of the Institute of Terrestrial Ecology) measured several plant nutrients in precipitation at sites in south Cumbria and at Moor House on the Pennine (eastern or inland) border of Cumbria. Few measurements of sulphate and pH were made, except by Gorham and Sutcliffe et al.

Wraymires Hatchery, on the eastern shore of Esthwaite Water, has been in continuous use as a sampling site for atmospheric precipitation since April 1970, when it was selected for study in a programme, initially sponsored by the Natural Environment Research Council, to determine (weekly and then monthly) major ions and many trace elements in airborne dust near ground level, in rainwater and in dry deposition. A few analyses were done initially at the Windermere laboratory of the FBA but otherwise at the Environmental and Medical Science Division of the Atomic Energy Research Establishment, Harwell (Cawse & Peirson 1972, and a series of annual reports, e.g. Cawse 1977, 1981; Peirson et al. 1982; Cambray & Eakins 1982). For bulk precipitation the same site was used for our studies in 1975-76 (weekly to monthly samples) and since 1977 it has been a sampling site (monthly) for work done by the Institute of Terrestrial Ecology in Scotland.

Acid precipitation at Wraymires

In maritime regions such as the Lake District, rainwater contains relatively large quantities of sodium and chloride ions, the components of NaCl (common salt), accounting for almost half the total concentration of ions at Wraymires (Fig. 1). The two ions probably originate largely from seawater, in small drops (aerosols) picked up from the surface of the sea; after circulating in the atmosphere they are deposited on land, returning

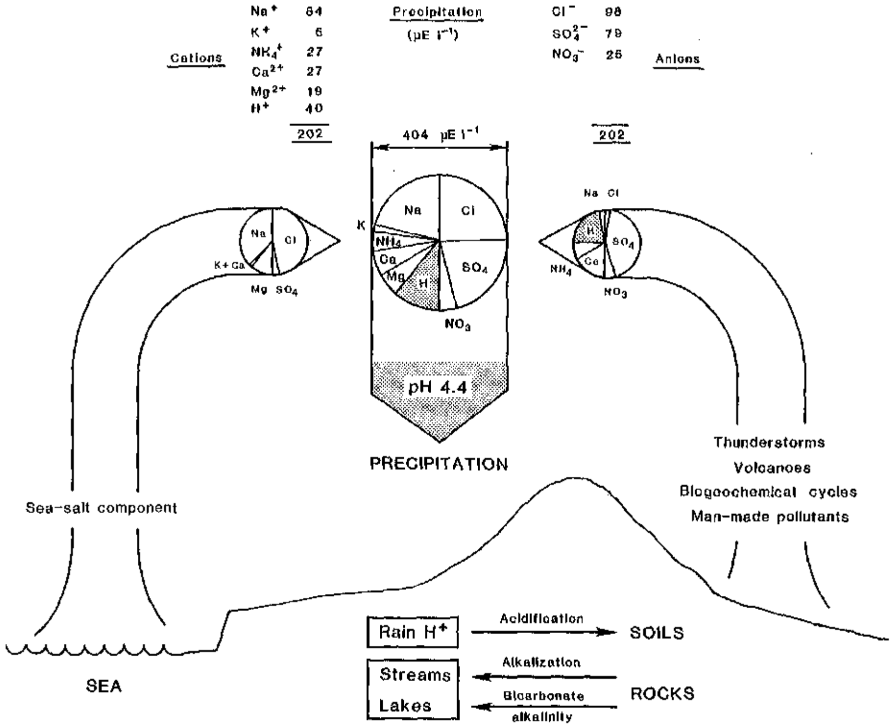


FIG. 1. Sources of major cations and anions in precipitation at Wraymires Hatchery, showing relative proportions of ions and (at the top) volume-weighted mean concentrations for 1975-76.

to the sea by way of streams and rivers in a continuous recirculation of salt. Smaller amounts of other ions are presumed to come from seawater in the same manner; their proportions are calculated from the ratios of each ion to chloride in seawater. Concentrations or amounts derived in this way constitute a 'sea-salt component' of precipitation, shown on the left-hand side of Fig. 1. At Wraymires the sea-salts represent half the total concentration of major ions in precipitation.

Rainwater is naturally acid. In the absence of basic materials such as ammonia and calcium carbonate ($CaCO_3$), average pH values of *c.* 5·2 may be expected to occur in pristine locations but values ranging between *c.* 4·5 and 5·6 may occur locally due to geographical variability in the natural biogeochemical cycle of sulphur and patchiness of other components in the atmosphere, e.g. water and nitrogen (Charlson & Rodhe 1982). In 1975 and 1976, precipitation at Wraymires had a mean pH of 4·4. In individual samples, pH ranged from 3·6 to 6·9. Similar values were found at Grasmere and the upper catchment of Brotherswater (Sutcliffe et al. 1982). Acidity was chiefly due to sulphuric (H_2SO_4), nitric (HNO_3) and hydrochloric (HCl) acids, the latter being present in small amounts according to calculations from Na^+/Cl^- ratios. A pH value of 4·4 is (approximately) equivalent to a hydrogen ion concentration of 40 µE l^{-1}. Assuming that H^+ is balanced by most (80%) of the nitrate and some sulphate, half the acidity can be attributed to nitric acid and half to sulphuric acid. Most of the sulphate ions must then be balanced by basic ions; calcium, magnesium, potassium, and ammonia plus ammonium, because it is believed that 86% of the chloride is balanced by sodium as part of the sea-salt component. Much of the H^+, $NH_3+NH_4^+$, Ca^{2+}, NO_3^- and SO_4^{2-} ions are probably derived from terrestrial sources, including emissions resulting from man's activities (Fig. 1). Gaseous emissions of sulphur (some from burning fossil fuels) and nitrogen (some from vehicle exhausts) are oxidized in the atmosphere to form SO_4^{2-} and NO_3^-. These may be partly neutralized by ammonia and ammonium ions, which must also balance some of the chloride. Apart from anthropogenic (man-made) sources, sulphur is continually released into the atmosphere by natural processes such as volcanic activity and biogeochemical cycles in the oceans and on land. Total emissions from natural sources are difficult to estimate but may be of the same magnitude (*c.* 100×10^{12} g S $year^{-1}$) as those from anthropogenic emissions (Charlson & Rodhe 1982). Nitrogen is the most abundant element in the atmosphere, derived from volcanic activity, and part of this gaseous nitrogen enters the biogeochemical cycle by photochemical fixation. It is therefore very unlikely that atmospheric precipitation in Cumbria – or elsewhere – would be naturally free from sulphate and nitrate ions.

The sea-salt component of sulphate in precipitation at Wraymires is 13% of the mean value of 79 µE l^{-1}. The remaining 87% represents non-marine or 'excess' sulphate that might be formed in the atmosphere by oxidation of S or H_2S, producing hydrogen ions in the process. A maximum of 40 µE l^{-1}, or 58% of the remaining sulphate ions (see Fig. 1), is potentially linked to production of acidity (H^+). But some H^+ must be linked to production of NO_3^- from nitric oxide (NO_x). Also, as biogeochemical cycles are a source of some 'excess' sulphate in addition to SO_4^{2-} entrained in sea-salt from the ocean surface (as aerosols), it appears that less than half of the total sulphate in precipitation is directly linked to acidity produced from anthropogenic sources. With these facts in mind some possible combinations of the main components in precipitation are given in Table 1. This shows common chemical substances and the relative amounts that might be deposited in a year, but it must be emphasized that we do not know if any of the combinations given (Table 1) actually exist in the atmosphere or, if they do (for example in dry deposition), what their proportions are in relation to the masses of ionized particles in wet precipitation. Nevertheless, bulk precipitation is an important source of plant nutrients.

		Annual deposition	
Combination	*Formula*	*Wraymires (kg per hectare)*	*Windermere catchment (Tonnes)*
Sodium (and potassium) chloride	Na (K) Cl	85	2350
Ammonium chloride	NH_4Cl	3	100
Ammonium sulphate	$(NH_4)_2SO_4$	40	1100
Calcium sulphate	$CaSO_4$	65	1800
Magnesium sulphate	$MgSO_4$	38	1050
Sulphuric acid	H_2SO_4	27	750
Nitric acid	*HNO_3	18	500
Hydrochloric acid	HCl	3	80

TABLE 1. Some possible combinations of ions in precipitation at Wraymires Hatchery (1975-76) and calculated amounts for the entire catchment of Windermere (230 km^2).

* Some nitrate may be neutralized by ammonium ions.

In Cumbria, precipitation is noticeably 'salty' during stormy weather in autumn (October-December) and winter (January-March) when westerly winds blow from the Atlantic Ocean. Occasionally a fine layer of common salt is deposited on vegetation and other exposed surfaces, particularly near the coast. Of the total annual deposition of sodium and chloride at Wraymires, 60-80% occurred between October and March in 1975 and 1976. In both years, chloride was deposited in slightly greater amounts than sulphate, when expressed as equivalents. Winds from the south and east tend to carry more sulphate and calcium into Cumbria, accompanied by hydrogen ions thought to be derived from industrial pollution outside the Lake District (Gorham 1958).

