The Influence and Importance of Daily Weather Conditions in the Supply of Chloride, Sulphate and Other Ions to Fresh Waters from Atmospheric Precipitation

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THE INFLUENCE AND IMPORTANCE OF DAILY WEATHER CONDITIONS IN THE SUPPLY OF CHLORIDE, SULPHATE AND OTHER IONS TO FRESH WATERS FROM ATMOSPHERIC PRECIPITATION

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CONTENTS

This paper deals with chemical analyses for hydrogen, sodium, potassium, calcium, chloride, sulphate and nitrate ions in daily precipitation samples collected in the English Lake District, and examines the correlations of these analyses with (*a*) one another, (*b*) the amount of precipitation, (*c*) wind direction, (*d*) wind velocity, and (*e*) temperature.

Highly significant correlations are found between estimates for H, K, Ca, NO_3 and SO_4 ions, and atmospheric pollution appears to supply much of the sulphate in Lake District rain, since it comes largely as sulphuric acid from the south-east. The correlation between Na and Cl is also extremely close, with the proportion between the two ions very similar to that in sea water. Since these two ions are supplied mainly from the south-west, in amounts which are greatly increased by high winds, sea spray may be inferred as the principal source. Nevertheless, evidence is presented for some small supply from atmospheric pollution, and it is furthermore suggested that mixed droplets of sea salt and sulphuric acid may, upon abstraction of moisture by freezing or evaporation, release gaseous hydrogen chloride to the air and so alter the balance of Na and Cl in precipitation. The supply of Na and Cl is also considerably higher in cold than in warm weather, a phenomenon possibly connected with stormier conditions and greater evaporation over the Atlantic Ocean.

The atmospheric contribution of ions to natural waters via precipitation is shown to be of great importance, in particular to bog pools, to upland tarns on hard rocks, and to the soil solution in highly organic *mor* humus layers overlying heavily leached hillside soils. Sodium and chloride in most surface waters appear to be almost wholly supplied by sea spray, while calcium and magnesium bicarbonates are the main products of soil weathering. A net loss of rain acids is evident in all soil waters, although some may be more acid than normal rain water owing to considerable concentration by evaporation. The soil waters are relatively rich in potassium, presumably supplied from decaying vegetation.

INTRODUCTION

The presence of dissolved substances in rain and snow raises many problems, among them those of moisture condensation and precipitation, the cycle of materials between soils, fresh waters and the sea, and the distribution and dissipation of atmospheric pollution. However, while nitrogen compounds, chlorides and sulphates in rain and snow have been analyzed frequently and in many parts of the world (see Eriksson 1952, and recent issues of *Tellus*), rather little is known of the ways in which day-to-day changes in the weather may affect the supply of these ions in precipitation, and even less is known of the distribution of other ions. The chief aim of this paper is to provide information upon such matters, with reference mainly to chloride and sulphate, but also incidentally to sodium, potassium, calcium, hydrogen and nitrate ions.

The English Lake District, where the investigation has been made, is eminently suitable for the purpose, being a mountainous region with numerous peaks of just under 1000 m within a circle of about 40 km diameter. Most important, there is an abundance of rain, with much of the area receiving over 1250 mm per annum. In addition, chlorides and sulphates, which together account for well over 90% of total dissolved anions, are supplied in similar and easily measurable amounts, but from largely different sources.

As shown in an earlier investigation (Gorham 1955), most of the chloride comes from sea spray, while a great part of the sulphate is derived from atmospheric pollution, much of it falling as sulphuric acid. The mechanism of sea spray entry into the atmosphere, which has been studied recently by American scientists (Woodcock, Kientzler, Arons & Blanchard 1953; Woodcock 1955), appears to lie in the bursting of small bubbles at the sea surface, as, for example, in foam patches. Upon collapse these bubbles form jets, which eject minute droplets of sea water into the air where—if sufficiently small—they may be swept up as a fine aerosol and carried away by the wind. Whether they subsequently collect more water by condensation or evaporate to form solid particles of sea salt depends upon atmospheric humidity. If the latter, such solid particles may of course serve as condensation nuclei upon entering a damper environment and pick up moisture again. Twomey & McMaster (1955) also report that the drying of large salt droplets may in certain circumstances release a multitude of much smaller condensation nuclei, by fragmentation during the crystallization process. Much of the sulphur produced by fuel combustion must enter the air in gaseous form as sulphur dioxide, either free or absorbed by soot particles. Gradual oxidation then takes place, resulting in the accumulation of extremely hygroscopic sulphuric acid droplets in the atmosphere.

The apparent abundance of atmospheric pollution in this predominantly rural area seemed rather surprising at the time of the earlier work, and provided one of the main reasons for undertaking the present study, since the influx of large amounts of sulphuric acid during the past century or so must have considerable ecological significance.

METHODS

Sampling

From 21 January 1955 to 25 January 1956 precipitation was collected at about 9 a.m. on the day following each day on which at least 0·1 mm fell. The sampling site was located in a firebreak in young pinewoods at High Man, about 280 m above sea level on Hawkshead Moor between Windermere and Coniston Water, in the southern part of the English Lake District. The sample container was a 1-gallon Polythene bottle, with a Polythene funnel 30 cm in diameter projecting to about 0·5 m above the ground. The funnel and container were exposed continuously, so that any substances falling as dry particles would be included in the next wet precipitation sample. However, the humid climate of the Lake District, with 178 rain days in this particular site, may be expected to minimize such contributions of dry materials.

Chemical analyses

Each daily sample was analyzed for chloride and for sulphate plus nitrate by the technique of Mackereth (1955). Because of the small size of many samples a separate nitrate estimation could not always be carried out, but it may be convenient to note that there is a good logarithmic correlation between nitrate and sulphate ($r = 0{\cdot}83$ for the 126 samples analyzed for both ions), and that the regression is nearly linear, with nitrate amounting on the average to just under 10 % of sulphate. Next sodium and potassium were measured on all but the smallest samples, by EEL flame photometer with Calor-gas fuel. pH was then determined by glass electrode. About 70 % of samples yielded enough water to allow estimation of nitrate nitrogen by the phenoldisulphonic acid method, evaporation being preceded by addition of excess calcium carbonate to these, often very acid, waters in order to prevent loss of nitrate. Finally, calcium was measured in the remaining 65 % of samples, by versenate titration with ammonium purpurate as indicator (Heron & Mackereth 1954).

Weather data

Precipitation was measured by pouring the daily samples into appropriate Pyrex volumetric cylinders. Wind records were taken from Sellafield, on flat land near the coast and about 25 km from the sampling site. (Records from the Ferry House laboratory were not suitable owing to strong bias from the physiographical situation). The hourly wind speeds were averaged to each 24 h period, while hourly wind directions were plotted as frequency distributions and the daily modes estimated by eye. Daily temperature was taken as the average of daily maximum and minimum readings recorded each morning at Ambleside, about 35 to 40 m above sea level and 9 km from the sampling site.

Statistics

The statistical procedures used in summarizing and analyzing the grouped data follow Brooks & Carruthers (1953). Ion concentrations and daily precipitation figures were grouped logarithmically to facilitate correlation and regression analysis, this transformation being chosen empirically by inspection of scatter diagrams and correlation tables, because it gave frequency distributions much more closely resembling the normal frequency curve than those utilizing untransformed data, and also because it yielded, as far as could be discerned, reasonably straight regression lines. Since the logarithmic transformation appeared satisfactory, no others were tested.

RESULTS

Statistics for chloride, sulphate plus nitrate and weather conditions are presented in table 1, for the 163 rain days on which complete sets of data could be assembled. Table 2 gives the correlation coefficients (r) between daily ion supply per unit area and the various weather conditions, both before (zero order) and after (third order) elimination of the influence of other weather variables. Table 3 shows these coefficients transformed to Fisher's z' values, which enable comparisons of the significance of differences between the various coefficients. Table 4 presents the zero- and third-order regression coefficients (b) for the same data. Changes in the concentrations of different ions during a single shower are illustrated in table 5. In table 6 statistics are given for daily supply of the various other ions analyzed in this study, and in table 7 the corresponding correlation and regression coefficients between the supply of these ions and the supply of either chloride or sulphate plus nitrate. The original data are available for inspection at this laboratory.

TABLE 1. STATISTICS FOR THE DAILY SUPPLY OF CHLORIDE AND SULPHATE PLUS NITRATE, AND FOR DAILY WEATHER CONDITIONS (163 RAIN DAYS)

	chloride	sulphate plus nitrate	precipitation	wind direction		wind speed	temperature
	($\log_{10}$ mequiv./100 m^2)		($\log_{10}$ mm)	for chloride*	for sulphate plus nitrate†	(km/h)	(°C)
range	0·05 to 3·2	0·3 to 2·8	$\bar{1}$·0 to 1·8	—	—	4 to 46	−2 to 17
mean	1·78	1·70	0·68	3·56	3·87	21·9	8·2
S.D.	0·61	0·56	0·62	2·01	2·49	8·0	4·4

* Units of 22·5° from 236°. † Units of 22·5° from 124°.

TABLE 2. COEFFICIENTS (r) FOR THE CORRELATION OF ION SUPPLY WITH WEATHER CONDITIONS

	$\log_{10}$ chloride		$\log_{10}$ sulphate plus nitrate	
	zero order	third order	zero order	third order
$\log_{10}$ precipitation	0·71	0·73	0·84	0·82
wind direction	−0·24	−0·23	−0·45	−0·45
wind speed	0·55	0·49	0·30	0·20
temperature	−0·21	−0·39	−0·06	−0·13

N.B. If r exceeds 0·16 it is significant at the 5 % level; if r exceeds 0·20 it is significant at the 1 % level.

TABLE 3. FISHER'S z' VALUES FOR THE CORRELATION COEFFICIENTS RELATING ION SUPPLY TO WEATHER CONDITIONS

	$\log_{10}$ chloride		$\log_{10}$ sulphate plus nitrate	
	zero order	third order	zero order	third order
$\log_{10}$ precipitation	0·89	0·93	1·22	1·16
wind direction	−0·25	−0·23	−0·49	−0·49
wind speed	0·62	0·54	0·31	0·20
temperature	−0·21	−0·41	−0·06	−0·13

N.B. If the difference between z' values exceeds 0·22, it is significant at the 5 % level, if it exceeds 0·29 it is significant at the 1 % level.

Table 8 provides analyses of extracts from smoke solids, while table 9 gives the ionic composition of a stream water percolating through powdered slate from a quarry working. In table 10 analyses of some blanket bog waters are compared with those of rain, and in table 11 the influence of distance from the sea upon tarn water composition is demonstrated. Tables 12 and 13 are concerned with the ionic composition of waters pressed from oakwood soils, and the contribution of rain ions thereto.

The relation of ion supply to precipitation

As might be expected, daily ion supply is most closely related to daily precipitation, the correlation coefficients given in table 2 being a little above 0·7 and 0·8 for chloride and for sulphate plus nitrate, respectively. The latter coefficient appears from the z' values in table 3 to be significantly higher (at the 5 % level) than the former, reflecting the greater total influence of other factors upon chloride supply.

