On the acidity and salinity of rain

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ABSTRACT

Analyses of pH, Na, K, Ca, Mg, HCO_3, Cl, SO_4, NO_3, and PO_4 are recorded for forty-two rain samples collected in the English Lake District between 14 May and 23 October 1954.

NaCl was often an important constituent, and the main source of Na, Mg, and Cl appeared to be sea-spray. SO_4 was clearly correlated with soot, and free H_2SO_4 frequently accounted for an appreciable proportion of total ions. Ca, K, and SO_4 were correlated to some extent. HCO_3 was absent from more than half the samples. NO_3 and PO_4 were usually low in concentration. Sea-spray influence appeared greatest in autumn, while industrial pollution reached its highest concentration in spring.

The ecological significance of the ions in rain is pointed out.

Introduction

Although the geochemical importance of rain has long been emphasized, its ionic composition has seldom been investigated except for Cl, SO_4, NO_3, and NH_4 (Eriksson, 1952). This paper presents six months' analyses for pH, Na, K, Ca, Mg, HCO_3, Cl, SO_4, NO_3, and PO_4 at a site in the English Lake District.

The Area

Samples were collected between 14 May and 23 October 1954 at Wise Een Tarn on Claife Heights, above the western shore of Windermere and about 50 kilometres east of the Irish Sea. Rainfall is highly variable in this region of marked relief. At Ferry House and Wraymires Hatchery, just east and west of Claife Heights, the range is between about 150 and 200 centimetres per year. Monthly fall is about 10 centimetres in spring, rising to 15–18 centimetres in autumn and winter. South-westerly winds prevail.

Methods

Rain was sampled by a polythene funnel 30 centimetres in diameter, surrounded by short stainless-steel wires for protection against birds (Egner *et al.*, 1949), and leading to a gallon polythene bottle. Whatman-541 filter papers (washed with distilled water) were tied over the end of the funnel to trap soot and insects, and were replaced after each collection. Samples averaged about 2 litres, and ranged from 0·7 to 4·5 litres. They were stored in polythene bottles.

pH was measured by glass electrode; Na and K by EEL flame photometer with Calor-gas fuel; Ca and Mg by versenate titration; HCO_3 by titration to a methyl red/bromocresol green end point buffered at pH 4·5; and Cl and SO_4 conductimetrically after ion-exchange treatments, using a method devised in this laboratory by F. J. Mackereth (in press). NO_3 was estimated by visual colorimetry with phenol-disulphonic acid, adding excess $CaCO_3$ before evaporation to neutralize the rain-acids. PO_4 was also determined by visual colorimetry, employing the usual ammonium molybdate/stannous chloride technique. A rough index to soot was obtained by grading the blackness of the filters from 0 to 5 and dividing by sample volume in litres.

TOTAL IONS

Fig. 1 shows the modal concentration of total ions to have been slightly more than 0·1 milli-equivalents per litre. In rains of this concentration SO_4 usually exceeded Cl; at the higher levels Cl was the dominant anion. If anion and cation values for the entire period (see Table 1) are summed, the former amount to 0·165 and the latter to 0·155 milli-equivalents per litre. The slight excess of anions, much less in autumn than in spring and summer, would be balanced to some degree by NH_4.
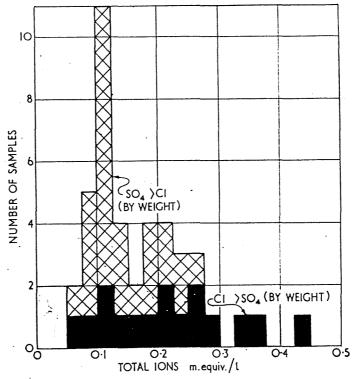

Fig. 1. Frequency distribution of total ion concentrations in Lake District rains.

Dissolved NO_3 and PO_4 usually made a negligible contribution to total ions. NO_3—N was less than 0·02 parts per million in the majority of samples, most of the higher values being encountered in spring. PO_4—P was below 0·001 parts per million in thirty-eight of forty-two samples.

Ion concentrations similar to or little greater than those of rain have been observed in pools on raised or blanket bogs in northern Britain (GORHAM, in preparation), and in many upland tarns of the Lake District (F. J. MACKERETH and J. HERON, private communication). Atmospheric precipitation must therefore be the principal source of nutrients for their plankton. As to the larger lakes, Windermere itself has only 0·5 milli-equivalents of total ions per litre. three times the concentration in rain. Its ionic proportions are of course very different, with Ca and HCO_3 the dominant ions.