Input of hydrogen ions at Wraymires

Acidity can be expressed in various ways; three are shown in Fig. 2. When pH of precipitation (Fig. 2*a*) is converted to equivalent concentrations of H^+, 'peaks' of high concentrations occur (Fig. 2*b*) at low values of pH and they would also occur in unbuffered waters receiving direct runoff from rainfall. These high concentration peaks are thought to be important to fish and invertebrates. When multiplied by volume of rainfall, concentrations of H^+ may be converted to amounts deposited per unit area (Fig. 2*c*). The largest amounts of H^+ are deposited when rainfall is high and pH has a low value. Rocks and soils respond to this input of hydrogen ions either by neutralizing them at once or storing them for later release. In the latter case, concentration peaks of H^+ might occur in

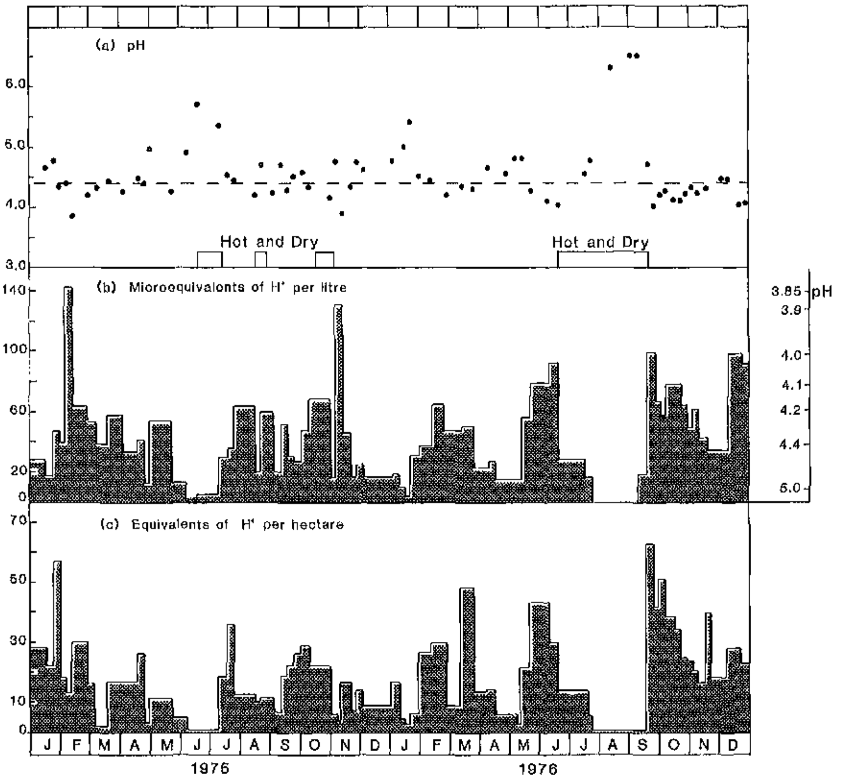


FIG. 2. (a) pH of precipitation, with dashed line indicating the 2-year mean; (b) converted to hydrogen ion concentrations, and (c) multiplied by rainfall and expressed as equivalents of hydrogen per hectare of catchment.

streamwater in addition to those in direct runoff (Fig. 2*b*); they also occur in snowmelt when acid deposited in snow is released as runoff during a rapid thaw (Sutcliffe & Carrick 1973c).

Figure 2 is also useful for considering the effects of increasing or decreasing the hydrogen ion content of precipitation. If this were to be halved, for example from 40 to 20 μE H^+ l^{-1} as a volume-weighted annual mean, pH would rise from *c.* 4·4 to *c.* 4·7 and the amounts of H^+ deposited annually on the catchment would be halved from *c.* 600 to *c.* 300 equivalents per hectare. Chemical weathering of rocks and soils would then decelerate as smaller amounts of base were exchanged with soil water. However, the pH and alkalinity of water in strongly buffered streams and lakes would alter little, and overall changes might not be detectable. Even in base-poor waters containing little or no alkalinity at present, with pH in the range *c.* 4·5–5·5, it is doubtful if pH would rise to the levels (>5·7) necessary to sustain a varied biota (see later section; Fig. 9). Some or all of the high concentration peaks of acidity in precipitation (Fig. 2*b*) *might* be reduced and, if a similar reduction occurred in runoff to streams, this could be of importance to the biota. On the other hand there might be no reductions in these peaks of high acidity, whose frequency and duration in both precipitation and streamwater are dependent on many variables. Detailed studies are urgently needed to examine the causes of concentration peaks in water-bodies and their frequency of occurrence throughout the year.

In 1975 and 1976, two relatively dry years, annual rainfall at Wraymires was respectively 157 and 163cm, and mean pH for the two years was 4·4. Hence the annual deposition of H^+ (Equivalents per hectare) was *c.* 600. However, the average annual rainfall at Wraymires (1903-1979) is 184cm. If mean pH is also 4·4 in wetter years, the annual rate of deposition will be *c.* 740 for H^+.

In the wettest areas round Scafell, where average annual rainfall exceeds 300cm, deposition rates of *c.* 1200 may occur. Thus the annual deposition of hydrogen ions in precipitation over Cumbria is *c.* 0·6–1·2kg ha^{-1}.

Variation between years (1954-1979) at Wraymires

Differences in deposition rates of ions occur between years and between sampling sites. This is part of a natural variation, some of it due to differing amounts of rainfall and other meteorological variables. Even so the mean pH of precipitation was practically identical in 1954-55 and 1975-76, and deposition of sulphate was similar in the two periods, ranging between *c.* 20 and 40kg S ha^{-1} $year^{-1}$. Nicholson et al. (1980) also found a mean pH of 4·4 at Wraymires in 1978-79 but a smaller amount of 'excess' sulphur. Cawse & Peirson (1972) tabulate monthly pH, ranging from 3·5 to 6·8 for June 1970–March 1971 at Wraymires. From their values, geometric mean pH is 4·1, lower than the means of 4·4 obtained by others. This difference is partly due to the very low value of 3·5 (316 μE H^+ l^{-1}). However Cawse (1977) also gives a value of 4·1 for Wraymires in 1976. Values are not quoted for other years. From an analysis of quarterly deposition in 1971-79, Cawse (1981) concludes there was no trend for an increase or decrease in rainfall, nitrate and sulphate at Wraymires.

Acid precipitation elsewhere in northern Britain

North of the Lake District, mean pH of precipitation ranges between *c.* 4·0 and 4·7. In 1978-80, the highest mean (4·7) occurred in north-west Scotland and the lowest mean (4·2) occurred in eastern Scotland and in Northumberland, just south of the Border at Redesdale. The amounts of H^+ deposited each year are similar to those found in Cumbria, i.e. 0·5 kg ha^{-1} in the drier parts of east Scotland, increasing to over 1 kg ha^{-1} in the wetter north-western areas (Fowler et al. 1982). At a rural site (Rothbury) in Northumberland, a few kilometres east of the Redesdale site referred to above, I recorded pH 4·0-4·1 in precipitation collected in July 1963-October 1965. At a neighbouring site (Black Lough) nearer the east coast, pH was 4·2-4·3 compared with 4·65-6·0 at Whitley Bay, an urban site on the east coast near the city of Newcastle upon Tyne. During the same period, six peaty moorland water-bodies in Northumberland, containing virtually unmodified rainwater, had pH values between 3·9 and 4·2 (Sutcliffe 1972).

Historical changes in acid precipitation in northern Britain

The evidence summarized above shows that precipitation in Cumbria has been strongly acid (pH 4·1-4·4) for a period of at least 25 years. In Northumberland in the mid-1960s, pH was similarly low and the values are consistent with recent measurements for northern Britain, so again the evidence indicates there has been little or no change in regions adjoining the Lake District. Industrial conurbations to the south and east are probable sources of some sulphate and nitrate acidity (plus HCl). The effects of industrial smoke and other emissions, producing an acid precipitation containing large quantities of free acids, sulphate, nitrate and ammonia, were known for Manchester in the middle of the last century (Gorham 1982) and Leeds in the first decade of this century (Crowther & Ruston 1911; Crowther & Steuart 1913). Thus one may presume that acids from these and other anthropogenic sources have been deposited on Cumbria for a long period of time, probably since the beginning of the Industrial Revolution in Britain and possibly with pH values similar to those found during the past 25 years.

It is pertinent to add that although anthropogenic emissions of sulphur approximately doubled in west Europe between 1950 and 1970, in some western regions the deposition of non-marine or 'excess' sulphate either decreased or remained relatively constant, albeit with considerable variability at each site (Granat 1978). There may have been small increases in sulphur deposition over Ireland and at a Border site in Scotland but the evidence is meagre. Small decreases in pH of precipitation at some sites in Ireland are thought to be caused mainly by local sources of pollution; all sites had annual mean pH values higher than 4·5 in 1960-79 (Mathews et al. 1981). Evidence for a substantial increase in deposition of nitrate in southern England is given by Brimblecombe & Stedman (1982).

Alkalization, neutralization and buffering of acid rainwater in water-bodies

When rainwater reaches the ground some of it seeps through the soil but some, especially during heavy or continuous rainfall, runs over the surface and enters the nearest watercourse. The runoff is similar in composition to that of rainwater. During spates (floods) it may retain this composition as it travels downstream, diluting the normal streamwater and lowering the pH en route. Normally however, in streams as in soils, when strong acids are present the chemical composition of the water begins to alter quite rapidly. H^+ is exchanged for mobile cations in rocks and soils, and pH of the water rises in the first stage of an alkalization process that eventually leads to neutralization of strong acids, where sufficient base is present for this to occur. The process has not been studied in detail for Cumbrian waters but has been elsewhere on igneous rocks in Galloway (Scotland) and Norway (Henriksen & Seip 1980), and in North America (Johnson et al. 1981). Organic acids enter the water from soils, along with silicic and carbonic acids, forming a weakly buffered solution (Mackereth et al. 1957). At the same time aluminium may be released in various forms, including free (aquo) Al^{3+} (at pH <5) and aluminium hydroxides derived from silicates – major components of rocks and soils. Basic ions then enter the water in increasing amounts and bicarbonate alkalinity (HCO_3^-) becomes dominant (Fig. 3), forming a more strongly buffered solution.