Table 4. Coefficients (b) for regression of ion supply upon weather variables given in table 1

	$\log_{10}$ chloride		$\log_{10}$ sulphate plus nitrate	
	zero order	third order	zero order	third order
$\log_{10}$ precipitation	0·70	0·59	0·76	0·67
wind direction	−0·073	−0·042	−0·10	−0·057
wind speed	0·042	0·026	0·022	0·007
temperature	−0·029	−0·033	−0·008	−0·008

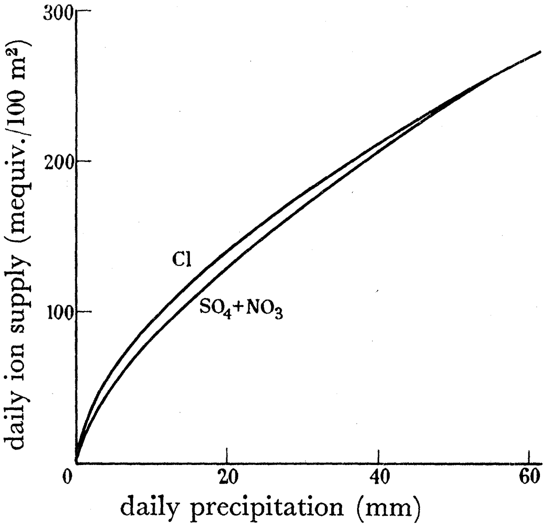

Figure 1. The supply of chloride and of sulphate plus nitrate in relation to daily precipitation.

The general relation between ion supply and amount of precipitation (third-order regression) is shown graphically in figure 1, which demonstrates the great similarity of precipitation effects upon chloride and sulphate plus nitrate in this area, both components reaching levels of 270 mequiv/100 m^2/day with 60 mm of rainfall. Figure 2, in which daily ion supply per unit area has been divided by daily precipitation to give ion concentrations for different amounts of precipitation, is a further illustration of this point; but shows in addition the rapidity with which ion concentrations decline in light showers as the amount of rainfall increases. In heavy rains this drop in concentration is much less marked. For example, between 1 and 10 mm precipitation the chloride concentration falls by 0·15 mequiv./l., while from 10 to 20 mm the fall is 0·02 mequiv., and from 50 to 60 mm only 0·003 mequiv. (It is necessary to remark here that both figures 1 and 2, although plotted upon arithmetic scales for the sake of clarity, represent logarithmic rather than arithmetic regressions, since they are constructed of antilogarithms from the straight-line logarithmic relationship. No attempt has been made to approximate the true arithmetic regression through adjustments such as those proposed by Quenouille (1952).)

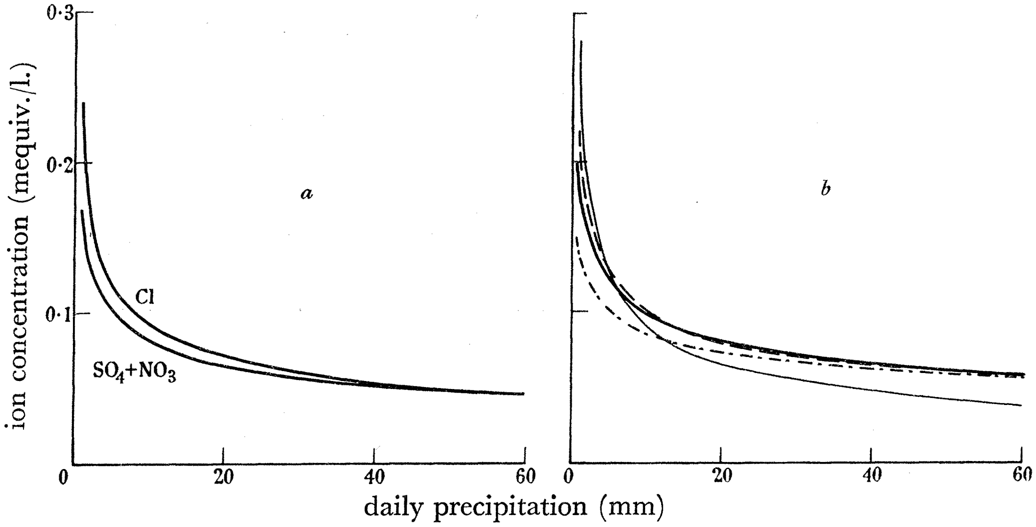

FIGURE 2. The concentration of chloride and of sulphate plus nitrate in relation to daily precipitation, for third-order (*a*) and zero-order (*b*) regressions. For (*b*) only, all rain days, Cl, —; SO_4+NO_3, – · –. No rain on previous day, Cl, —; SO_4+NO_3, – –.

A number of factors may be suggested as contributing to the initial sharp decline in ion concentration with increasing rainfall. If there is only a limited amount of hygroscopic saline or acid material in the atmosphere the first part of a shower may carry down a fairly large part of it, so that there is a much lower (and constantly decreasing) air concentration available for capture by subsequent precipitation. Hence, heavier rains may be expected to exhibit lower salt concentrations. In this connexion too it appears from inspection of the daily weather maps that the smallest Lake District showers are rather local. In contrast, the heaviest downpours reflect a pattern of more general rain accompanying the Atlantic depressions, with (presumably) a considerable likelihood of aerosol precipitation and depletion within an air mass before it reaches the Lake District. Moreover, the heavier rainfalls tend to be more intense, and therefore more subject to the operation of the law of diminishing returns, with too many raindrops chasing too few salt particles. Finally, in small showers there is likely to be a greater chance of droplet evaporation on the way to the ground (cf. Turner 1955).

From the picture given in figure 2 one might be led to suspect a similar drop in ionic concentration during individual precipitations. Table 5 shows that this was so in a single short shower sampled during a calm period on 7 September 1956. In the first sample taken the total anion concentration was 0·36 mequiv./l., while by the end of the shower—

after half an hour's rain amounting to 0·9 mm—the concentration had fallen to 0·22 mequiv./l. Here rain intensity seemed not to be the controlling factor, since ion concentration (apart from potassium) did not rise in proportion to the decline in rainfall rate during the later stages of the shower. However, Mordy (1953) and Woodcock & Blanchard (1955) report instances in which ionic concentration appeared to show a marked response to changes in rain intensity.

Table 5. Changes in ion concentrations throughout a single shower during calm weather

	duration of successive sampling periods (min)				
	15	5	2	5	4
rain delivery rate (mm/min)	0·007	0·040	0·130	0·056	0·012
sodium (mequiv./l.)	0·027	0·019	0·008	0·012	0·015
chloride (mequiv./l.)	0·031	0·027	0·018	0·013	0·015
sulphate (mequiv./l.)	0·27	0·24	0·18	0·13	0·16
hydrogen ion (mequiv./l.)	0·18	0·14	0·12	0·08	0·10
nitrate (mequiv./l.)	0·063	0·057	0·057	0·046	0·043
calcium (mequiv./l.)	0·04	0·04	0·02	0·02	not done
potassium (mequiv./l.)	0·008	0·005	0·003	0·005	0·006

A last point to be noted about table 5 is that the change in concentration with time is not the same for different ions, either absolutely or proportionally, although in general the trends are similar. For instance, while all anions declined in concentration during the course of this shower, the decline was proportionally much less for nitrate than for sulphate, while the fall in chloride concentration was proportionally a little greater. Both nitrate and chloride were present in much smaller amounts than sulphate.

Yet another point to be considered about the relation of ion concentration to amount of precipitation concerns the effect of previous precipitation. Figure 2*b* provides information about this, since it shows the zero-order regressions of chloride and of sulphate plus nitrate upon precipitation, not only for all rain days, but also for the fifty-five occasions when there had been no rain on the previous day. While there is a general resemblance between all the curves, three differences may be remarked. First, during those rain days not preceded by rain on the day before, the concentration of sulphate plus nitrate was distinctly higher than usual, in spite of the fact that the average daily precipitation, wind speed, temperature, and indeed chloride supply, were all a trifle lower than normal, and the distribution of wind directions showed no obvious abnormality. No explanation of this phenomenon can be suggested by the writer. Secondly, the maximum concentration is higher, and the fall in concentration with increased rainfall more rapid, in those samples taken after a dry day. This may possibly suggest some slight deposition of material in the collector during dry weather, though the evidence is not strong. Thirdly, the fall in chloride concentration with increasing precipitation appears generally somewhat more pronounced than that of sulphate plus nitrate.

In connexion with the last point, the observation by Junge (1954) that atmospheric chloride particles may be an order of magnitude larger in diameter than sulphate particles suggests that the former may grow to raindrop size more rapidly, and hence be precipitated to a greater extent than the latter during the early stages of rainfall. Since the degree of vapour pressure reduction is rather similar for sodium chloride and for sulphates such as sulphuric acid and ammonium sulphate, the different chemical nature of the respective particles may be expected to have less effect than their difference in size.

An Australian observation by Squires (1956) is also of interest in regard to this matter. He found that while there is little difference in liquid water content between maritime and continental cumulus clouds, the former contain many fewer but larger droplets; and he suggests that the more frequent production of non-freezing rain by these maritime cumuli may be connected with this difference in microstructure. It seems reasonable to suppose that the larger size of the maritime droplets is associated with the initially larger size of the maritime chloride particles as compared with continental sulphate particles.

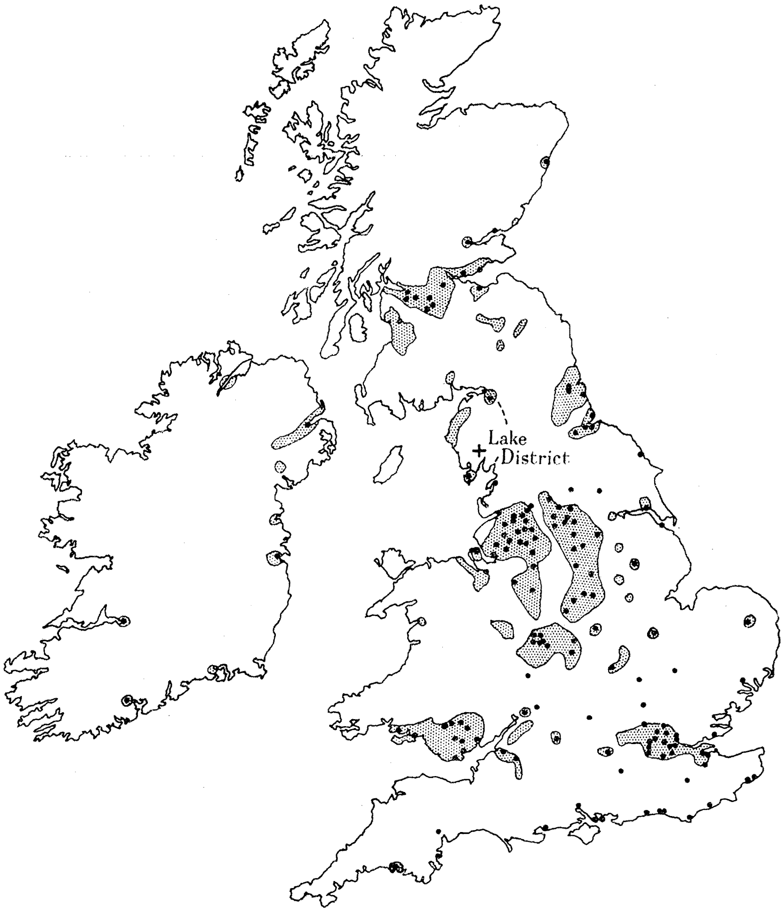

FIGURE 3. The location of the Lake District rain sampling site, marked by a cross, in relation to the distribution of population and industrial centres, marked by dots (towns over 30 000) and stippling. (After the *Times Survey Atlas of the World*, 1920.)

The relation of ion supply to wind direction

The location of the rain collector used in this study is indicated in figure 3, where also are shown the main industrial areas and centres of population in the British Isles. It is evident that the greatest seaward exposure is between west and south, while the major centres of atmospheric pollution lie to the south and east. The influence of these two sources of aerosols is illustrated in figure 4, in which the average rain day's supply of chloride and of sulphate plus nitrate is plotted on polar co-ordinates round the compass. (Once again the values shown are antilogarithms of the logarithmic averages, on this occasion the latter have been smoothed by the well-known formula $\frac{1}{4}(a+2b+c)$.) It will be seen that daily chloride supply is much greater to the south-west than to the north-east, being usually well above 100 mequiv./100 m^2 in the former direction and less than 50 mequiv. in the latter. On the other hand, sulphate plus nitrate shows, as expected, a maximum daily accumulation in the south-east quarter, where it almost reaches 100 mequiv./100 m^2, while to the north-west it is below 25 mequiv.