SODIUM, MAGNESIUM, AND CHLORIDE

Na and Mg are examined in relation to Cl in Figs. 2 and 3. the straight lines representing the proportions in sea-water. The close correspondence strongly suggests derivation almost entirely from sea-spray: it may be remarked that the two highest NaCl values followed the two heaviest gales from the sea. Mechanisms

of sea-salt entry into the atmosphere have recently been much discussed (BOYCE, 1951; WOODCOCK *et al.*, 1953; KNELMAN *et al.*, 1954; KIENTZLER *et al.*, 1954; BLANCHARD, 1954).

In most Lake District tarns and lakes Na and Cl are likewise present in proportions similar to that of sea-water, so that rainfall—and hence sea-spray—may be inferred as the chief source.
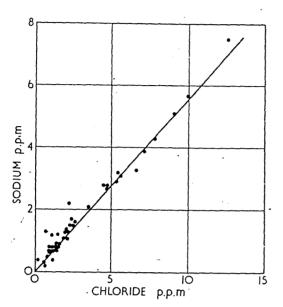

Fig. 2. The relation between sodium and chloride in Lake District rains. Straight line = proportion in sea-water.
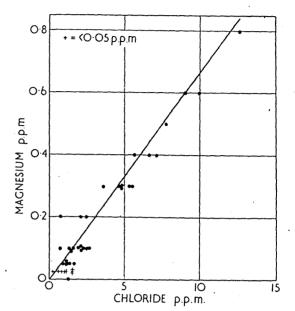
Fig. 3. The relation between magnesium and chloride in Lake District rains. Straight line = proportion in sea-water.
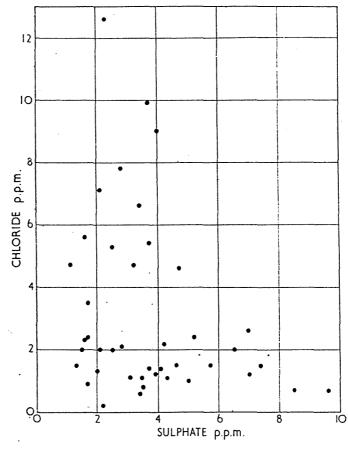
Even the rain highest in NaCl may not have derived its whole ion content from the sea. The ratios of H-ions and HCO_3 to Cl were far higher than in sea-water, and the ratio K : Cl was half as high again in this rain as in the sea. The ratios SO_4 : Cl and Ca : Cl were also slightly high. Alternative hypotheses might, however, be invoked. Japanese workers (KOYAMA and SUGAWARA, 1953) have postulated a differential separation of atmospheric salts by rain, hygroscopic chloride particles being washed out most easily and quickly. And CONWAY (1942) has inferred a supply of SO_4 by diffusion of H_2S from the muds of the continental shelf, which might perhaps account for a small amount of H_2SO_4 in rain from the sea.
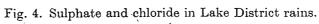
The concentrations of Na, Mg, and Cl rose during the period studied, particularly in autumn. Preliminary examination of wind-speeds and directions has so far offered no clear explanation. It is hoped to investigate the matter further.
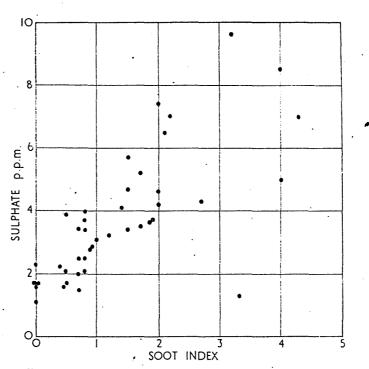
SOOT, SULPHATE, AND HYDROGEN IONS

Fig. 4 shows SO_4 plotted against Cl. While individual rains were often low in both ions, none was high in both, indicating that Cl and SO_4 came from different sources. Sea-spray has been suggested as the origin of the former, and must necessarily supply some SO_4 as well. However, a large amount of the latter ion appears to come from atmospheric pollution, as shown in Fig 5—where SO_4 is plotted versus soot index. Five samples with very little soot contamination (see Table 3) yielded an average of 1·7 parts per million of SO_4; all but one of the ten sootiest rains had
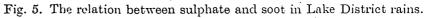
Fig. 4. Sulphate and chloride in Lake District rains.

Fig. 5. The relation between sulphate and soot in Lake District rains.

more than four parts per million. It may be noted that filter contamination was always very black; on no occasion did a brown soil coloration prevail.