The term *alkalinity* refers to the sum of the anions of weak acids, plus hydroxyl ions and bicarbonate, in a sample of water (Mackereth et al. 1978). At pH above *c.* 6·0, bicarbonate ions (HCO_3^-) are normally the dominant component of alkalinity in Cumbrian waters. As the concentration of HCO_3^- increases, so does pH, but the concentration of carbon dioxide dissolved in the water is also an important regulator of pH (Talling 1973, 1976).

The term *alkalization* refers to the addition of alkali cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) to a water-body by ion exchange from soils. Apart from the direct exchange of alkali cations in soils and rocks for H^+ in acid rainwater as it percolates through a catchment there may be additional cation exchange, resulting from production of H^+ in soils following transformations of $NH_3+NH_4^+$ and SO_4^{2-} in rainwater. The net result would be an increase in alkalis that may not be balanced by an equivalent amount of alkalinity but by 'strong acid' ions instead. In immature forests the soil accumulates hydrogen ions that have been exchanged for alkalis taken up by the roots of growing trees. When these die and decay the alkalis are normally returned to the soil and hydroxyl ions (OH^-) neutralize the hydrogen (Nilsson et al. 1982), but some of the latter may be washed out of soils under an immature forest and thus acidify the nearest watercourse. The removal of timber or other crops from a catchment is another form of acidification, because bases are removed.

The exchange of ions between acid rainfall and basic rocks and soils is part of the natural process of chemical weathering which, in the long term, leads to acidification of the catchment and leaching of soils (Pearsall 1938,

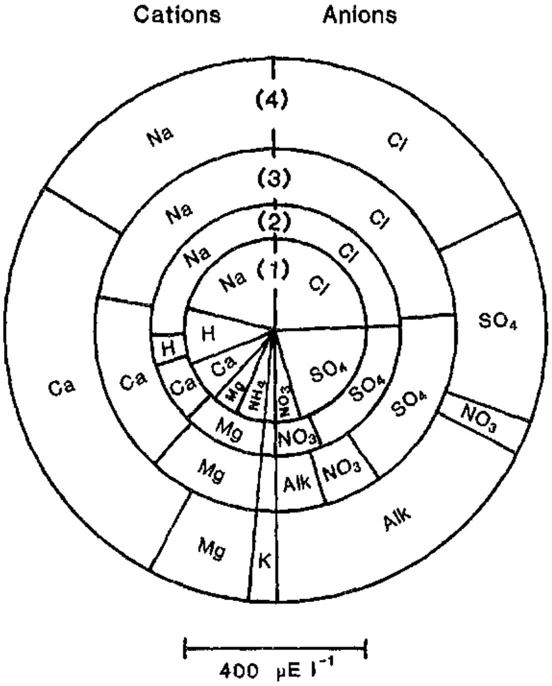


FIG. 3. Composition of (1) precipitation at Wraymires Hatchery (pH 4·4), (2) Levers Water (pH 4·7), (3) Goats Water (pH 6·4), (4) Windermere South Basin (pH 7·1). Each circle shows the relative proportions of cations (left half) and anions (right half); diameters indicate the total concentration of ions. Hydrogen represents less than 0·5% in (3) and (4).

1950; Mackereth 1965; Pennington 1981). Additional inputs of acids derived from anthropogenic (man-made) sources may accelerate the rate of weathering and modify its course, but they are not the sole cause of acidification.

Composition of tarns and lakes in Cumbria

On igneous rocks of the Borrowdale Volcanic Series, forming the central core of the Lake District hills (Fig. 4), some of the high tarns contain water with pH 5·0-5·2 and only traces of alkalinity. A few are known with lower pH, notably Levers Water (pH 4·7). The latter contains no measurable alkalinity and its major ion composition differs from that of bulk precipitation in having less H$^+$, some being exchanged for the alkali and alkaline earth metals: Na$^+$, K$^+$, Ca^{2+} and Mg^{2+}. Most of the ammonium ions have also disappeared, presumably through assimilation by algae and other micro-organisms. The total concentration of ions is greater than in precipitation, due partly to evapotranspiration but also to the increase in alkalis, balanced mainly by increased Cl^- and a little SO_4^{2-} (Fig. 3(2)). The water retains a surprisingly high concentration of nitrate (30 μE l^{-1}) derived largely if not entirely from precipitation. Thus Levers Water contains *c.* *20 μE H^+ l^{-1} balanced by strong acids, i.e. HCl, HNO_3 and H_2SO_4.* Nearby Seathwaite Tarn is slightly less acid, with *c.* 8 μE H^+ l^{-1} (Fig. 5). From alkalinity titrations done in 1949-50 (Knudson 1954) it is inferred that pH was *c.* 4·5-5·0 at that time in these two tarns and in some others on Borrowdale Volcanics, i.e. these tarns have been 'acid' for at least 30 years.

Other high tarns on Borrowdale Volcanics contain water with pH *c.* 6·0-6·4, as in Goats Water which is only *c.* 2 km from Levers Water and Seathwaite Tarn. In Goats Water the process of neutralization has gone further. It contains measurable alkalinity, though in relatively small amounts (mean 34 μE l^{-1}), balanced by a considerable increase in Ca^{2+} and Mg^{2+} derived from rocks and soils in the catchment (Fig. 3(3)). Hydrogen ions have been largely neutralized: pH 6·0 is approximately equivalent to only 1 μE H^+ l^{-1}, and pH 6·4 is *c.* 0·4 μE H^+ l^{-1} (Fig. 5).

The composition of upland tarns lying on Skiddaw Slates resembles those on Borrowdale Volcanics but the former contain more Na^+ and Cl^- (Fig. 6). Some are poor in calcium, and have little or no alkalinity; pH was not determined when the tarns were sampled (1953-54).

Some 'hard' waters occur on the Carboniferous Limestone rocks surrounding the Lake District (Fig. 4) but most of the larger lakes and tarns in the National Park lie on the central Borrowdale Volcanic Series, Skiddaw Slates to the north and Silurian Slates (a series of slates, grits and shales) to the south. On these rocks the waters are all relatively 'soft'; many are slightly acid with pH 6-7 and alkalinities of *c.* 50-200 μE l^{-1} (Fig. 5). Even in the more productive lakes, Blelham Tarn, Esthwaite Water and Windermere (Fig. 3(4)), mean pH of the water column is only 7·0-7·1, although on occasions during hot fine weather in summer the pH of surface water sometimes rises above 10.0 due to photosynthesis by dense populations of algae, which deplete the CO_2 content of the water (Talling 1976; Heaney & Talling 1980).

Thus the upland tarns and becks (streams) of the central Lake District are typically low in dissolved ions, especially on the Borrowdale Volcanics and Skiddaw Slates where the water contains less than 600 μE l^{-1} of total ions, half of which are Na^+ and Cl^- (Sutcliffe & Carrick 1983 a, b). As altitude decreases, both the total concentrations of ions and the proportions of Ca^{2+} and bicarbonate alkalinity increase. These increases are greatest in water-bodies on the Silurian Slates and younger sedimentary rocks surrounding the central hills, where total ion concentrations of 2000 μE l^{-1}

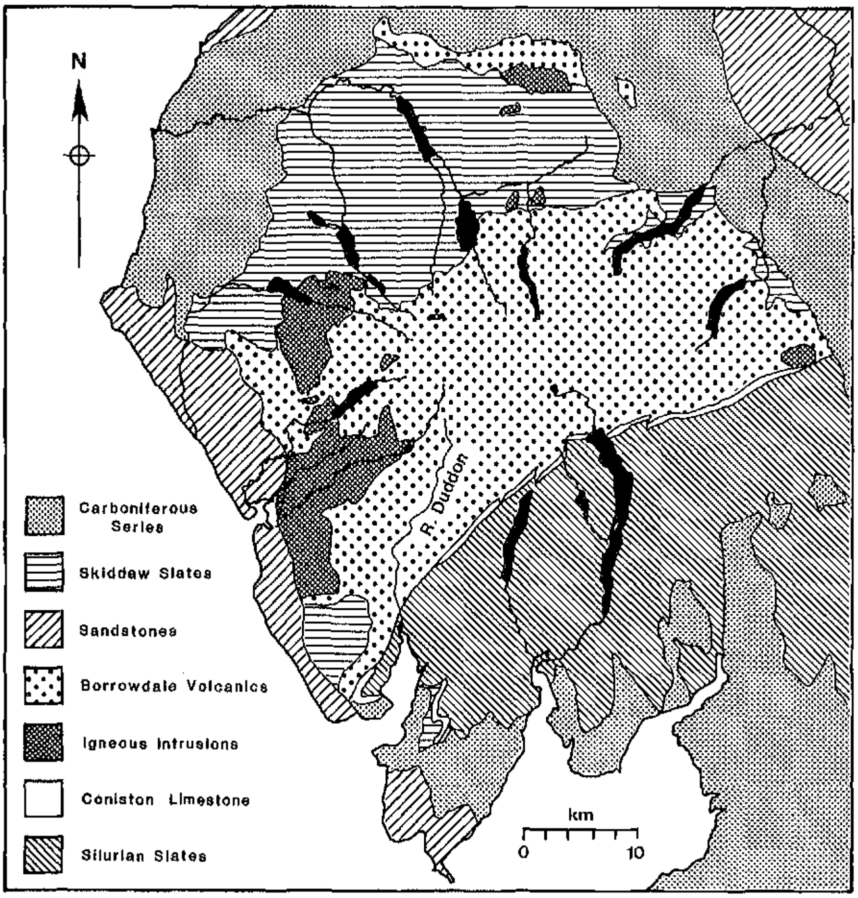


FIG. 4. The English Lake District, showing major boundaries of solid geology, some larger lakes and tarns, and location of the River Duddon.

or more can occur (Mackereth et al. 1957; Carrick & Sutcliffe 1982). Here, bicarbonate concentrations may exceed the combined concentrations of chloride and sulphate, the other two predominant anions in Cumbrian waters. Both Cl^- and SO_4^{2-} attain their highest concentrations in lowland productive lakes such as Coniston Water, Windermere, Blelham Tarn and Esthwaite Water. In the last two, sulphate concentrations are double those in Levers Water and Buttermere, representing 12-13% of the total ions; Cl^- represents 13-15% and HCO_3^- represents 21-22%.