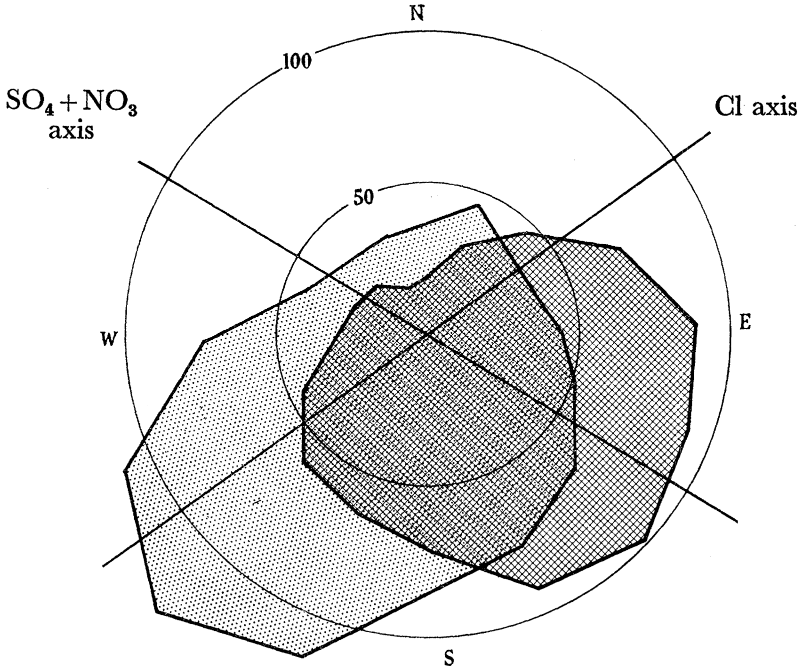

FIGURE 4. Mean daily supply of chloride (stippled) and sulphate plus nitrate (hatched) in relation to wind direction. The inner and outer circles delimit 50 and 100 mequiv./100 m^2, respectively. Diagonal axes are those used in figure 5. (Data smoothed by formula $\frac{1}{4}(a+2b+c)$.)

The chloride and sulphate plus nitrate axes shown in figure 4 form the bases of the correlation and regression analyses of the relation between ion supply and wind direction, the units being given in table 1. The results of these analyses are given in tables 2 and 4, and illustrated in figure 5. The conditions for such an analysis are far from ideal, with the estimates of effective wind direction liable to many obvious errors, and with, in addition, distinctly asymmetrical polar distributions of values about the chosen axes. Nevertheless, the correlation coefficients in table 2 are significant at the 1 % level for both zero and third orders. It further appears from the z' values in table 3 that the correlation coefficient for sulphate plus nitrate and wind direction is significantly higher at the 5 % level than that for chloride and wind direction. No doubt the great concentration of atmospheric pollution centres in the industrial midlands of England forms something approaching a point source of sulphate plus nitrate, while the sea supplies chloride from all directions, although reaching closest to the Lake District in the south-west.

The third-order regressions of ion supply on wind direction are demonstrated in figure 5, which reveals that the influence of this factor is much less great than that of rainfall volume. For example, over the whole range of wind directions the difference in sulphate plus nitrate supply is only a little above 50 mequiv./100 m^2 (figure 4 gives a difference of about 80 mequiv./100 m^2), in comparison with a difference of a little more than 250 mequiv./100 m^2 between maximal and minimal rainfalls.

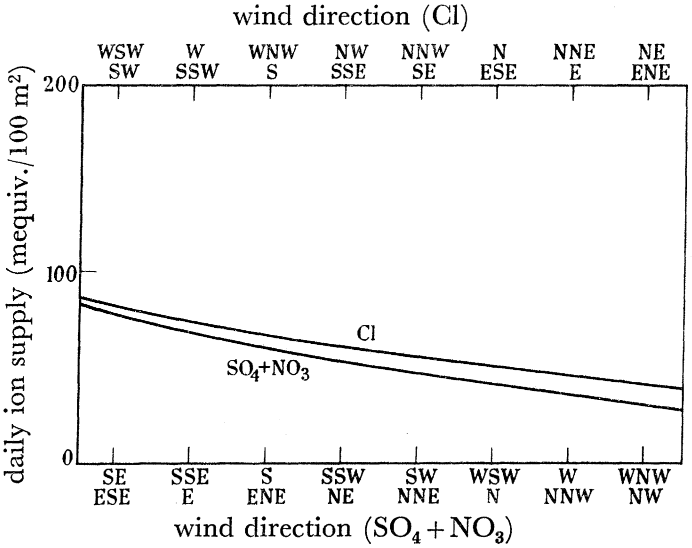

FIGURE 5. The daily supply of chloride and of sulphate plus nitrate in relation to wind direction.

The relation of ion supply to wind speed

The amounts of both chloride and sulphate plus nitrate brought down in rain vary considerably with changes in wind speed, the relationship being closest and the response particularly marked in the former case. Again, despite deficiencies in measurement, since mean hourly wind speed at Sellafield over 24 h is not necessarily an accurate reflexion of the average wind speed over the area while rain was falling, the third-order correlation coefficients are both significant, being 0·49 and 0·20 for chloride and for sulphate plus nitrate, respectively (see table 2). The difference of 0·34 in the third-order z' values (table 3) is significant at the 1 % level.

The third-order regressions illustrating the effect of wind speed are shown in figure 6, where the contrast between its influence upon chloride and upon sulphate plus nitrate supply is clearly brought out. Between the minimum and maximum wind speeds the supply of sulphate plus nitrate is approximately doubled, whereas chloride supply increases more than tenfold. Another point to be noted is that at low wind speeds chloride supply is less than that of sulphate plus nitrate, although the reverse very definitely obtains in stormy weather. The explanation of these differences probably lies in the fact that while entry of pollution into the atmosphere is continual and largely independent of wind strength, the production of foam patches on the ocean and the entrainment of sea salt particles in the air increases sharply with rising winds. Thus, the Lake District's supplies of sulphate and nitrate from pollution depend on wind speed only to the extent that high winds carry the larger aerosols a longer distance from their point of origin; while chloride supply is additionally dependent on the wind actually to produce the sea spray carried inland. In calm weather little chloride will escape into the air, and so the supply inland may fall below that of sulphate plus nitrate. The greater size of the chloride particles (Junge 1954) may also involve a greater chance of fall-out near the source in calm weather.

The nature of the wind effect upon atmospheric chlorides has been demonstrated more directly by Woodcock (1953; Woodcock & Mordy 1955) in studies of sea salt in Hawaiian air. These have shown that the numbers and weight of salt particles in the Hawaiian atmosphere rise exponentially with increasing wind speed, as does the weight of chloride deposited on land in the Lake District.

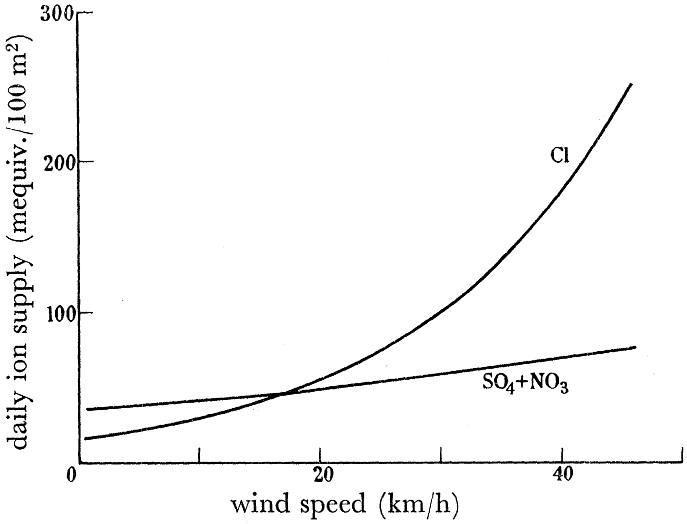

FIGURE 6. The supply of chloride and of sulphate plus nitrate in relation to daily wind speed.

Of interest in connexion with the abundance of atmospheric chlorides during periods of high wind is the possibility, suggested also by Woodcock & Mordy (1955), that the increased number of condensation nuclei thus provided may intensify precipitation. In the present instance there is a positive correlation between the logarithm of rainfall and the wind speed, significant at the 1% level ($r = 0{\cdot}29$, $b = 0{\cdot}022$). While this might be taken, in conjunction with the *chloride supply*:*wind speed* relation, to suggest a causal connexion between atmospheric chlorides and rainfall, it must be borne in mind that increased wind speed also involves a more rapid flow of moist air over the Lake District hills, and this too may increase rainfall. At present suitable data are not available to evaluate the relative importance of these two factors.

The relation of ion supply to temperature

The influence of temperature was investigated because it was believed that greater fuel combustion during cold weather would increase atmospheric sulphates. In the event the expected negative correlation between temperature at Ambleside and sulphate plus nitrate falling on Hawkshead Moor proved not to be significant (third-order $r = -0{\cdot}13$), a puzzling result, especially in view of Meetham's (1950) demonstration that smoke and sulphur dioxide concentration in the air over the major industrial districts of England is distinctly higher in winter than in summer. The writer can only suppose that the decline of atmospheric turbulence in winter (see Bilham 1938) leads to a much greater fall-out of air pollution near its source during this season.

Expectation was again confounded when the third-order correlation coefficient for chloride supply and temperature turned out to be highly significant ($r = -0{\cdot}39$). The regression is given in figure 7, which shows that as temperature drops from summer levels around 17° C to a degree or two below freezing point, chloride supply increases about fivefold, even with the effects of winter gales eliminated by the methods of partial regression.

It may of course be that this negative correlation is merely a reflexion of the generally increased storminess in winter over the Atlantic Ocean, which may raise the level of atmospheric sea salt even on days without local high winds in the Lake District. On the other hand, the greater degree of evaporation over the North Atlantic in winter (Jacobs 1951) may also be concerned, since by vaporizing the water accompanying sea salt in the entrainment of sea spray droplets into the atmosphere, the droplets are made lighter and hence less likely to fall back into the sea. It is tempting to see the zone of maximum evaporation, located where cold dry air from America blows over the warm Gulf Stream between latitudes 35° and 40° N. and longitudes 60° and 65° W., as a major centre for the production of at least those chloride particles small enough to drift long distances with the wind. That oceanic particles may in fact penetrate in appreciable numbers far into even the larger land masses has been shown by the investigations of Twomey (1954, 1955), Junge (1956) and Byers (1957).

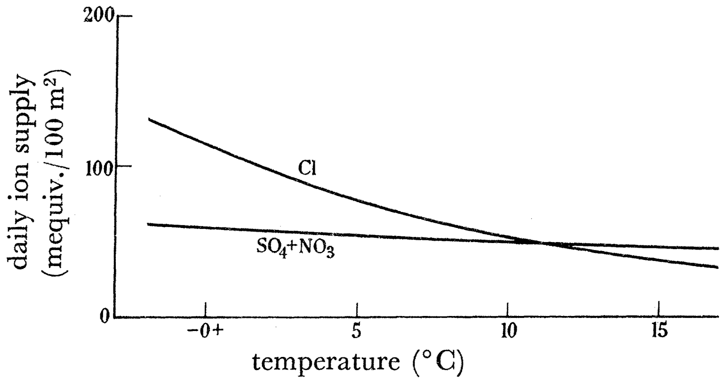

FIGURE 7. The daily supply of chloride and of sulphate plus nitrate in relation to temperature (daily max. + min./2).