Fig. 6, illustrating a correlation between SO_4 and H-ion concentration, demonstrates that H_2SO_4 may be a substantial component of Lake District rains. The straight line represents equivalent proportions of the two ions. While pitting of building stone in industrial cities is well known, the writer has encountered in the
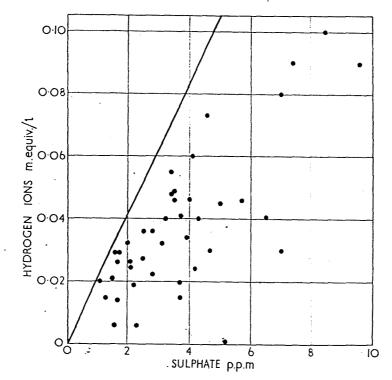

Fig. 6. Sulphuric acid in Lake District rains. Straight line = equivalent proportions of sulphate and hydrogen ions.

literature very little evidence of free mineral acid in country rain. Conway (1942) speculates that acids produced by oxidation of sulphur compounds may react with most or all of the bicarbonates deriving from dust or ash in the rain. In contrast, Tamm (1953) gives a pH range of 4·3–5·9 for rain in open fields in east Sweden, but no anion analyses.

Such a supply of dilute mineral acid must be an appreciable factor in rock and soil weathering, especially where vegetation is sparse. Moreover, if soot is the main source, its influence must have increased enormously during the past century, and be still growing. As to vegetation, two somewhat antithetical effects may be postulated. Bathing with dilute H_2SO_4 may well be inimical to many species. On the other hand, the addition of extra Ca and K in the rain, and in particular an increased degree of weathering, may lead to greater nutrient supply. While upland tarns owe most of their acidity to rain, which enters them chiefly as superficial run-off, they may also receive added Ca and K from atmospheric pollution. Lowland waters may also obtain more nutrients due to neutralization of rain-acids by bases from soil and rock minerals.

Although soot and SO_4 decrease from May to October, acidity varies rather little and is greatest in summer, because of an even larger decrease in Ca and K from the first to the middle period (see Table 1).

Comparison of the present data with figures for atmospheric precipitation in industrial cities should be of much interest. Table 2 gives analyses for pH, Ca, Cl, and SO_4 in rain subject to extreme industrial contamination. That the acidity is lower than in Lake District rains, despite a lower rainfall, is especially noteworthy. Furthermore, Cl is about half as much as SO_4 in city rain, while in the sootiest Lake District samples the concentrations of SO_4 were usually several times those of Cl. Such dissimilarity of proportions suggests a differential separation of the components of industrial pollution. Another possibility might be oxidation of sulphides in soot to H_2SO_4 while in the atmosphere. In this connection, black soot collected above a grate in which no fire had been lit for two or three weeks gave a strong odour of H_2S upon acidification.

The regression of SO_4 on Cl in Lake District tarns and lakes shows a proportionality markedly similar to the mean SO_4 : Cl ratio in rain. It may be supposed that atmospheric precipitation is the main source of both ions.

Table 1. Ion concentrations in Lake District rain

	Rain period				Range in 42 individual samples
	May 14 to 30 June	1 July to 31 Aug.	1 Sept. to 23 Oct.	Entire period	
Amount of rain (cm)	26	39	58	124	
Total ions (m. equiv./1)	0·152	0·154	0·177	0·165	0·054–0·439
pH	4·45	4·38	4·50	4·45	4·0–5·8
Na	1·3	1·6	2·4	1·9	0·2–7·5
K	0·3	0·2	0·2	0·2	0·05–0·7
Ca (parts	0·5	0·2	0·2	0·3	0·1–2·0
Mg per	0·1	0·1	0·3	0·2	nil–0·8
HCO_3 million)	0·4	0·4	0·4	0·4	nil–2·8
Cl	2·0	2·7	4·2	3·3	0·2–12·6
SO_4	4·3	3·5	2·4	3·2	1·1–9·6
Soot index	1·5	1·3	0·7	1·0	0–4·3

CALCIUM, POTASSIUM, AND BICARBONATE

Fig. 7 reveals some correlation between Ca and SO_4; while Fig. 8 shows a rise in the upper limit for K with increasing SO_4 concentration. Fig. 9 further demonstrates that these two cations follow generally similar trends. While many of the sootiest rains had no more Ca and K than the purest, the highest concentrations were distinctly limited to the more contaminated samples, notably in spring. Perhaps the relatively dry spring weather, following a winter of fuel-burning, builds up atmospheric pollution at this time.