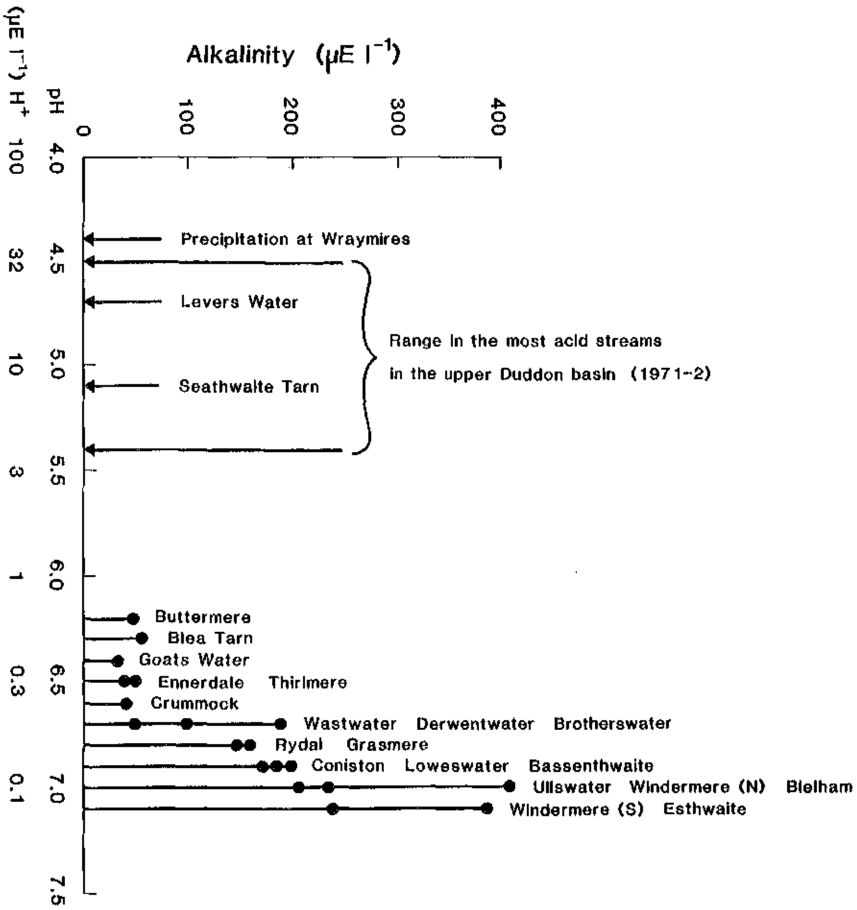


FIG. 5. Mean alkalinity (●) shown against mean pH and hydrogen ion concentrations in surface waters of main lakes and tarns, 1974-78. Also shown are bulk precipitation and range of pH for stream waters in the upper Duddon catchment, 1971-72.

Thus sulphate concentrations increase with higher alkalinity and pH and are normally lower than those of chloride (Fig. 6*a*). In productive lakes (Gorham et al. 1974; Jones et al. 1979), equivalent concentrations of Ca+Mg greatly exceed Na+K (Pearsall 1921), as indicated in Fig. 6*b* where Na^+ is plotted against Ca^{2+} for a series of lakes. Molar concentrations (expressed as μmoles l^{-1}) are included in Fig. 6 because they are more relevant than equivalent concentrations (μE l^{-1}) when considering ion uptake by animals.

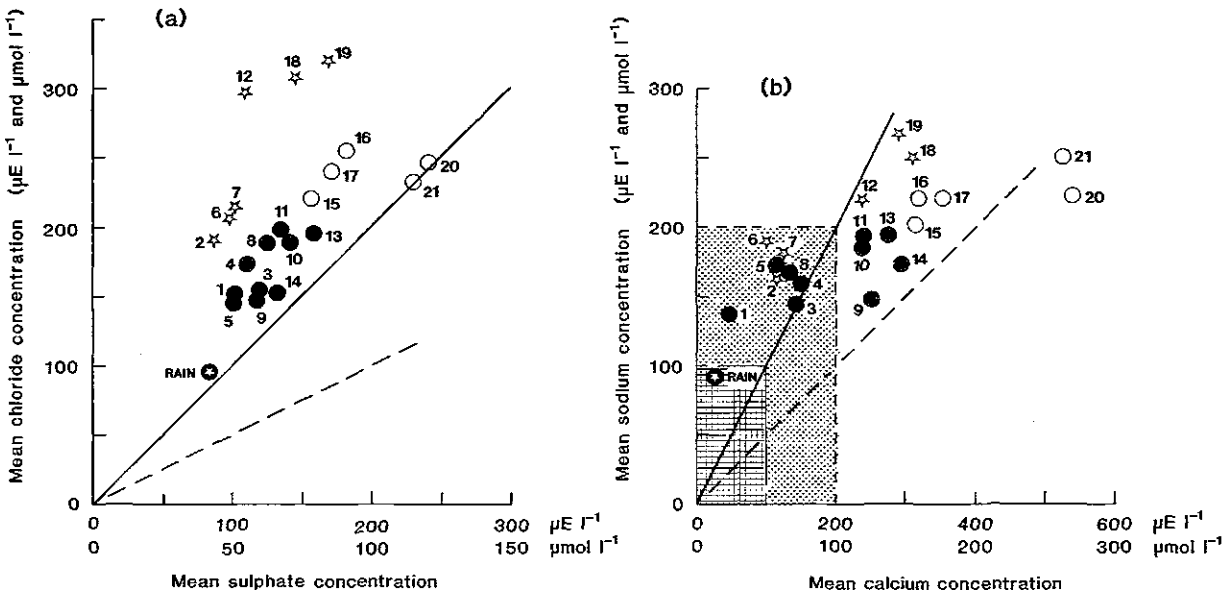


FIG. 6. Mean concentrations of some ions in precipitation and surface waters of twenty-one lakes and tarns, 1974-78. Symbols indicate type of rocks in the catchments: ●, Borrowdale Volcanics; ☆, Skiddaw Slates; ○, Silurian Slates. Diagonal lines indicate equal concentrations expressed as equivalents (——) and moles (– – –). Lakes are numbered 1-21 in order of increasing total concentrations of anions and (approximately) increasing productivity. In (b) the hatched section indicates concentrations that are probably too low for survival of *Gammarus pulex* and the stippled zone is one of suboptimal concentrations. 1, Levers Water; 2, Buttermere; 3, Blea Tarn; 4, Thirlmere; 5, Wastwater; 6, Ennerdale Water; 7, Crummock Water; 8, Goats Water; 9, Haweswater; 10, Grasmere; 11, Rydal Water; 12, Derwentwater; 13, Brotherswater; 14, Ullswater; 15, Windermere North Basin; 16, Coniston Water; 17, Windermere South Basin; 18, Bassenthwaite Lake; 19, Loweswater; 20, Blelham Tarn; 21, Esthwaite Water.

For Cumbrian waters, the following equations describe the general relationships between pH, alkalinity (μE l^{-1}) and calcium (μE l^{-1}): pH = 4·85+0·86 $\log_{10}$ Alk, and pH = 2·51+1·74 $\log_{10}$ Ca^{2+} (Sutcliffe et al. 1982).

The acidity of some bog and fen waters was studied by Gorham (1956) and Gorham & Pearsall (1956).

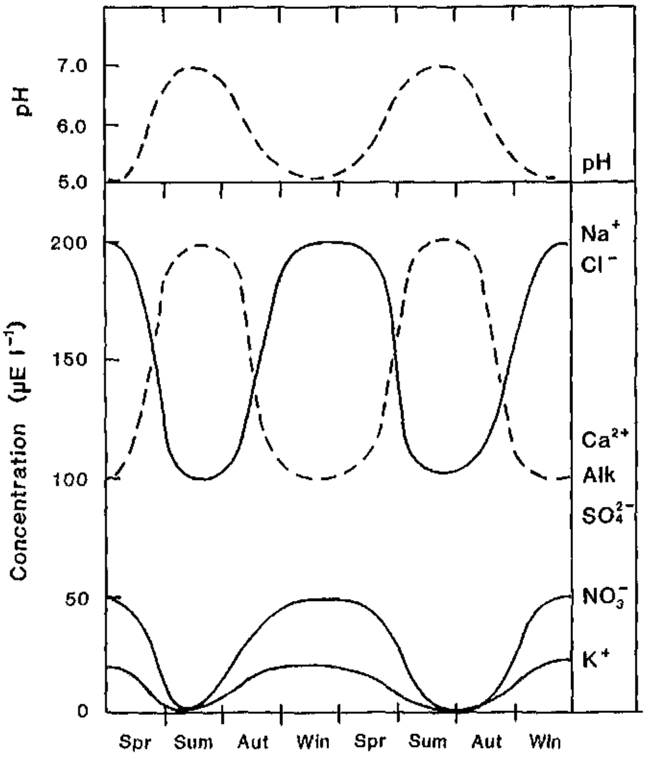


FIG. 7. Diagram of seasonal cycles of major ions in Cumbrian streams and lakes. Actual concentrations vary in different water-bodies (Sutcliffe et al. 1982; Sutcliffe & Carrick 1983 a,b).