The supply of other ions in relation to the supply of either sulphate plus nitrate or chloride

Throughout the present study sulphate and nitrate have been treated together, owing to exigencies of the analytical techniques employed. Fortunately the correlation between supplies of these two ions is close (r for 126 samples $= 0{\cdot}83$, in this as in subsequent cases based upon logarithmic transformations). In the samples analyzed, nitrate amounts on the average to just under 10 % of sulphate. Moreover, the regression of nitrate upon sulphate plus nitrate, shown in figure 8, is approximately linear ($b = 1{\cdot}03$, again for logarithmic values). It therefore appears inescapable that air pollution is responsible for a great deal of the nitrate brought down by precipitation in the Lake District.

In confirmation of this view, the eighteen samples showing least pollution, with chloride making up more than 80 % of total anions, are uniformly low in nitrate. The average concentration is 0·0035 mequiv./l., and no sample exceeds twice this figure. Nor is there among these samples any apparent correlation of nitrate with other ions analyzed. Similar low nitrate values have been recorded recently from the presumably rather little polluted atmosphere of western Ireland (Gorham 1957*a*). Junge (1956) has, however, expressed the view that cities and industrial areas are not great sources of nitrate. Nevertheless, it may be that nitrates do not enter the air of cities as such, but as other oxides of nitrogen, or alternatively they may derive from ammonia in air pollution by oxidation in the atmosphere, perhaps photochemically as has sometimes been suggested.

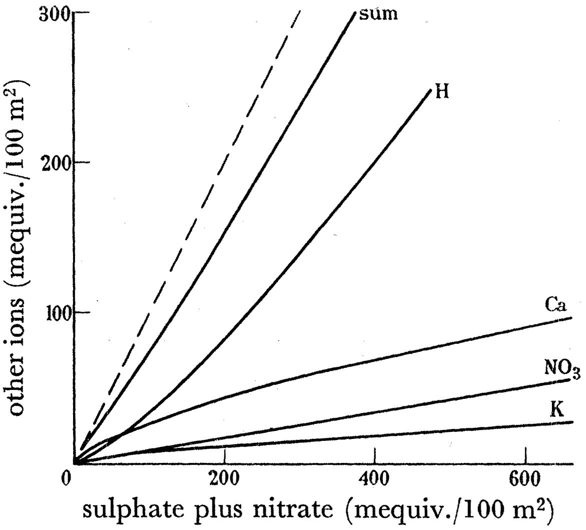

FIGURE 8. The daily supply of hydrogen, calcium, potassium and nitrate ions in relation to that of sulphate plus nitrate. (Dashed line shows equivalent proportions.)

TABLE 6. STATISTICS FOR THE DAILY SUPPLY OF THE OTHER IONS ANALYZED, AND FOR THE SUPPLY OF CHLORIDE OR SULPHATE PLUS NITRATE IN THE SAME SAMPLES*

number of daily samples …	126		157		116		152		166	
	nitrate	sulphate	hydrogen ion	sulphate plus nitrate	calcium	sulphate plus nitrate	potassium	sulphate plus nitrate	sodium	chloride
	(log$_{10}$ mequiv./100 m^2)									
range	$\bar{1}$·6 to 1·9	—	$\bar{2}$·3 to 2·4	—	0·5 to 2·3	—	$\bar{1}$·4 to 2·0	—	0·1 to 3·2	—
mean	0·81	1·87	1·23	1·77	1·38	1·94	0·66	1·76	1·71	1·78
S.D.	0·51	0·41	0·78	0·52	0·38	0·42	0·47	0·52	0·58	0·60

* These figures are given merely as a complement to the subsequent regression and correlation analyses. They do not represent annual averages, since the smaller rainfalls could not be analyzed for all these ions.

TABLE 7. CORRELATION AND REGRESSION COEFFICIENTS FOR THE SUPPLY OF OTHER IONS IN RELATION TO SUPPLY OF SULPHATE PLUS NITRATE OR OF CHLORIDE

y	x	correlation coefficient	regression coefficient
(log$_{10}$ mequiv./100 m^2)		r_{yx}	b_{yx}
nitrate	sulphate	0·83	1·03
hydrogen ions	sulphate + nitrate	0·85	1·29
calcium	sulphate + nitrate	0·77	0·69
potassium	sulphate + nitrate	0·80	0·72
sodium	chloride	0·97	0·93

N.B. For the minimum number of 116 samples, if r exceeds 0·18 it is significant at the 5 % level; if r exceeds 0·24 it is significant at the 1 % level.

The strongly acid nature of Lake District rain, established in an earlier study as largely due to sulphuric acid from air pollution (Gorham 1955), is confirmed by the present analyses, of which half yielded pH values of less than 4·5. 8% were below pH 4, while in contrast only 19% were above pH 5 and 4% above pH 6. The correlation between hydrogen ions and sulphate plus nitrate is high (*r* for 157 samples = 0·85) and on the (logarithmic) average hydrogen ions account for about 30% sulphate. Figure 8 shows that this percentage rises considerably with increasing sulphate supply, as is indicated by a regression coefficient in excess of unity ($b = 1{\cdot}29$). In this connexion it must be borne in mind that when little sulphate is being supplied, as with westerly winds, an appreciable part of what does come down will be of marine origin and therefore not acid. On the other hand, when there is a great influx of sulphate it is almost always the result of acid air pollution drifting in with easterly or southerly winds from the great industrial areas. Incidentally, Twomey (1953) has observed small hygroscopic nuclei which seem likely to be sulphuric acid droplets in the air near the large Australian city of Sydney. It is also evident from figure 8 that with low sulphate supply calcium ions are in excess of hydrogen ions. While undoubtedly a good deal of calcium comes from the industrial towns, since the correlation between this ion and sulphate plus nitrate is high (*r* for 116 samples = 0·77), there is probably also a small, but not insignificant supply from blown soil dust which is likely to contain some carbonate and so neutralize a part of the pollution acids, though not a large part when sulphuric acid pollution is heavy.

Incidentally, it may be remarked that in the great cities rain appears to be less acid than on Hawkshead Moor, suggesting that basic substances are liberated during fuel combustion, but fall out within a more restricted area near their point of origin than does sulphuric acid, which may of course be partly liberated in the air itself, by oxidation of sulphur compounds in drifting smoke. Of interest here is the fact that precipitation analyses from large cities (Gorham 1955, table 2) show calcium as being equivalent to 67% (mequiv.) of sulphate, whereas in the Lake District it accounts for a much smaller proportion, particularly in those precipitations supplying large quantities of the latter ion. For example, with a sulphate plus nitrate supply of 500 mequiv./100 m^2, calcium only amounts to about 17% of sulphate.

Potassium follows much the same trend as calcium in relation to sulphate plus nitrate (*r* for 152 samples = 0·80; $b = 0{\cdot}72$ as opposed to 0·69 for calcium). However, it only amounts on the average to about a quarter of calcium on an equivalent basis.

It may also be seen from figure 8, in which the dashed line marks off equivalent proportions, that the sum of hydrogen, calcium and potassium ions balances a large part of total sulphate. Presumably ammonia makes up most of the remainder; Herman & Gorham (1957) have demonstrated a correlation between this ion and sulphate in the more acid samples of Nova Scotian precipitation, while Junge (1954) has shown a similar correlation in the case of atmospheric particles in Europe and America.

For chloride it was shown previously (Gorham 1955) that both sodium and magnesium exhibit a high degree of correlation with this anion, and since the proportions closely resembled those in sea water it was evident that sea spray must be the major source of these ions. In the present instance only the former cation has been analyzed, and an exceptionally high correlation between the logarithmic values for supply of sodium and chloride is observed (r for 166 samples = 0·97). The regression is illustrated by figure 9, in which the dashed line represents the proportion between these two ions in sea water. This figure gives a very clear warning of the danger of interpreting such a logarithmic regression too rigidly at the high end of the scale, since it would appear that on days exhibiting a large fall of sea salt the *sodium/chloride* balance departs from that of sea water to a marked extent. This is in fact not true, for the 10 days with a supply of chloride greater than 500 mequiv./100 m^2 exhibit an average *sodium/chloride* ratio of 0·86, almost identical with that of sea water. These individual data are also shown on figure 9, as small dots which follow the dashed seawater line very closely. The explanation of the above discrepancy is that in spite of a very high degree of correlation the relationship between chloride and sodium is actually a trifle curvilinear, with a number of the samples at the low end of the range giving *sodium/chloride* ratios above that of sea water, and several of the intermediate samples low ratios, with the result that the few samples representing exceptionally heavy chloride supply are outweighed in the logarithmic regression analysis. These variations in *sodium/chloride* balance will be dealt with in the next section.

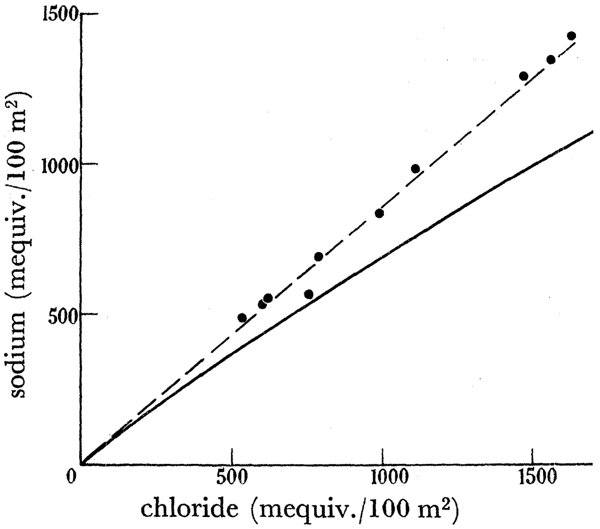

FIGURE 9. The daily supply of sodium in relation to that of chloride. (Dashed line shows seawater proportion, dots show ten highest individual values.)

The balance of sodium and chloride in Lake District precipitation

That disintegration of salt particles in the air may be responsible for variations in the *sodium/chloride* ratios of rain and snow has been suggested by Cauer (1951), and more recently by Rossby & Egnér (1955). However, the writer wishes first to examine another possibility, that an appreciable amount of chloride may be liberated by fuel combustion, partly as sodium chloride but also in other forms and probably as hydrochloric acid. According to Meetham (1950) British coals contain about one-fifth as much chlorine as sulphur, and chloride is certainly much more plentiful in precipitation over the larger British cities than would be expected from their geographical situation (cf. Gorham 1955, table 2), so it seems reasonable to suppose that such a chloride source exists.

It remains, however, to establish how far this chloride is balanced by sodium, and hence indistinguishable from sea salt. To examine this matter a series of five samples of smoke solids recovered from London chimneys (supplied through the courtesy of Dr E. T. Wilkins of the Fuel Research Station there) were investigated. The technique adopted involved suspension in distilled water at 1:100 dilution by weight, rapid shaking in a machine for 6 h, and subsequent occasional shaking by hand over a period of 2 months, after which the liquid was filtered off and analyzed. The results are presented in table 8, and show *sodium/chloride* ratios very much lower than that of sea water (average = 0·47 as against 0·85 in the sea), or in other words, considerable 'excess chloride'.