At any given SO_4 level, rains with HCO_3 naturally contain more Ca and K, since Na and Mg are commonly balanced by Cl. The source of these bicarbonates may be industrial, agricultural, or natural (i.e., soot or ash, fertilizer or dust from

cultivated fields, or dust from uncultivated ground). The highest Ca value, two parts per million, lay well above the normal regression of Ca on SO_4, due presumably to an abnormal local supply of $CaCO_3$ to the atmosphere from one of these sources.
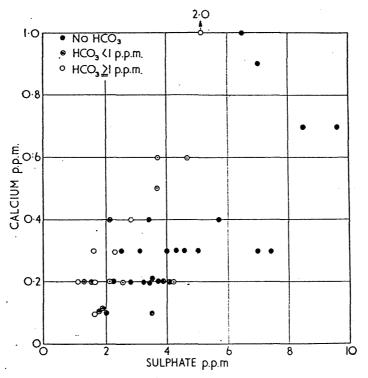

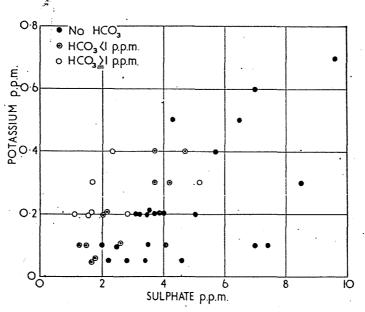Fig. 7. Sulphate and calcium in Lake District rains with or without bicarbonate.

Fig. 8. Sulphate and potassium in Lake District rains with or without bicarbonate.

The ratio of Ca to SO_4 is much higher in city rains (see Table 2) than in the sootiest of the present series. Again, this may signify differential separation of atmospheric salts, or a gradual H_2SO_4 production from drifting soot.

Rain may be an important source of K for many natural bodies of water in the Lake District, in which it makes up only a small proportion of total dissolved ions.

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The median K : Cl ratio for tarns and lakes is in fact somewhat less than for the present rain series. In this connection it should be borne in mind that K is subject not only to a much stronger biological demand than Cl, but also to fixation in non-exchangeable form by soil colloids.
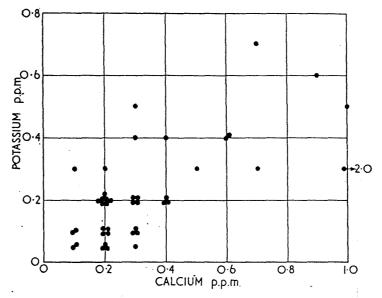

Fig. 9. The relation between calcium and potassium in Lake District rains.

Table 2. *Ion concentrations in atmospheric precipitation over industrial cities (Leeds, London, Manchester, Sheffield, Glasgow, and Newcastle, 1944–49)* *

Rain (cm/yr)	pH	Ca	Cl	SO$_4$
		(parts per million)		
73	4·8	5·8	10·9	20·6

COMPOSITION OF SOOT-FREE RAIN

Table 3 presents data for five rain samples on whose filters only faint traces of soot were discernible. One of these was collected after a gale from the sea. The others, while obtained after or during fairly high winds, were not exceptionally rich in NaCl, although it was the dominant component. H-ions, HCO$_3$, Ca, K, and SO$_4$ were present in much more than the proportions of sea-water (relative to NaCl). Part of the SO$_4$ may have originated, as previously noted, from H$_2$S diffusing out of the muds of the continental shelf (CONWAY, 1942).

H$_2$SO$_4$ was much lower, and HCO$_3$ much higher, than in sooty rains. At the same time Ca and K were in general lower in the clean rains, which makes it unlikely that the relatively high winds brought into the atmosphere more than the usual amount of soil-dust, rich in CaCO$_3$ and K$_2$CO$_3$. Rather it would seem that the light soot particles were more widely dispersed than usual, or settled out more

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* Data provided through the courtesy of D. MacDougall, Chief Chemist, Fuel Research Station, Department of Scientific and Industrial Research.

slowly—so that the HCO_3 derived from soil particles was not neutralized by H-ions from soot.

Table 3.   Ion concentrations in five soot-free rains

		Mean	Range
pH		4·8	4·5–5·2
Na		3·1	1·5–7·5
K		0·2	0·05–0·4
Ca	(parts	0·2	0·1–0·3
Mg	per	0·3	0·05–0·8
HCO_3	million)	1·2	0·5–2·2
Cl		5·1	2·3–12·6
SO_4		1·7	1·1–2·3

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