Seasonal changes in concentrations of major ions in water-bodies

Concentrations of most ions vary in a pronounced seasonal manner (Fig. 7) although amplitudes vary for different ions and water-bodies for a number of reasons (Sutcliffe et al. 1982). Concentrations of sodium and chloride are highest in midwinter and lowest in midsummer, when they fall to *c.* 100 μE l^{-1} in hill-streams, reflecting the seasonal input of both ions in atmospheric precipitation. The effect is most noticeable in hill-streams on Borrowdale Volcanics but occurs in all water-bodies, accompanied by seasonal changes in the ratio of Na^+/Cl^- which often exceeds 1·0 in summer due to an 'excess' of Na^+ derived from the catchment. Potassium has a similar cycle, partly for the same reasons but also because much of the K^+ is held in growing vegetation during summer, when concentrations in hill-streams may be as low as 1 $\mu E\ K^+\ l^{-1}$. The annual cycle of the above ions is important because the midsummer concentrations in upland waters may be too low for some invertebrates (crustaceans and molluscs), especially where the acidity is high. Productivity of moorland catchments may be limited by the input of K^+ in precipitation (Heal & Perkins 1978).

Calcium, magnesium and alkalinity generally have an annual cycle that is the reverse of the above, with the lowest concentrations in midwinter, though not exclusively so, because these ions are discharge-dependent in streams and hence in surface waters of lakes; concentrations are lowest when streams are in flood. Seasonal and sometimes spatial variation (George 1981) in concentrations of all major ions, including nitrate with its very pronounced seasonal cycle in productive lakes and sulphate which behaves rather unpredictably, makes it difficult to compare results within and between lakes over a span of years unless a substantial number of representative measurements is obtained.

Long-term changes in Cumbrian water-bodies (1928-1980)

Pearsall (1921, 1930) and Mortimer (1941-2) describe the main features of the chemical composition of some central lakes. Knudson (1954) tabulates alkalinity for 120 tarns and lakes, sampled in 1949-50. In 1953-56, all of the major ions (but not pH) were determined in a survey of tarns and lakes in Cumbria (Mackereth et al. 1957); the results are tabulated by Carrick & Sutcliffe (1982). Between then and 1974-1978, few chemical determinations were made in Cumbrian water-bodies except for Blelham Tarn, Esthwaite Water, Grasmere and Windermere where very detailed studies have been made of some chemical components, mainly plant nutrients. In these productive lakes, except Grasmere, alkalinity (Alk) and nitrate were determined weekly for many years, starting in 1939 or 1945 (Sutcliffe et al. 1982). Alk, conductivity and pH of surface waters have all increased markedly in the past 10-15 years, by *c.* 50% for Alk (Fig. 8), associated with increased winter concentrations of NO_3-N and PO_4-P. Sources of the increased Alk are thought to be treated sewage (containing high concentrations of Alk) and generation of Alk within the lakes as a byproduct of increased biological productivity. In the latter case Alk is produced by two processes. In one, biological reduction of NO_3^- (to NH_3 or N_2) and SO_4^{2-} (to HS^-) produces hydroxyl ions (OH^-); these combine with dissolved carbon dioxide (CO_2) to form bicarbonate ions, i.e. $OH^- + CO_2 \rightarrow HCO_3^-$ (e.g. see Kelly et al. 1982; Kilham 1982). In the other process, metabolism of

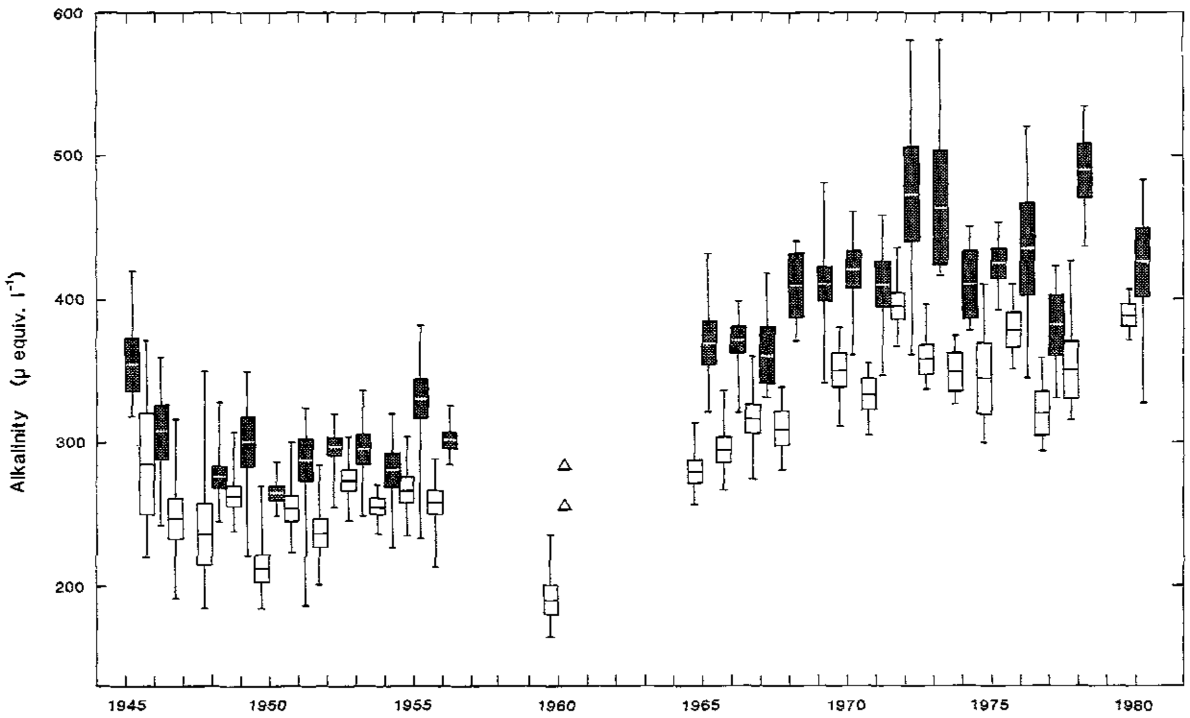


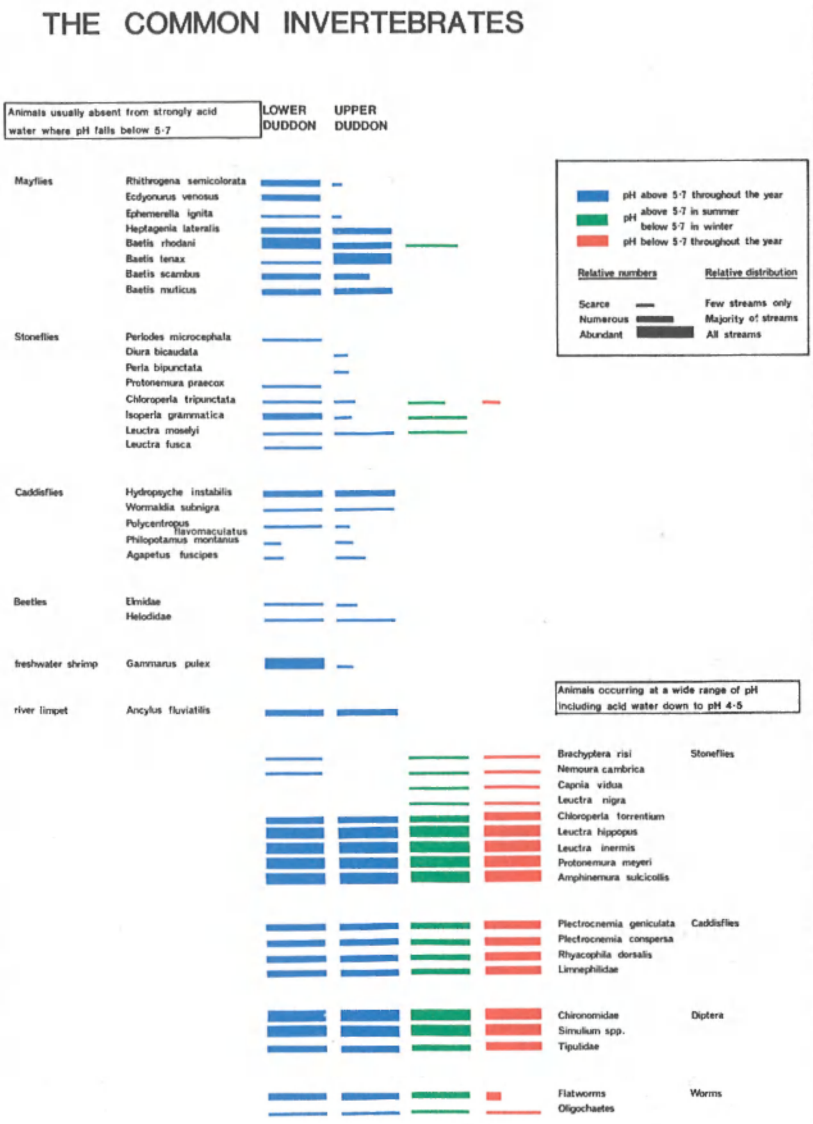
FIG. 8. Alkalinity in Esthwaite Water at 0-5 m depth (integrated tube samples), 1945-80. Boxes are 95% confidence limits of the mean concentrations, with ranges (vertical bars), for weekly samples in January-June (unshaded) and July-December (shaded); △, individual measurements. Redrawn from Sutcliffe et al. (1982).

micro-organisms raises the concentration of CO_2 in the hypolimnia of stratified lakes and this will promote the release of HCO_3^- from carbonates held in lake sediments. Increased productivity of algae and other micro-organisms has followed a rise in nutrients derived from treated sewage and agricultural runoff (Lund 1972a,b, 1978; Sutcliffe et al. 1982). Other lakes where Alk may have increased, though to a much smaller extent, are Coniston Water, Ullswater, Bassenthwaite Lake and Loweswater. The latter is a peculiarly productive lake (Gorham et al. 1974; Jones et al. 1979). There is no urban development round it and no large input of treated sewage, but nitrate concentrations apparently have risen in recent years. Loweswater appears to perpetuate the mediaeval condition of Esthwaite Water and Blelham Tarn (Pennington 1981).