TABLE 8. SOLUBLE MATERIALS IN SMOKE SOLIDS

sample	source	optical density* ($\log_{10} I_0/I$)	pH before aeration	pH after aeration	sodium (mequiv./g dry weight)	potassium (mequiv./g dry weight)	calcium (mequiv./g dry weight)	magnesium (mequiv./g dry weight)	chloride (mequiv./g dry weight)	sulphate (mequiv./g dry weight)	nitrate (mequiv./g dry weight)
A	brush type cleaner, Fuel Research Station, London, 1952	0·65	6·7	7·2	0·22	0·12	0·97	0·03	0·5	1·8	0·01
B	brush type filter, Palace of Westminster, 1956	0·61	6·7	7·5	0·58	0·10	1·54	0·17	1·1	1·9	0·01
C	filter at Royal Festival Hall, 1952	0·55	5·1	5·0	0·29	0·10	2·20	< 0·01	0·6	2·5	0·02
D	electrostatic precipitator, Palace of Westminster, 1954	0·36	5·3	5·6	0·06	0·02	0·25	0·03	0·1	0·4	0·01
E	baffle type cleaner, supplied by Ministry of Works, 1956	0·55	6·8	7·0	0·47	0·14	1·82	0·10	1·5	1·9	0·12
	average	0·54	5·6	5·6	0·32	0·10	1·36	0·07	0·76	1·70	0·03

* Measured with Unicam SP500 spectrophotometer, in 1 cm glass cells at 320 mμ, in order to provide a rough estimate of dissolved organic matter (cf. Gorham 1957*b*).

It is interesting that these smoke samples yield proportionally more sulphate and less chloride than the city rains mentioned above. Also noteworthy is the fact that in these smoke extracts nitrate amounts to only about 2% of sulphate, as opposed to about 10% in Lake District rain. These facts suggest that of the acid anions liberated by fuel combustion sulphate is the least volatile and most easily trapped in air filters. However, once escaped from the chimneys it seems likely that sulphate is less easily precipated than chloride, as appears from further examination of rain in the larger British cities. Their precipitation shows average sulphate and chloride concentrations of 0·43 and 0·31 mequiv./l., respectively, and even if all the sulphate were assumed to derive originally from coal it would entail a chloride contribution from this source of only about 0·04 mequiv./l., leaving 0·27 mequiv./l. to be supplied by sea spray. Since this is about twice the concentration of chloride in rain on Hawkshead Moor, a place much more exposed to sea spray than the majority of the cities from which the above data come, it seems reasonable to conclude that a much larger proportion of coal chloride than of coal sulphate falls out near its point of origin.

The observation that sulphate is trapped in filters to a greater extent than chloride, while not so quickly brought down once out of the chimney, suggests that a good deal more of it than of chloride may be intimately associated with smoke particles, perhaps partly in the form of either sulphide or of sulphur dioxide absorbed by the smoke. These particles, while easily trapped by filters, would presumably be rather resistant to capture by raindrops, owing to their non-hygroscopic nature (which was very evident in preparing the extracts). They may thus drift long distances before being precipitated, during which time associated sulphur compounds can presumably become oxidized to sulphate, much of it in the form of sulphuric acid. Chloride particles, on the other hand, might be expected to form or be captured by raindrops rather easily, owing to their hygroscopic properties, and gaseous hydrogen chloride would likewise be easily dissolved.

A final point to note about these smoke extracts is that calcium ions are more, and hydrogen ions much less, abundant in relation to sulphate than in both city and country rains. These facts are in line with the earlier argument that basic substances in air pollution are more easily and quickly precipitated than the acidic ones.

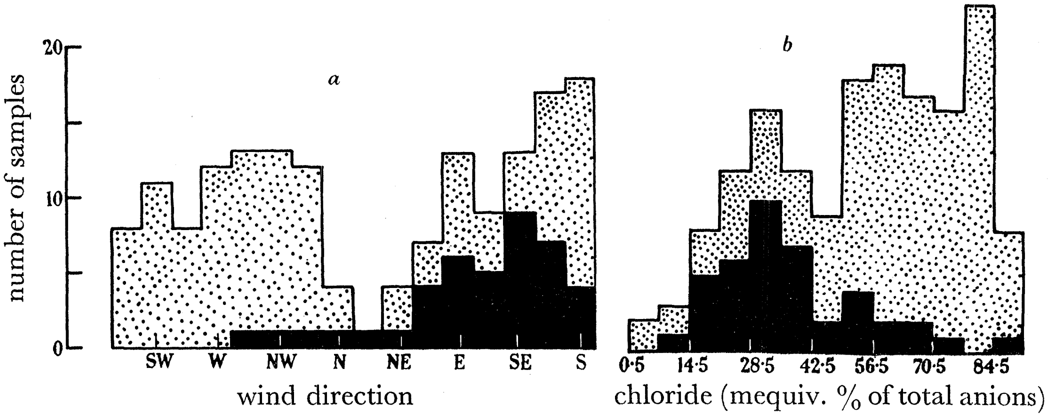

Figure 10. Frequency distributions of (*a*) wind direction and (*b*) chloride as a percentage of total anions, for all samples (stippled areas) and for samples with 'excess chloride' (solid areas).

Next the Lake District precipitations must be examined for chloride which cannot be ascribed with certainty to sea spray, that is, examples must be sought in which the *sodium/chloride* ratio is distinctly less than 0·85. In practice it was decided to separate those samples for which this ratio fell below 0·8, and for which the 'excess chloride' also amounted to more than 0·004 mequiv./l. Data for some forty-two samples were segregated in this way, when it became apparent that a source in atmospheric pollution was highly probable. Figure 10, which compares the frequency distributions of the 'excess chloride' samples and the whole range of samples for both wind direction (10*a*) and proportion of chloride to total anions (10*b*), provides the main evidence in support of this hypothesis. It is easily seen that the 'excess chloride' comes mostly with easterly winds, bringing predominantly acid sulphate rains in which chloride forms a relatively small proportion of total anions. As it happens, the demarcation of the two chief chemical types of precipitation, westerly chloride rains and easterly sulphate rains, is rather well illustrated in figure 10*b*, where a trough in the frequency distribution at the point of approximately equal chloride and sulphate proportions separates the two groups. The major peak on the right-hand side of the chloride rain type marks a series of winter gales from the sea, but even these do not appear to bring pure sea spray, in which chloride accounts for about 90 % of total anions.

A last point to be remarked about the possibility of chlorides in air pollution is that Junge (1956) has provided some evidence for the view that there are two kinds of chloride particles in the atmosphere, viz. larger ones derived from sea spray, and smaller ones of continental origin. However, his tests so far indicate that the smaller particles have an excess of sodium, and so cannot be postulated as the source of 'excess chloride' in the present instance.

In searching among the Lake District data for 'excess chloride' rains, some thirty samples were found exhibiting 'excess sodium' values, the criteria here being *sodium/chloride* ratios of at least 0·95 together with a sodium excess of not less than 0·006 mequiv./l. The chief characteristic of this group is that the majority of the samples were collected from fairly small showers when only a few millimetres of rain fell (see figure 11). They covered the whole range of wind directions, but westerlies predominated, presumably because the tendency for 'excess chloride' to come from easterly directions acts as a counterbalance to 'excess sodium' coming from the same points of the compass. Wind speeds were a little below normal, averaging 18 instead of 22 km/h.

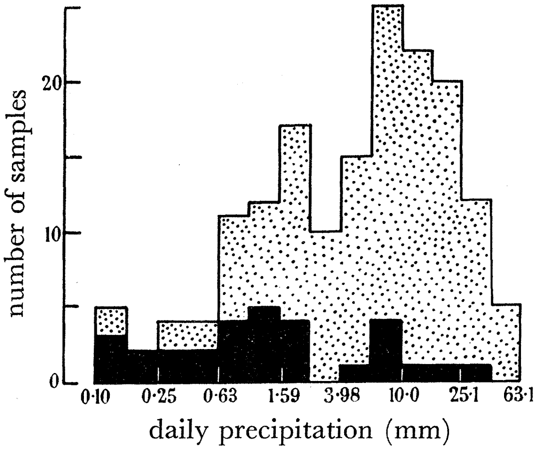

FIGURE 11. Frequency distribution of daily precipitations for all samples (stippled areas) and for samples with 'excess sodium' (solid areas).

As to other chemical properties, the main distinguishing feature of these 'excess sodium' precipitations was their generally higher-than-average pH, although sulphate was not particularly low. No 'excess sodium' was recorded in any of the twelve samples with pH below 4, and the median pH was about 4·8 in contrast to 4·4 for the whole group of samples. Moreover, six of the seven least-acid samples, with pH greater than 5·7 (incidentally the pH of distilled water in equilibrium with atmospheric carbon dioxide) yielded 'excess sodium'.

To account for these thirty samples, the writer was first inclined to invoke wind-borne rock or soil dust (cf. Kalle 1953/4). Rocks usually contain sodium greatly in excess of chlorine, and an example of this may be seen in table 9, which provides analyses of a stream flowing through crushed slate from a quarry in the Langdale valley. Here the *sodium/chloride* ratio is 1·2, a good deal higher than that of sea water. Another point seemingly in favour of a dust origin is the fact that, in an 8-month comparison of the present 'ground' sampler (about 0·5 m above the soil surface) with a 'tower' sampler on top of a nearby forestry tower (about 20 m above ground), some fifteen out of the twenty 'excess sodium' precipitations collected were found to come from the sampler near the ground.

It is also worth mention in connexion with this problem, that in Florida, Junge (1956) has found an increase in the *sodium/chloride* ratio of the larger maritime air particles over that of sea water when the breeze blows from the land (ratio with sea breeze = 0·83, with land breeze = 1·05).

One difficulty in the way of the dust theory, however, is the absence of appreciable 'excess sodium' in the lakes of the district, as may be seen from figures 12 and 13. This suggests that not much sodium is released from weathered soil materials. However, there is a possibility of some supply of fresh rock dust from either a small quarry a few hundred metres away from the rain sampler, or from local dumps of crushed gravel used for road repairs. Even so there may be objections, since most rocks in the area, though not limestones, are rather rich in calcium (cf. table 9), while the few 'excess sodium' samples large enough to be analyzed are not notably rich in this element.

TABLE 9. IONIC COMPOSITION OF WATER FROM A STREAM LEACHING POWDERED SLATE

cations	concentration (mequiv./l.)	anions	concentration (mequiv./l.)
sodium	0·37	chloride	0·32
potassium	0·09	sulphate plus nitrate	0·45
calcium	1·85	bicarbonate	2·09
magnesium	0·55		

pH = 8·0.

Another factor which occurred to the writer as possibly affecting *sodium/chloride* ratios was insect contamination, which led to rejection of a few rain analyses during the year. On extracting a mass of freshly caught chironomids with distilled water for several days a ratio of about three was in fact observed, but such contamination seems unlikely to be of any importance owing to the enormous ammonia and pH values in the extract, making it impossible to mistake a sample contaminated badly enough to alter its *sodium/chloride* ratio appreciably. The following cation and anion proportions were recorded from this extract (as mequiv. %): ammonia 89, sodium 5, potassium 6, calcium and magnesium 0, hydrogen ions 0 (pH 7·9); alkalinity 91, sulphate 3, chloride 2, nitrate 1, phosphate 3.

Since the dust theory of 'excess sodium' supply does not seem to be securely founded, though by no means disproved, the hypothesis of atmospheric separation of sodium and chloride from sea salt nuclei may be re-examined. One possible mechanism was suggested to the writer by analysis of a single sample of hail, kindly collected by Miss Vera Collins at this laboratory. This hail yielded the highest *sodium/chloride* ratio so far observed in the Lake District, 6·5. The analytical data are as follows (ions as mequiv./l.): pH 4·63, sulphate plus nitrate 0·12, chloride 0·012, sodium 0·078, potassium 0·004.

The hail fell from a sudden storm in mid-afternoon of 12 July 1955, precipitation records being as follows: Ferry House laboratory 32 mm, Wraymires hatchery 3 km, west-north-west 9 mm, Huyton Hill school about midway to Ambleside 4 mm, Ambleside trace. Wind speeds were generally low, except for a sharp rise to about 45 km/h at about the time of the storm, after which fairly calm conditions returned. There was also a shift on the Ferry House wind recorder from west-south-west to north when the wind rose.