For unproductive lakes and tarns on Borrowdale Volcanics and Skiddaw Slates there are insufficient data to draw detailed conclusions, except that pH and Alk have not altered markedly in the last 50 years. If there have been any changes they are too small to detect with certainty but concentrations of alkalis (Na^+, $Ca^{2+}+Mg^{2+}$), Cl^-, Alk and (in some upland tarns) $SO_4^{2-}+NO_3^-$ may have been slightly higher in 1974-76 than they were in 1955-56. Such increases would be consistent with an enhanced alkalization of water-bodies due to increased inputs of acid (also see Kelly et al. 1982; Kilham 1982), but there is no evidence for a complementary increase in the acidity of atmospheric precipitation at Wraymires. An alternative explanation is that upland tarns had slightly higher concentrations in 1974-76 because the study period and the preceding six years were all relatively dry. From 1968 to 1979, annual rainfall at Wraymires was mainly below the average for 1903-79 and the summers were exceptionally dry (Sutcliffe et al. 1982). Apart from greater evapotranspiration, which would increase the concentrations of all solutes, streams and tarns would contain smaller proportions of runoff (except during heavy rainfall) and larger proportions of soil-seepage ground water that naturally contains higher concentrations of most ions. If this explanation is correct, mean concentrations in tarns will decrease during a period of relatively wet years, including a decrease of Alk and pH.

Effect of pH and ionic concentration on the distribution of invertebrates in Cumbria

The pH regime of stream waters has a profound effect on the distribution of many benthic invertebrates and this has been clearly revealed by FBA work on the River Duddon (Fig. 4) and its tributary streams (Fig. 9; Sutcliffe & Carrick 1973a). In the lower Duddon, streams are relatively rich in bases and Alk derived from glacial till overlying Borrowdale Volcanics. pH is usually 6·0–7·0, rarely falling below 5·7 and then only temporarily when streams carry snowmelt. The streams have a rich (diverse) assemblage of invertebrate species (Fig. 9*b*) typical of hill-streams in



THE COMMON INVERTEBRATES

FIG. 9a

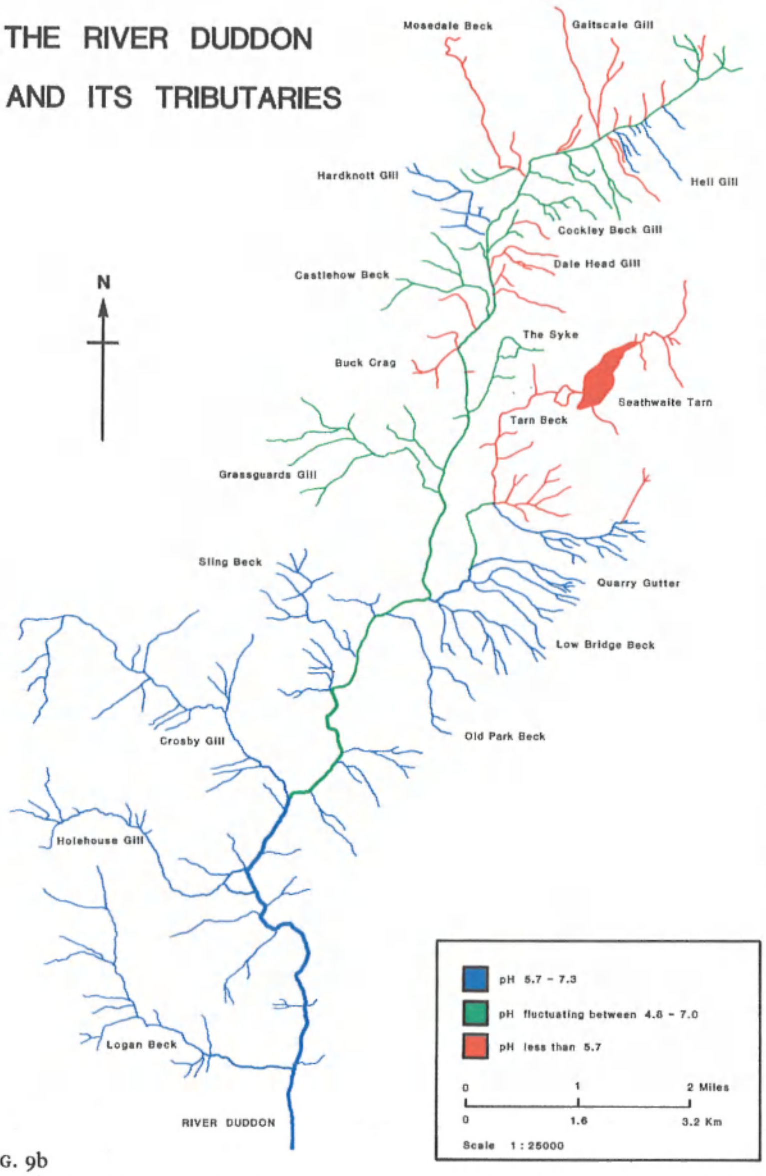

THE RIVER DUDDON
AND ITS TRIBUTARIES
Mosedale Beck
Gaitscale Gill
Hardknott Gill
Hell Gill
Cockley Beck Gill
Dale Head Gill
Castlehow Beck
N
The Syke
Buck Crag
Seathwaite Tarn
Tarn Beck
Grassguards Gill
Sling Beck
Quarry Gutter
Low Bridge Beck
Old Park Beck
Crosby Gill
Holehouse Gill
Logan Beck
RIVER DUDDON
🟦 pH 5.7 - 7.3
🟩 pH fluctuating between 4.8 - 7.0
🟥 pH less than 5.7
0
1
2 Miles
0
1.6
3.2 Km
Scale 1 : 25000

FIG. 9b

pristine condition; numbers (densities) of animals are relatively high (Elliott & Minshall 1968; Minshall & Kuehne 1969). The same taxa also occur in streams in the upper Duddon wherever pH remains above 5·7 during autumn and winter, although the freshwater shrimp *Gammarus pulex* occurs rarely, in only one stream (Sutcliffe & Carrick 1973a). But wherever pH falls below *c.* 5·7 in autumn–winter (green in Fig. 9) and where it remains low at pH 4·5–5·4 throughout the year (red in Fig. 9), fewer species are found in an impoverished fauna that is dominated by stonefly larvae (e.g. Minshall 1969). Most of the taxa in this impoverished fauna occur at low densities. Those absent are larvae of the common species of mayflies (though *Siphlonuris lacustris* does occur in some streams), certain stoneflies, caseless caddis flies and beetles, *G. pulex* and the freshwater limpet *Ancylus fluviatilis*. The latter is common in streams with pH>5·7, even at the top of the Duddon which suggests, because it is a somewhat sedentary animal, that *Ancylus* was once distributed throughout the upper Duddon. If so its present distribution may reflect the adverse effects of acidification that occurred decades ago, certainly before 1965 when the Duddon was first sampled and perhaps much earlier still in the era of the Industrial Revolution (19th century). It is important to note that extensive leaching and production of acid organic soils (Pearsall 1938, 1950) are thought to have first occurred *c.* 5–7 thousand years ago (Pennington 1981) and one may speculate that at the time some hill-streams could have had low or zero concentrations of Alk, with pH<5·7, as they do today.

The other taxa absent at pH<5·7 are nearly all insects with winged adults capable of flying to any part of the Duddon. In late summer, females of the mayfly *Baetis* spp. lay their eggs in streams with pH>6·0 but generally avoid those with pH<6·0. In Grassguards Gill where *Baetis* larvae were found in October 1972 (Sutcliffe & Carrick 1973a), pH subsequently decreased to its lower winter levels (<5·7) and the larvae had disappeared by late November. Very little is known about the physiological effects of low pH on stream invertebrates. *Baetis* larvae may have died from toxic effects or drifted out of the stream (Elliott & Minshall 1968) in response to lowered pH, or they may be unable to find suitable food. Sutcliffe & Carrick (1973a) suggest this is the reason why so many herbivorous taxa appear to be sensitive to low pH whereas most carnivorous taxa are not. Some algae (especially diatoms) and other benthic micro-organisms are also sensitive to low pH or low Alk (e.g. Louis & Aelvoet 1969; Ziemann 1975; Muller 1980) and these, plus decomposing vegetable matter (detritus), are the principal food supply of herbivores in streams. Thus the pronounced effect of pH<5·7 on benthic animals in the Duddon and elsewhere may be viewed as an extension, albeit a dramatic one, of the well-known fact that densities of animals and number of taxa are greatest in hard waters and decrease in softer waters low in Alk and other ions. This applies to most stream invertebrates (and those in the littoral of lakes) in Britain, northern Europe and elsewhere. Reasons for this phenomenon are much debated but the quality and quantity of food for herbivores are almost certainly of central importance (e.g. Willoughby & Sutcliffe 1976).

I believe that the concentrations of some ions in upland water-bodies are physiologically important when they are at very low levels, at least for some invertebrates, e.g. crustaceans and molluscs. These animals are permeable and have to actively take in ions from the water in order to maintain their internal concentrations. In very dilute water this ion uptake (against a large concentration gradient) becomes progressively more difficult, as the ion-transporting systems are concentration-dependent and rate-limited at low external concentrations (Sutcliffe 1978). For *G. pulex*, and *G. duebeni* in Ireland (Sutcliffe 1967a), the concentrations of Na^+, K^+, Ca^{2+}, Cl^- and Alk may all be too low in some hill-streams and tarns, where ionic regulation is stretched to its limits even at $pH>6{\cdot}0$ (Fig. 10). A lower pH may then impose a further, fatal stress on the animals because the small mobile hydrogen ion can compete with larger cations at the ion transporting sites and H^+ will be increasingly transported instead of other cations as the concentration of H^+ rises (and pH falls). *Gammarus duebeni* is remarkable because although it does not occur in acid hill-streams (in Ireland) it does occur in acid lakes where the salt content is sufficiently high, and *G. pulex* is reported to occur in acid streams (pH 4·0-5·0) in France. These examples serve to illustrate the impossibility of finding absolute concentration limits for H^+ (pH) or any other ion(s) because the physiological tolerances of populations vary in space and time. What *can* be done is to find zones of concentrations that represent *suboptimal conditions*, based on field observations and experiments on carefully defined physiological responses (Figs 6 and 10; Sutcliffe 1978). Økland (1980) gives a limiting zone for *Asellus aquaticus* in Norway, from fieldwork relating pH and total hardness of the water.

The combination of low pH and low ionic content of the water produces an impoverished, species-poor fauna in some tributaries of the upper Duddon whereas adjacent streams have a normal diverse fauna because pH and ionic strength are higher, due to very local geological sources of carbonate, e.g. calcite, and alkali feldspars. Although detailed studies have not been made we have found the same phenomenon in the upper parts of neighbouring catchments in Langdale, Eskdale, Wasdale, Ennerdale, Buttermere, Thirlmere, Easedale Tarn and Harrop Tarn (the latter two have been 'acid' for at least 30 years), and at the top of Borrow Beck, a tributary of the River Lune (Macan 1976a,b). All are located in high rainfall areas on igneous rocks of the Borrowdale Volcanic series or on base-poor Skiddaw Slates, and all drain leached soils with a covering of peat and *Sphagnum* bog which may be a local source of H^+, perhaps part of the reason why some streams have a low pH ($<5{\cdot}7$) throughout the year whereas others do not (Fig. 9*a*). Nothing comparable has been found on the base-richer Silurian Slates in the southern part of the Lake District.

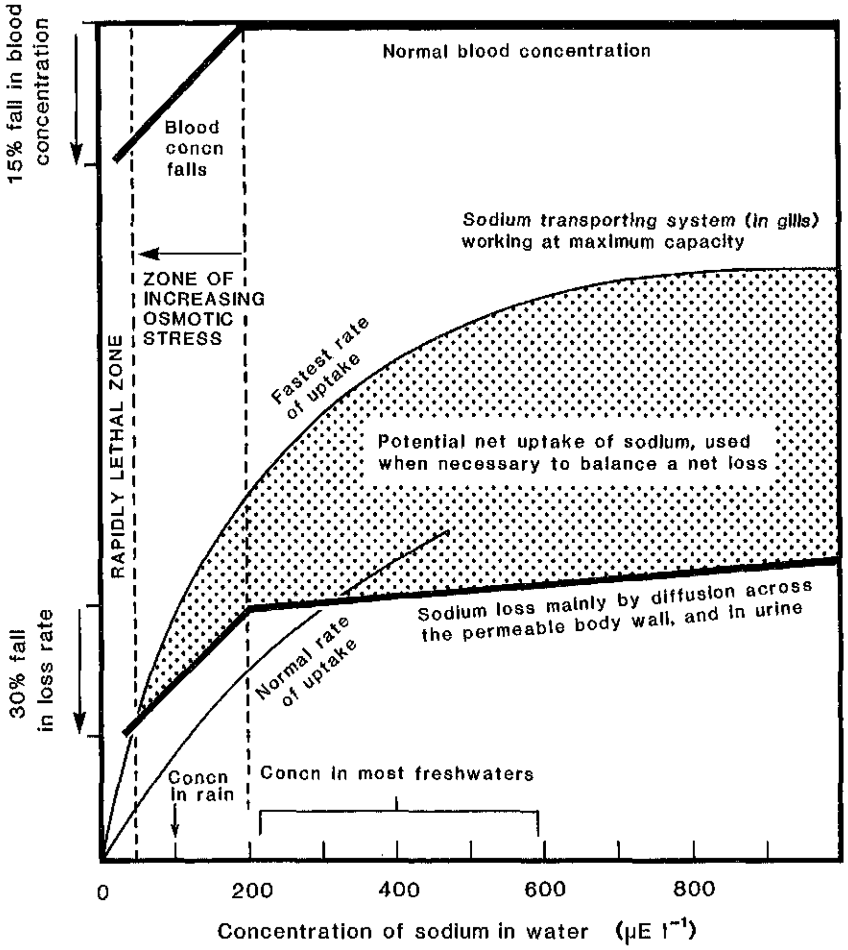


FIG. 10. Diagram (not to scale) of sodium balance in *Gammarus pulex*, in relation to the sodium concentration in the water. Further details are given by Sutcliffe (1967b, 1968, 1971, 1978).

Similar relationships between fauna and pH are also found in streams in central Scotland (Harriman & Morrison 1982) and in lakes in Northumberland where many taxa (e.g. *Gammarus*, *Asellus*, molluscs, leeches) are absent at pH 3·9-4·2 although some, e.g. *Aeschna*, *Sialis*, *Phryganea* and corixids, are numerous (Sutcliffe 1972). In my experience these very acid, peaty moorland water-bodies, and those on the Pennines, are often much more productive than rocky mountain tarns in the Lake District where the littoral fauna, and zooplankton (Smyly 1958), are extremely sparse. The economy of peaty waters appears to be based on micro-organisms and invertebrates utilizing the organic materials in peat and *Sphagnum* (McLachlan et al. 1979); the waters are also usually richer in ions, especially sodium and chloride. The invertebrate fauna of Cumbrian lakes and tarns has been related to ionic content, especially calcium and alkalinity (Macan 1950, 1970; Mackereth et al. 1957) but not pH, although this has been done elsewhere in northern Britain for crustaceans. pH has a marked effect on species diversity (Fig. 11) but some species are very tolerant of acid waters; a few occur at pH down to 3·0 on the southern Pennines (Fryer 1955, 1980; Fryer & Forshaw 1979; Potts & Fryer 1979).

Effects of pH on salmonids in Cumbria

The Duddon is a salmonid river with runs of salmon (*Salmo salar*) and sea trout (*S. trutta trutta*), and resident brown trout (*S. t. fario*). In Mosedale Beck, where pH is normally below 5·7 throughout the year and there is an impoverished invertebrate fauna (Fig. 9), brown trout were found to be relatively small in size. The largest trout that we caught in 1974-75 was 17 cm in length and those greater than 4 cm length (age 1+) were few in numbers (density was *c.* 0·06 fish m^{-2}). But trout in the neighbouring Hardknott Gill, where the pH is usually above 5·7 and a diverse invertebrate fauna occurs, were similar in number (*c.* 0·09 fish m^{-2}) and size. Estimating the age of fish from both streams was extremely difficult, because most of them had no obvious annular growth rings on the scales; interpretations are at best likely to have an error of 2–3 years. Some fish of 15-17 cm length may have been at least 4–5 years old. This size-for-age is similar to that of trout in some Pennine moorland streams (Crisp et al. 1975; Crisp & Cubby 1978), where densities ranged from 0·1 up to 0·9 fish m^{-2}. Compared with Hardknott and Mosedale becks, trout were five to ten times more numerous (*c.* 0·5 fish m^{-2}) in Great Gill, a less acid tributary of Crosby Gill in the lower Duddon (Fig. 9*a*) where the invertebrate fauna is more abundant. The largest fish caught here was 23·6 cm in length. Relating fish growth and size to the abundance of benthic invertebrates is complicated by the fact that much of the food of fish in moorland streams may be terrestrial in origin (Crisp 1966; Elliott 1973). Moreover, using equations developed by Elliott (1975) from his experimental work on brown trout (also see Elliott 1977), Edwards et al. (1979) showed that the water temperature of the habitat can be a major factor determining the growth rates of brown trout living in waters of differing hardness.