The weather during this general period was exceptionally sunny, hot and dry, 12 July being the sixth consecutive day with maximum temperature at Ambleside reaching 27° C or more, and the ninth day without rain. A belt of high pressure extended from Norway across the British Isles, and local thunderstorms were forecast for several days.

In seeking to account for the high *sodium/chloride* ratio it was conjectured that the freezing process might be concerned, and that if a mixture of sulphuric acid and sea salt nuclei were collected together in a single droplet, the concentration brought about by abstraction of moisture during ice crystallization might lead to volatilization of hydrogen chloride gas. Whether this process can operate effectively in the atmosphere has yet to be ascertained, but the possibility deserves investigation.

In an attempt to test the above hypothesis in the laboratory, the following experiment (suggested by my colleague Mr F. J. Mackereth) was performed. A mixture of 150 g of sulphuric acid and 50 g of sodium chloride was diluted to 1 l. with distilled water, making up a solution sufficiently concentrated to depress the freezing point to almost −10° C at normal temperature and pressure, and thus representing the ultimate concentration of a relatively dilute rain droplet after abstraction of moisture by freezing at about this temperature. Compressed air was then bubbled into the mixture through a fine air-breaker of sintered glass, led through a vertical column of Terylene wool, and bubbled through another air-breaker into 100 ml. of distilled water. After 2 h the distilled water was analyzed, and found to contain 0·16 mequiv./l. of hydrochloric acid with no detectable sulphate ($<$0·01 mequiv./l.) and only a trace (0·002 mequiv./l.) of sodium, which on the basis of subsequent tests may be ascribed to solution from the sintered glass in this rather acid solution. The small amount of potassium found (0·001 mequiv./l.) probably came from the same source. From this experiment it appears likely that the proposed mechanism is in fact capable of bringing about the required ionic separation and volatilization of hydrogen chloride in the atmosphere, especially as the rate of escape will no doubt be enhanced by the lower pressures at cloud levels. It may also be that evaporation of mixed droplets in warm dry air would have a similar result. The small volume of most of the 'excess sodium' samples may be significant here, presumably the escape of gaseous hydrogen chloride would be favoured in air masses of lower water content. The lower acidities of these rains, in spite of the unusually small volume of precipitation in many samples, might also be accounted for by such a separation process.

Some observations by Twomey (1954) may be considered pertinent to this problem. In sampling aerosols at high levels in subsiding air masses in Australia he found some hygroscopic particles with a solid-liquid phase transition at 91 to 93% relative humidity, which he suggested might perhaps be particles of sodium carbonate. However, his laboratory data show that sodium sulphate (a likely product of the postulated freezing mechanism) also exhibits a phase transition at this point; and he further states that he was unable to observe any response to phenolphthalein on slides exposed for long periods to both continental and maritime air, although the response was given by sodium carbonate particles of an appropriate size in the laboratory. It seems not impossible that the freezing process outlined above may have been operating in these high-level descending air masses.

Whatever the mechanisms by which these variations in *sodium/chloride* ratio are produced, differences between Scandinavia and the Lake District appear to be pronounced, and require elucidation. For Sweden it seems that in general 'excess sodium' predominates (Emanuelsson, Eriksson & Egnér 1954), whereas if all the present year's Lake District samples were added together there would be a slight 'excess' of chloride (ratio = 0·83). This contrast seems reasonable on many grounds: the latter area is much more subject to air pollution from nearby industrial centres; while the former is not only much dustier (and with rocks poorer in lime), but also has much greater extremes of climate, so that freezing and evaporation effects, if important, would be strongly accentuated. Moreover, as regards the possible importance of freezing, Rossby & Egnér (1955) state that the minimum chloride concentrations, and the maximum *sodium/chloride* ratios, are observed mainly in precipitation from arctic or polar continental air masses. Presumably whatever chloride escapes from the aerosols over Sweden is brought down elsewhere, augmenting the supply of 'excess chloride' due to pollution.

Ecological aspects of ion supply by atmospheric precipitation

The total supply of chloride, sulphate and nitrate

In comparison with other parts of the world where analyses have been made, the Lake District is interesting in that it receives rather large quantities of both chloride and sulphate; on Hawkshead Moor the estimated income for the twelve months studied was 92 kg/hectare of chloride and 24 kg/hectare of sulphate sulphur. The winter months December to February—with the heaviest rainfall and especially high winds—provided the largest amounts; in the period under review about 60% of chloride and nearly 40% of sulphate fell during these months. In the summer months June to August chloride supply was only about 4% of the total, due to the low rainfall and in particular to the calm weather then. Sulphate supply during this season did not decline to anything like the same extent, and was only a little lower than during spring and autumn, presumably because the industrial production of air pollutants is not so greatly reduced in calm weather as is the production of sea spray.

As regards nitrate, in the present instance the annual supply was a little more than 2 kg/hectare of nitrogen. This figure is not much above the median of the values compiled by Eriksson (1952), although the annual precipitation is among the highest recorded in the localities mentioned by him.

While the present investigation demonstrates the predominance of sea spray in supplying chloride, and of air pollution in supplying sulphate, it is rather difficult to assess quantitatively the contribution of either ion from each of these sources, although it might seem a comparatively simple matter, given their proportions in sea water and in coal. One difficulty is the previously mentioned likelihood that the two elements behave dissimilarly when released from coal into the air, and there is also the possibility that sodium and chloride in sea spray aerosols may separate if mixed with sulphuric acid droplets under certain conditions. Moreover, it seems from Conway's (1942) geochemical balance sheet for sulphur that a good deal of this element in rain and river waters cannot be accounted for by rock weathering, sea spray, vulcanism and fuel combustion, and he suggests that an appreciable supply may be provided by diffusion of gaseous hydrogen sulphide from the muds of the continental shelf into the atmosphere, where it becomes oxidized to sulphuric acid. In this connexion several samples of western Irish rain, presumably little polluted, yielded a concentration of about 0·035 mequiv./l. of sulphate not ascribable to sea spray (Gorham 1957*a*), while the cleanest Lake District rains sampled in 1954 (Gorham 1955, table 3) yielded about 0·02 mequiv. A similar level of about 0·02 mequiv./l. is given on subtraction of the sea spray contribution to sulphate in precipitation at Riksgränsen in northern Sweden (twelve monthly samples from December 1954 to December 1955, excluding May 1955, see Brodin (1955, 1956)); and a series of ice samples from North East Land in Spitsbergen showed a slightly lower concentration (Gorham 1958). From these data then, it seems likely that about 0·02 mequiv./l. of sulphate may come from some source other than sea spray and coal, and this concentration represents about one-quarter of the total sulphate concentration in the year's samples on Hawkshead Moor. (The rather higher level in western Ireland may perhaps be ascribed to a hydrogen sulphide—sulphate cycle between the extensive blankets of waterlogged anaerobic peat in the area and the atmosphere.)

The supply of ions to bog waters

Of all land areas, raised and blanket bog peats must be most dependent upon atmospheric precipitation for their ion supply, since their surfaces are almost if not wholly isolated from the mineral soil beneath by deep and relatively impermeable organic deposits, and the humid climate prevailing where such bogs occur prevents much capillary rise of subsoil water consequent upon strong evaporation in dry weather. This dependence may be examined in table 10, where the ionic composition of waters from some British blanket bogs is compared with that of Lake District rain analyzed in 1954. Allowing for considerable evaporation of the water in these stagnant pools, fed from spongy *Sphagnum* moss with vast surface area, rain is probably capable of producing the observed ion concentrations (cf. also Gorham 1956). The very high sodium chloride concentration in the Sutherland bog pools is clearly a result of greater exposure to storms from the sea than in the other localities. In contrast, these Scottish bog waters are much less acid and lower in sulphate than the English ones situated closer to sources of air pollution.

TABLE 10. IONIC COMPOSITION OF SOME WATERS FROM BRITISH BLANKET BOGS

location	hydrogen ion	sodium	potassium	calcium	magnesium	chloride	sulphate
	(mequiv./l.)						
Lake District rain, 1954	0·036	0·083	0·005	0·015	0·016	0·092	0·066
Druimbasbie and Strathy bogs, Sutherland*	0·03	0·60	0·02	0·03	0·09	0·67	0·11
Coom Rigg bog, Northumberland	0·13	0·23	0·01	0·05	0·09	0·26	0·23
Ringinglow bog, near Sheffield	0·58	0·23	0·005	0·35	0·15	0·37	0·96

* Data from Pearsall (1956), analyses by E.G.

Ringinglow bog is especially subject to pollution, lying very near to one of the largest industrial centres in the country. This explains the extremely high level of sulphuric acid in its waters, and also the exceptionally large concentration of calcium, far greater than in similar habitats farther removed from industrial districts. The high concentration of this cation also supports the view that it tends to fall out relatively near the pollution source.

The abundance of calcium in the water of Ringinglow bog fails, however, to counterbalance the deleterious effects of pollution upon the bog vegetation, which is notably poor in the floristic sense and has changed its character greatly within fairly recent times (Conway 1949). Whether air pollution is harmful chiefly on account of its acidity or because of other properties is at present uncertain, but it may be remarked that water from this bog gave a strong heavy-metal coloration on testing with dithizone, as did the smoke extracts when tested with this reagent. Moreover, in a few analyses of Lake District rain, Mackereth (private communication) has found as much as 130 μg/l. of zinc. Morita (1955) has also found much lower but still appreciable amounts of both zinc and copper in precipitation collected at Nagoya (Zn up to 12 μg/l., Cu up to 2·3 μg/l.), so that heavy-metal toxicity seems not inconceivable in sites receiving much atmospheric pollution.

A last point to note about the Ringinglow water is that it contains considerable 'excess chloride', with the *sodium/chloride* ratio of 0·62 lying well below that of sea water, 0·85. Such a result is of course to be expected so close to an industrial city.

The supply of ions to lake waters

For sulphate, and especially for chloride, it seems probable that atmospheric precipitation provides by far the largest part of the total amounts in natural waters of the Lake District, since most rocks are exceedingly poor in sulphur and chlorine (Rankama & Sahama 1950). It should therefore be worth while to compare the rain concentrations of these two ions with those of lake waters nearby. To enable such a comparison fourteen analyses from the two large lakes on either side of Hawkshead Moor—Coniston Water and Windermere—have been kindly made available by F. J. Mackereth and J. Heron of this laboratory. The average chloride and sulphate plus nitrate concentrations, which vary little from one sample to another within each lake, are 0·204 and 0·158 mequiv./l., respectively, while the Hawkshead Moor precipitation samples, when weighted for volume and averaged, yield concentrations of 0·142 and 0·092 mequiv./l. In order to make an approximate correction of the rain analyses for evaporation before comparison with the lake data, a factor of 1·25 has been used (cf. Penman 1950; McLean 1940). This factor increases the rain concentrations to 0·177 mequiv./l. of chloride and 0·115 mequiv./l. of sulphate plus nitrate, leaving 0·027 and 0·043 mequiv./l., or 13 and 27 % of lake chloride and sulphate plus nitrate, respectively, to be accounted for.

It may of course be that the Hawkshead Moor station is not representative of rain over the whole Coniston–Windermere drainage basin, or that the evaporation factor assumed is incorrect, so that the above differences are more apparent than real. However, there is reason to believe that some chloride may be supplied from the atmosphere apart from that falling in precipitation. In Sweden, for example, Eriksson (1955) has suggested that capture of giant sea salt particles by vegetation during dry weather may be a very important source of chlorides in river waters, these particles being washed from the plants by subsequent rain. Such a process may well supply a small part of lake chlorides even in the much more rainy Lake District. A certain amount must also come from rock weathering, but this is probably very small indeed, as chloride seldom amounts to more than a trace in Lake District rocks (see Guppy 1931, 1956).