Trout fry occur in several of the less acid streams in the upper Duddon and we caught 0+ fish in Mosedale Beck. Elliott & Minshall (1968) caught 2·5 cm fry at night in drift samples (May-June 1966) in the main Duddon

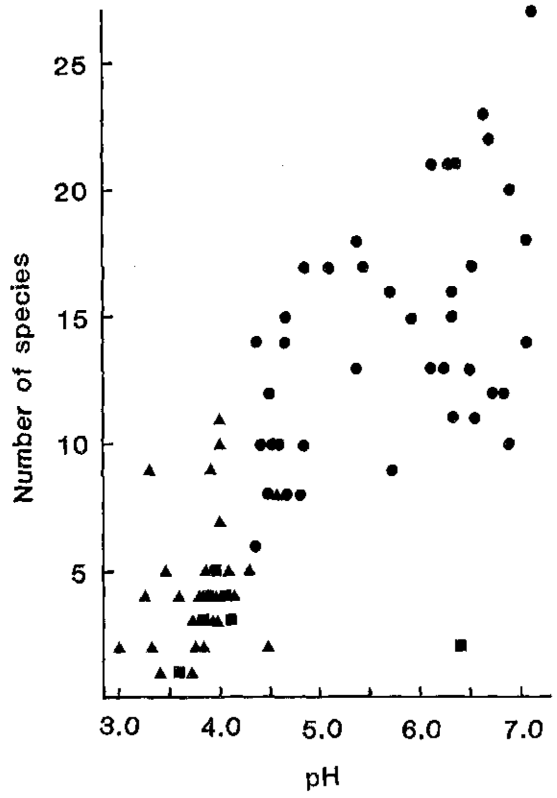


FIG. 11. Number of crustacean species related to pH in acidic moorland water-bodies on the Isle of Rhum (●), Yorkshire Pennines (▲) and North-East Yorkshire (■). Redrawn from Fryer (1980).

where pH fluctuates over a wide range of values (Fig. 9*a*). Attempts to examine the pH tolerance of trout eggs held in Vibert boxes in acid streams were unsuccessful, so this was done in the laboratory (Carrick 1979). Some eggs of salmon, sea trout and brown trout hatched at pH 4·5, even when they were fertilized in water of pH 4·5; some eggs hatched at pH 4·0 when fertilized at pH 7·0-7·8 (Fig. 12). At pH 3·5, all eggs of all three salmonids died within 10 days exposure. The effect of altering the total ionic content of acid water by dilution was also studied (Fig. 12). This approach has been extended by Brown (1981, 1982) and Brown & Lynam (1981). Carrick (1981) showed that oxygen consumption of very small trout fry was the same at pH 4·0 and 7·0. Alabaster & Lloyd (1980), Fromm (1980), Haines (1981) and McWilliams (1982) review the ecological and physiological effects of acid water on freshwater fishes.

The current status of fish in acid tarns in Cumbria is not known, but in the past both brown trout and charr (*Salvelinus alpinus*) have occurred in Seathwaite Tarn and Levers Water, at pH *c.* 4·7-5·1. Brown trout have also occurred in Harrop Tarn, another acid tarn. Prigg (1983) gives details of recent work done by the North West Water Authority on fish in acid streams, including the Esk and Duddon.

Salmonids, especially brown trout, have been known to occur in acid waters in northern Britain for most of this century (Frost & Brown 1967). In Ireland, rainbow trout (*Salmo gairdneri*) have existed at pH 4·5-4·8 in L. Shure since 1905 (Frost 1940, 1974) and there are numerous published reports of brown trout in acid waters (e.g. Went 1940, 1941; Frost 1945). Streams draining igneous rocks in Ireland were known to have low pH values (4·0-5·0) in the 1930s (references given by Sutcliffe 1967a) and it is clear that acid water was known to descend from the hills into pristine salmonid rivers. However, there is no mention of fish kills or deleterious effects on fisheries downstream, although there was an impoverished fauna of invertebrates and fish in the acid hill-streams. Where the depletion or absence of fish has occurred recently in Scotland, this appears to be linked to intensive afforestation (Harriman & Morrison 1981, 1982). Work needs to be done on the acidity of streams draining coniferous forests, on igneous rocks, in Cumbria.

Effect of pH and other major ions on the distribution of aquatic plants in Cumbria

The subject is too large to be adequately summarized here, but the following papers will provide an introduction to FBA work on aquatic plants, related to major ions in Cumbrian waters: Knudson (1954); Gorham (1956); Gorham & Pearsall (1956); Mackereth et al. (1957); Gorham et al. (1974); Talling (1976); Heaney & Talling (1980). Stokoe (1983) lists the species of macrophytes that have been found in mountain tarns and lowland lakes.

Summary and concluding remarks

The problem of 'acid rain' and its effects on aquatic systems is not a simple one, nor is it a recent phenomenon. Acid rain is a natural phenomenon that inevitably leads to progressive acidification of soils. Where the weathering of rocks is insufficient to provide an adequate supply of bases and bicarbonate alkalinity, water-bodies naturally become more acid when the catchment soils have 'acidified'. Man's activities may increase the rate of chemical weathering by increasing the acidity of rainfall.

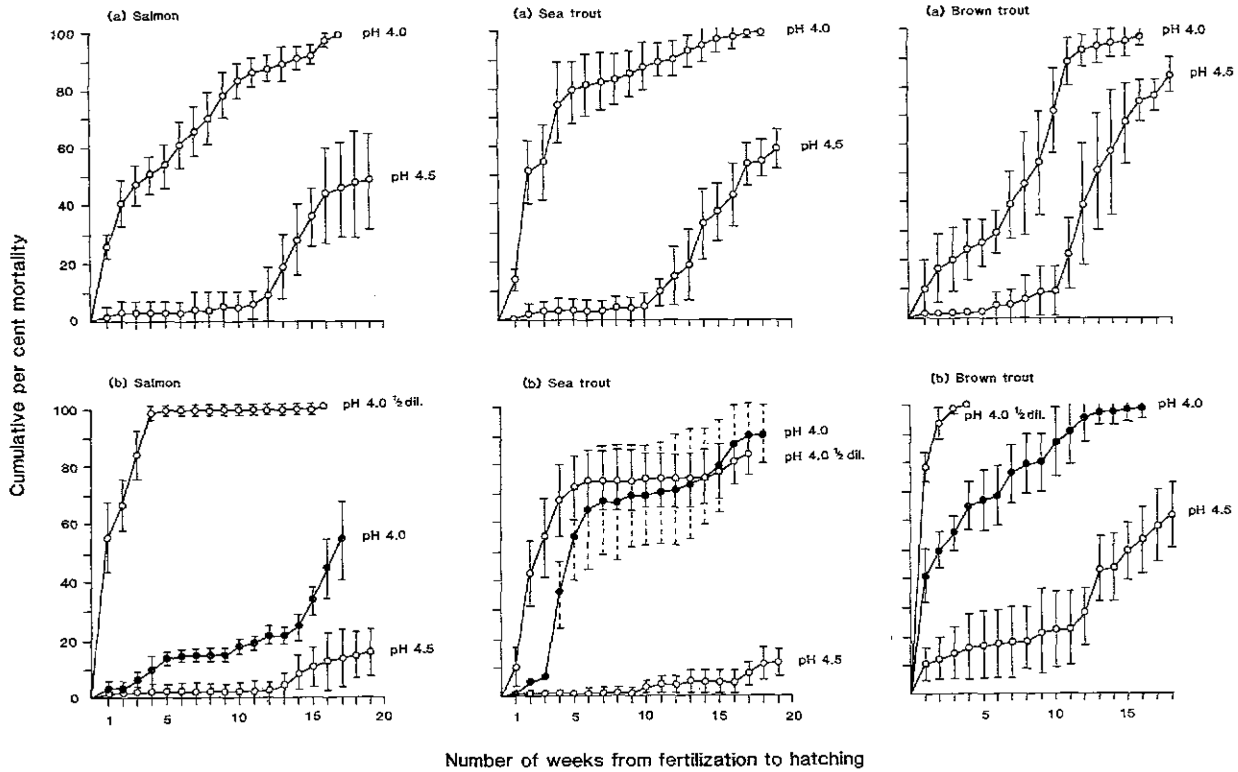


FIG. 12. Cumulative percentage mortality, with 95% confidence limits, for six replicate batches of salmonid eggs kept at 4 °C in Mosedale Beck water at pH 4·0 and 4·5. (a) Eggs fertilized in Mosedale Beck water; (b) Eggs fertilized in water from Windermere (pH 7·0) or the River Kent (pH 7·8). In (b), eggs were also kept in Mosedale Beck water diluted to half its ionic content with distilled water. Redrawn from Carrick (1979).

Intensive afforestation appears to have increased the acidity of water-bodies elsewhere but we do not know if it has had any effect in the Lake District. The proportion of acidity in rain that is due to anthropogenic (man-made) sources is not known, but acidity of rainfall rises when winds blow overland from the direction of industrial areas. These events have probably occurred in Cumbria for the last 100 years or more. Bulk precipitation at Wraymires has had a mean pH of *c.* 4·4 for at least 28 years. There is no evidence of an increase in the acidity (lower pH or alkalinity) of water-bodies in the Lake District over the last 50 years. Brown trout occur in acid streams and upland tarns where pH is 4·5-5·2 throughout the year. Their occurrence in such waters in Britain and Ireland has been known for most of this century and there is no previous evidence of harmful effects on salmonid fisheries, though numbers of fish are naturally low. However, many benthic invertebrates that are common in hill-streams where pH is above 5·7 do not occur in more acid streams. This phenomenon occurs in the headwaters of several western rivers in Cumbria. It is not a recent response to 'acid rain'. Harmful effects of pH are undoubtedly more pronounced in waters that are poor in other dissolved ions. Low concentrations of sodium, potassium, calcium and chloride are especially important and may limit the distributions of some aquatic animals even where pH is above 5·7. The concentration of sulphate ions is usually relatively high but this is not important to the fauna; concentrations are at least two times higher in productive alkaline water-bodies than they are in unproductive acid waters.

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