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY B BIOLOGICAL SCIENCES

It is probable that some sulphate may also be supplied from the air during rainless periods, either through the filtering out of sulphur-bearing smoke particles by plants, or through the absorption of sulphur dioxide by moist surfaces, followed by its oxidation to sulphuric acid. Nevertheless, it must be borne in mind that certain of the rocks in the area may be quite rich in sulphur. For instance, table 9 indicates that leaching of slate may increase the *sulphate plus nitrate/chloride* ratio of streams considerably above that of rain; in this admittedly exceptional example to 1·4 as against 0·6, with the Coniston Water–Windermere ratio being about 0·8.

TABLE 11. ION CONCENTRATIONS IN TARNS AT VARYING DISTANCES FROM THE SEA

tarn	approximate distance from sea (km)	approximate altitude (m)	pH	sodium (mequiv./l.)	chloride (mequiv./l.)	sulphate (mequiv./l.)	nitrate (mequiv./l.)	bicarbonate (mequiv./l.)
Gutterby	0·1	30	7·7	1·45	1·80	0·70	0·011	0·89
Braystone	0·1	15	7·3	1·11	1·29	0·37	0·020	0·20
Barfield	2·5	20	6·0	0·37	0·44	0·19	0·022	trace
Chapel Hill	5·0	175	4·7	0·56	0·64	0·28	0·001	nil
Parkgate	7·5	105	4·6	0·41	0·44	0·23	0·002	nil
Cleator Moor	10	185	6·7	0·28	0·33	0·16	0·043	0·08
Devoke Water	10	235	6·0	0·23	0·26	0·14	0·015	0·01
Blea (Eskdale)	13	215	5·4	0·25	0·27	0·17	0·017	nil
Torver Reservoir	18	105	6·8	0·23	0·27	0·17	0·002	0·02
Little Langdale	26	105	6·7	0·16	0·20	0·12	0·017	0·06
Blea (Langdale)	29	185	5·3	0·16	0·19	0·11	0·014	nil
Tewet	32	210	6·5	0·17	0·19	0·15	0·006	0·04
Brothers Water	38	160	6·7	0·15	0·20	0·13	0·019	0·11
Little Water	45	275	7·4	0·19	0·24	0·16	0·039	0·64
Berrier End	48	275	5·6	0·17	0·20	0·11	0·006	nil
Greystoke	51	220	7·7	0·22	0·27	0·21	0·036	1·99

Since the chloride concentration and *sodium/chloride* ratio of Swedish precipitation has been shown to vary systematically with distance from the sea, particularly to the south-west (Emanuelsson, Eriksson & Egnér 1954; Rossby & Egnér 1955), it seemed worth while to look for a similar effect in the Lake District. However, owing to the absence of a precipitation network it was decided to examine the relationship in tarns instead, as these probably derive their chloride mainly from rain and would serve as an integrator for precipitation over a considerable period. A rough transect was therefore taken from south-west to north-east across the area, and sixteen tarn waters were sampled during the very wet weather of February 1957, in order to minimize evaporation effects. The analytical results are given in table 11 and illustrated in figure 12, the latter clearly showing a very sharp rise in the chloride concentrations of waters from tarns less than 10 km from the sea coast. Incidentally, the Hawkshead Moor rain collector is located at a minimum distance of about 20 km from the sea, well outside the steeper part of the coastal gradient. The curve in figure 12 has been fitted to logarithmic values of both concentration and distance by the method of least squares, the formula being $c = 0{\cdot}71d^{-0{\cdot}33}$; but it is evident that while the fit is reasonably good, there is a distinct rise of concentration in the most inland waters, of which the formula fails to take account. This rise no doubt reflects the decrease of rainfall outward from the central hills across which the transect runs. It may be pointed out that the central values approach fairly closely to the average rain chloride concentration of 0·14 mequiv./l.; the winter rain concentration would of course be higher than this owing to the prevalence of gales from the sea at this season.

As to *sodium/chloride* ratios, the Lake District tarn waters fail to show the increase inland typical of Swedish precipitation, and in fact the ratios fluctuate around that of sea water throughout, the latter being represented in figure 12 by the dashed horizontal line and the former by the vertical bars (showing the range of ratios obtainable from the duplicate determinations of each ion). Evidently almost all of the sodium as well as of the chloride in these tarn waters is derived from sea spray.

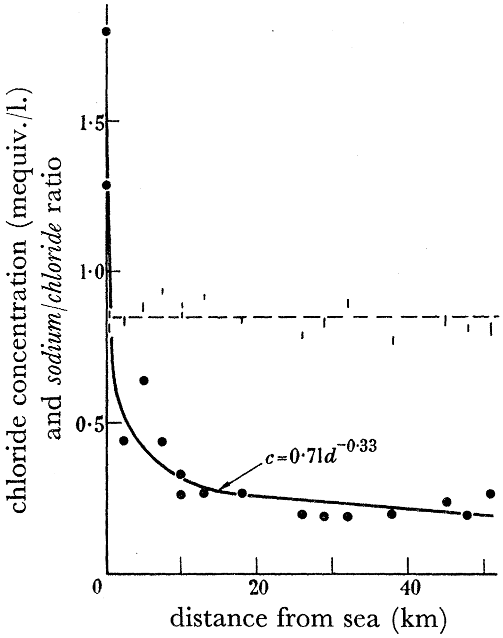

FIGURE 12. Chloride concentrations and *sodium/chloride* ratios in the waters of tarns at different distances from the sea. (Dashed line shows seawater ratio, and vertical bars the tarn ratios.)

Nitrate in these waters varies considerably, from 0·001 to 0·043 mequiv./l. The average concentration is 0·017 mequiv./l., or about 11 % of sulphate in those tarns at least 10 km from the coast. Since rain concentration is probably in the vicinity of 0·008 mequiv./l., it appears that atmospheric precipitation may play an important role in the supply of this ion, especially as some of the nitrate in the tarns with the higher concentrations may well come from oxidation of rain ammonia. In support of this view, ammonia measurements in nine of the present series of tarn waters show the concentrations of this ion to be negligible ($<0{\cdot}001$ mequiv./l.), whereas rain normally exhibits a marked excess of ammonia over nitrate (cf. British data quoted by Eriksson 1952). The two most acid waters, exhibiting pH values of 4·6 and 4·7, come from tarns with rather boggy margins, and yield the lowest nitrate concentrations. Since these are well below normal rain levels there may be an active removal or transformation of nitrate in such waters. This ion is known to be scarce in similarly acid bog pools (cf. Gorham 1956).

A last point deserving notice in table 11 is the occurrence of alkaline pH values and high bicarbonate concentrations at either end of the transect. These are associated with the presence of softer and more easily weathered sedimentary rocks of the Carboniferous and Triassic periods around the periphery of the Lake District.

Having examined the origin of chloride and sulphate in lake waters, the atmospheric contributions of other major dissolved ions remain to be considered. The extensive analytical data presented by Mackereth (1957) provide excellent material for this purpose, since he has given a detailed picture of the way in which ionic proportions in the waters of Lake District tarns and lakes alter in passing from the dilute upland tarns on the central volcanic massif through rather more concentrated waters in tarns and lakes on Silurian slates and flags to the tarn waters richest in salts on soft sedimentary Carboniferous and Triassic substrata around the margins of the district. From these data the concentrations of the various ions can be calculated in relation to chloride for successively richer groups of waters; and by assuming—without too much error—that only negligible amounts of chloride come from sources other than precipitation, and that inconsiderable quantities are bound by soils and vegetation, the proportions of any ion deriving from rain and from soil weathering may then be estimated. For instance, if a group of waters shows 86 parts of sulphate for every 100 parts of chloride, while rain shows only 64 parts, then the rain contribution of sulphate to this group of waters is 75 %. It will of course be evident that such calculations can yield only rather approximate results, since the present rain data cannot be assumed representative for the whole Lake District. Nevertheless, since the Hawkshead Moor collector is fairly centrally located, it is believed that the broad conclusions to be drawn from such calculations will not be invalidated by the deficiencies of the rain data.

On this basis figure 13 has been constructed, illustrating the different proportions of ions supplied by rain in the poorer and richer lake waters. (For the rain data, both 1954 and 1955 analyses have been used for sodium, potassium and sulphate, while only the 1954 data have been used for calcium and magnesium, since only the larger rainfalls were analyzed for calcium in 1955, and no magnesium determinations were made then.) Of the 222 waters analyzed by Mackereth, about one-seventh contain less than 0·2 mequiv./l. of total salts, almost half have less than 0·4 mequiv./l., and only about one-fifth contain more than 1 mequiv./l. At the top of figure 13 a rough indication is given of the transitions between the geological substrata, though there is naturally a good deal of overlapping between groups.

The picture presented is most interesting. It appears once again that almost the whole of the sodium in these waters is of marine origin and falls in rain, with no evident contribution from weathering of aluminosilicates in the soils. On the other hand, while in the more dilute waters most of the potassium also comes from rain, there is a steady decrease in the proportion from this source as total salt concentration rises, until in the richest peripheral tarns only about one-sixth of the potassium is supplied from precipitation. In this connexion it has been shown previously that waters on Triassic substrata elsewhere in Britain are rich in this element (Gorham 1957*c*).

As regards sulphate the general trend is similar to that of potassium, except that in the richest waters the proportion derived from rain remains a good deal higher, at about 50 %. The fact that the proportion of sulphate derived from rain is considerably higher in the dilute upland tarns than in Coniston Water and Windermere might be taken to indicate that atmospheric sulphate supply to the latter, apart from what falls in rain, is inconsiderable. However, a possibility to be borne in mind is that the extensive surfaces provided by woodland vegetation at lower levels may be of much importance in filtering soot or absorbing gaseous sulphur dioxide. The upland tarns whose sulphate appears to come almost wholly from rain lie mostly in rocky basins with rather sparse vegetation cover.

The divalent cations magnesium and calcium behave very differently from the other ions. Although in the most dilute groups of tarn waters about 85 % of the former ion and 57 % of the latter comes from precipitation, the proportions fall sharply as total salt concentration rises, gradually levelling off so that in the richest group of tarn waters only about 14% of magnesium and 3% of calcium derive from this source. The initial rapid decline mentioned above is owing to the fact that the chief products of soil weathering in this area are bicarbonates of magnesium and especially of calcium, as may be seen from the analysis of a stream flowing through powdered slate in a Langdale quarry (table 9). These ions predominate strongly in the richer lake waters, particularly in those of the peripheral tarns on soft Carboniferous and Triassic substrata. In this connexion it should also be noted that only the more dilute waters exhibit appreciable hydrogen-ion concentrations; above a total salt concentration of 0·4 mequiv./l. hydrogen ions are seldom more than 1 % of total cations.

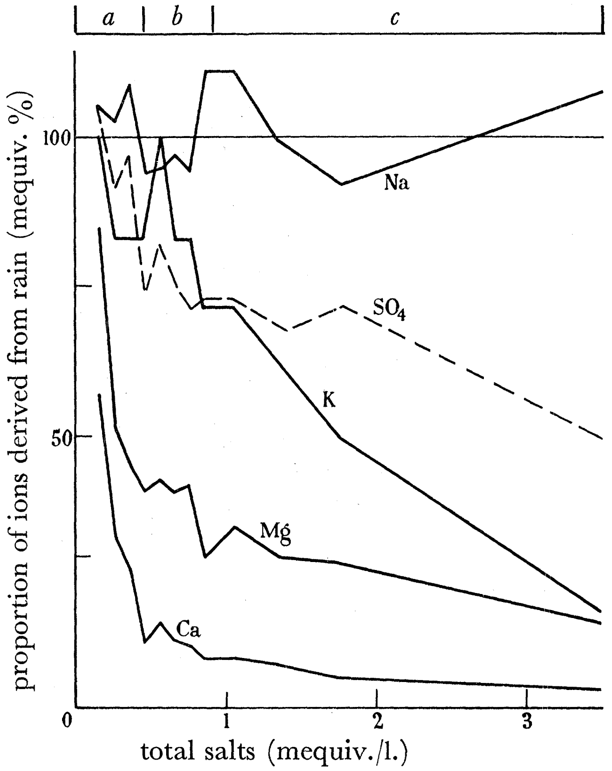

FIGURE 13. The proportions of ions derived from rain in tarn and lake waters of different salt content, on various geological substrata. (*a*) Upland tarns on hard volcanic rocks, (*b*) upland and lowland tarns and lakes on Silurian slates and flags, and (*c*) lowland tarns on softer sedimentary rocks of the Carboniferous and Triassic periods.

Although the tarns on the hard volcanic rocks of the central hills are poor in calcium, this does not reflect exceptionally low concentrations of this element in such rocks, indeed the Borrowdale volcanics contain quite large amounts of lime and other bases, as is evident from the analyses compiled by Guppy (1931, 1956). It therefore seems that the resistant nature of these hard rocks, which weather with great difficulty, is responsible for the low ionic concentrations in waters of the central upland tarns. It is interesting to remark here that the ecological importance of such a primary division of the English Lakes into rocky and silted types was long ago pointed out by Pearsall (1921, 1929).

While the peripheral tarns are very much richer in calcium and magnesium bicarbonates than the central ones, it should also be noted that they are a good deal richer in chloride as well. There is, for instance, a fivefold increase of chloride in passing from the most dilute to the most concentrated of the lake groups averaged by Mackereth. If all this chloride comes from rain, various factors connected with the moisture régime must be invoked to account for the above-mentioned increase. Figure 12 suggests that owing to its greater volume the rain in the central hills may be more dilute than that falling on the edges of the Lake District. Evaporation will also account for a much smaller part of total rainfall in the central hills than on the periphery, where rainfall is much lower, temperature presumably somewhat higher, soils deeper and vegetation cover more complete. Tarn waters in the uplands must be replaced by fresh inflow in a much shorter time than are the waters of tarns on the flat lands around the hills, where drainage is sluggish and many tarns have only negligible inflow and outflow streams, at least in summer. All in all, such differences may well be responsible for most of the increase in chloride concentration observed in the peripheral tarns, though it is also possible that a few high values for waters very near the sea may enhance evaporation effects in the richest tarns. In such conditions the rain contribution to other ions will be overestimated, but it is unlikely that the general picture given in figure 13 will be much altered, since there are so few tarns inside the steep part of the coastal chloride gradient shown in figure 12.

The supply of ions to the soil solution

When atmospheric ion supply proved to be of much importance in lake waters, the question arose of whether it might also provide an appreciable part of the ions dissolved in the interstitial water of the soil. Accordingly, this water was expressed under a pressure of about 100 kg/cm^2 from ten surface samples of oakwood soil, chosen to represent the very different types of humus layer which characterize the two extremes of the range of soils found in the area. Thus, five samples represent almost wholly organic *mor* humus layers from heavily leached knolls, and the other five are typical of the much less organic *mull* humus layers found in sites which are flushed by moving water percolating through the mineral soil (see Gorham 1953). The results of the analyses (which for calcium and magnesium involved gentle ignition of the evaporated samples, and for the latter also complexing of interfering heavy metals) are given in table 12.

It is evident that there are great differences between the two soil types. The heavily leached soils have strongly acid waters low in calcium and very low in nitrate; while the waters from the flushed soils are only faintly acid, with an appreciable proportion of bicarbonate, and are high in both calcium and nitrate. Judging from optical densities (cf. Gorham 1957*b*) the *mor* waters also contain far more dissolved organic matter than the *mulls*, in line with the greater humus content of the *mor* soils. They also exhibit a distinct excess (7 %) of cations over anions, which would be even greater if ammonia were included with the cations. Presumably these excess cations are balanced by organic anions of some kind.

The slight acidity of the *mull* waters appears to be due largely to carbon dioxide, since there is a considerable rise of pH (in three instances to above 7) upon aeration. The less acid of the *mors* also show a much less marked rise. The pH values of the fresh soils, measured by pressing them directly around a glass electrode without dilution, are on the other hand a good deal lower than those of the expressed soil solutions, owing presumably to contact between the electrode and the swarms of hydrogen ions adsorbed upon the soil colloids.

TABLE 12. THE IONIC COMPOSITION OF THE SOIL SOLUTION IN OAKWOODS ON CONISTON GRITS AND FLAGS

	pH												
	fresh soil	water before aeration	water after aeration	optical density* log (I_0/I) at 320 mμ	hydrogen	sodium	potassium	calcium	magnesium	bicarbonate	chloride	sulphate	nitrate
					(mequiv./l.)								
mors	3·52	3·87	3·89	1·15	0·14	0·64	0·21	0·05	0·13	nil	0·57	0·53	0·01 in mixed sample
	3·44	4·11	4·09	1·39	0·08	0·24	0·08	0·05	0·04	nil	0·15	0·29	
	3·40	4·28	4·30	0·96	0·05	0·28	0·11	0·05	0·05	nil	0·18	0·31	
	3·49	4·46	4·54	0·28	0·04	0·40	0·11	0·03	0·07	nil	0·35	0·28	
	3·28	4·64	4·76	1·32	0·02	0·45	0·23	0·09	0·07	nil	0·37	0·41	
mulls	4·64	5·86	6·5	0·08	—	0·28	0·10	0·26	0·13	0·03	0·21	0·23	0·32
	5·26	6·04	6·6	0·04	—	0·60	0·07	0·73	0·18	0·08	0·23	0·22	1·07
	5·44	6·24	7·1	0·25	—	0·27	0·20	0·63	0·14	0·21	0·21	0·15	0·63
	5·68	6·54	7·3	0·19	—	0·43	0·11	0·45	0·09	0·20	0·23	0·25	0·34
	5·38	6·55	7·1	0·14	—	0·31	0·08	0·42	0·10	0·14	0·19	0·15	0·43

* Measured as stated in table 8.

TABLE 13. THE RAIN CONTRIBUTION TO OAKWOOD SOIL SOLUTIONS AND TO LAKE WATERS OF SIMILAR CHLORIDE CONCENTRATION (ASSUMING ALL CHLORIDE TO COME FROM THIS SOURCE)

	sum of cations (mequiv./l.)	hydrogen	sodium	potassium	calcium	magnesium	sulphate
		(rain contribution as % of total supply)					
mors	0·74	157*	73	13	100	71	58
mulls	1·12	very high**	50	9	8	31	70
lake waters	0·55	very high	100	100	13	38	82
	1·05	very high	116	71	8	30	73

* 36 % of rain acids neutralized in *mors*.
** 99 % of rain acids neutralized in *mulls*.

As regards the rain contribution to dissolved ions, table 13 compares the figures for *mor* and *mull* waters (calculated as for figure 13) with those for lake waters of similar chloride concentration (data again from Mackereth 1957). The most striking feature of this table is the evidence it provides for a net loss of rain acids even in the strongly acid soil solutions of the *mor* humus layers, which owing to strong evaporation may yet be considerably more acid (on the average) than rain. This loss amounts in these *mors* to about one-third of the rain hydrogen ions. Presumably even in such highly organic soils there is sufficient base, either from weathered soil minerals or as ammonia from decaying organic matter, to neutralize some of the sulphuric acid brought down from the atmosphere (and perhaps also some produced by breakdown of organic sulphur compounds, since there is a good deal of sulphate in the *mor* waters that cannot be accounted for by rain, more even than in the waters of the less organic *mulls*).

Another interesting point in table 13 is the low proportion of potassium supplied by rain to the soil waters, in contrast to the high proportion from this source in comparable lake waters. Since potassium is commonly the most abundant of the alkali and alkaline earth metals in plant leaves, no doubt vegetable decay is the source of much of this element in the soil solution. As a univalent cation it will be much less strongly adsorbed by soil colloids than will the divalent ions calcium and magnesium, while the other univalent cation sodium is not nearly so abundant in most plant tissues, and is on the other hand much more plentiful than potassium in rain. It might of course be thought that much of this potassium comes from living organisms destroyed by the heavy pressure, and is not present in the actual soil solution; however, Troedsson (1955) has shown that not only expressed waters, but also the soil solutions seeping into lysimeters, are unusually rich in this element.

It further appears from table 13 that in the *mor* waters most of the calcium, magnesium and sodium comes from rain, although almost three-tenths of the magnesium and sodium come from other sources. In the *mulls* on the other hand only about half the sodium, three-tenths of the magnesium, and one-twelfth of the calcium appears to come from rain. As in the lake waters, calcium seems to be the main product of soil weathering. Unlike the lake waters, however, there is considerable weathering of sodium into the soil solution, which is of course in much more intimate contact with finely divided mineral particles than is much of the water reaching the lakes.

Nitrate in the *mor* waters is not much different in concentration from that in rain, while in the *mull* waters it is exceptionally high (0·3 to 1·1 mequiv./l.) and indeed accounts for about half of total anions. Probably this ion is at its maximum level, just prior to the start of a new growing season. In this connexion it may also be remarked that the *mull* soils bear a much more open ground flora than do the *mors*, so that soil ammonia concentrations will doubtless be more easily built up to the point where bacterial nitrification can proceed.

From the foregoing paragraphs it will be seen that the soil solution is by no means in equilibrium with the rain, nor with the lake waters which represent the ultimate composition of the rainwater leachate. As Troedsson (1955) has shown, most of the rain percolates rather rapidly through cracks and crevices, along root channels and the edges of stones, etc., without coming into nearly such intimate contact with the soil particles as does that small fraction held as soil solution and expressed by pressure. It would thus seem that aquatic organisms inhabit a medium of very different ionic composition from that bathing organisms in woodland soils around the lakes.

CONCLUDING REMARKS

From the data presented here it seems clear that local weather conditions play a very large part in determining the atmospheric supply of ions to natural waters in the Lake District. It is likewise evident that atmospheric precipitation is of the utmost importance as a source of many of the major dissolved ions, especially to bogs, to upland tarns on hard volcanic rocks, and to heavily leached soils with *mor* humus layers.

The dissolved ions in rain must therefore have considerable ecological significance, though little is known of this at present. On the one hand, appreciable amounts of plant nutrients, for example nitrogen, potassium, calcium and sulphur (and perhaps certain heavy metals), are supplied to habitats deficient in these elements; but on the other hand sulphuric acid, and probably also some of the organic compounds in smoke, may be toxic to many plants (as might also heavy metals in high concentration). In addition the large amounts of sulphuric acid provided by pollution of the atmosphere will presumably hasten deterioration of the already heavily leached Lake District soils.

Whether the effects of the industrial age upon air chemistry have as yet seriously influenced the ecology of the Lake District is difficult to say, but such influence might best be sought in the high tarns, since they are the most dependent upon rain for nutrients, and other factors such as local sewage pollution, agriculture, forestry operations, etc., could be discounted. Examination of mud cores for microfossils would no doubt throw much light upon the problem. Bog and moorland peat profiles might also repay investigation, since Mattson & Koutler-Andersson (1954) suggest that peat accumulation in Sweden may have been accelerated in recent times owing to combustion of fossil fuels and an increase in wind-blown dust from agricultural operations. But while there are regrettably few undisturbed peat deposits in the Lake District nowadays, there are fortunately a great many tarns in the central hills where mud cores might easily be taken with the aid of light instruments developed in recent years, and it is hoped that these matters will receive some attention in the future.

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