UNIVERSITY OF LONDON

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY

DEPARTMENT OF MATHEMATICS

The Atmospheric Transport of Natural and Man-made Substances

by

Mark Pryde Paterson

Submitted for the degree of Doctor of Philosophy

April 1975

ABSTRACT The atmospheric transport of natural and man-made substances.

Some aspects of the atmospheric transport of particles have been inferred from data on the chemistry of precipitation (rain and snow) collected in Europe and the islands of the northeast Atlantic. Bad data from some regions had to be identified and excluded from further analysis.

An analysis of the coherence of patterns in the amounts of magnesium, calcium, sodium and potassium in precipitation indicates that the northern and southern highlands of Norway shield large areas of the east slope from sea salt aerosol and enhance the washout of calcium aerosol from continental airmasses. The central saddle region of Sweden is not sheltered from sea salt aerosol. The high degree of coherence between north and south indicates that much of the magnesium and calcium aerosol travels long distances.

A comparison of island and inland data on sodium suggests the existence of an oceanic plateau and a continental floor in sea salt concentration in air with a difference in northwest Europe of at least a factor of thirty five. So large a difference cannot be explained by Junge's theory of increased vertical mixing over the continent. Calcium aerosol of land origin is well mixed in the atmosphere and is present over the North Atlantic in at least one quarter of the concentration present in air over Scandanavia. The atmospheric residence time of such continental aerosol is considerably greater than that of sea salt and much of it is thought to come from North America.

The apparent deviations in aerosol at coastal sites from the sea salt ratio of chlorine to sodium are mostly, if not totally, due to errors in measurement rather than to the "Cauer process" of aerosol dissociation. Some of the chlorine in German and Austrian precipitation seems to be from a land source but the suggestion that it arises from coal burning is not completely satisfactory. Most of the sodium and chlorine in rain samples in the interior of Australia comes from dry salt lakes.

In deciding the reliability of data and understanding the action of the atmosphere which it reveals the degree of order in the data is an important consideration. Where the order is an artefact of the monitoring system an independent set of measurements is needed to show up the effect. Where the order results from orderly behaviour of the atmosphere a single set of good measurements tells all.

It is concluded that the precipitation sampling by the European Air Chemistry Network suffers various defects and a basic re-examination of the project is now required. Small regional laboratories encounter special problems which have invalidated much of the data collected in the past twenty years. Defects in the operation of the largest laboratories could not have been discerned without the contribution of the smaller laboratories.

FOREWORD

For reasons which are to be found in the text of this thesis there is less reference to the literature than is customary. The basic works in this field of precipitation chemistry have been reported by later authors in such a way that a complete survey of the literature would amount to an opinion poll. This thesis questions the factual foundation of some of those basic references and re-evaluates the slim evidence on which some of them were based. If I have overlooked work which covers this ground I do apologise to the authors so treated.

The text is typed in Letter Gothic at one and a half spacing and a pitch of twelve per inch. The final copy has been made at a linear reduction of 15% on a Rank-Xerox Series 7000 copier. Tables and figures are printed on even-numbered pages opposite the relevant text whereever possible. One consequence of this is a number of blank pages which must be numbered in sequence with the pages of text and figures in accordance with the University of London regulations on the format of theses. By comparison with the traditional form of thesis there is a saving in paper of sixty percent, in the cost of copying of forty percent and in library shelf space and postage costs of fifty percent.

CONTENTS

Chapter 1. Introduction

The atmosphere carries many substances which are picked up from the surface of the sea and the land, from vegetation and, increasingly, from man's activities. The many factors which relate the sources, transformations in the atmosphere and the removal processes lead to each substance having its own peculiar history. Some of these have been subsumed traditionally under the definitions of elemental cycles such as the nitrogen, sulphur and carbon cycles, which presume to account for the history of the element from a nominal state, such as carbon in a living plant cell, through all the changes to its return to that state.

The true cycle is closed insofar as the atom which is at one time a part of a living plant cell stands a good chance of returning to that state in a hundred or a thousand or a million years. There are cycles in which only a small fraction of the material passes through living creatures. Calcium originates in the primitive rocks, is liberated by weathering and after a period in solution in ground water, lake, river or sea is deposited in a bed of carbonate sedimentary rock. Some of the calcium which undergoes this process is taken up by living creatures and used for life purposes, though its chances of returning a second time to the living state are rather low. Much of the calcium is deposited in oolitic limestone and other forms which have only a small fraction of material from living creatures. Where burial and re-exposure recur the cycle of calcium may be completed.

The atmosphere plays an important part in the elemental cycles for it transports and redistributes material to places where it may be caught up again in the biosphere. Carbon dioxide is removed directly from the air by growing plants which take about one hundredth of the total atmospheric content each year. As this is the larger of the two processes of removal, the other being solution in the sea, the turbulent mixing of the atmosphere lead to an almost uniform concentration of CO_2 being available to plants throughout the world. Most other elements are removed from the air more quickly than this by physical processes, among which are the washout by rain, sedimentation of particles and absorption of gases at the earth's surface. When these removal or "sink" processes are active the substance is quickly removed from the atmosphere and during its time of residence it will travel only a short distance from its origin. As it has insufficient time to mix well the atmospheric concentration varies greatly from time to time and place to place. For this reason Junge (1972) has taken the variability of atmospheric concentration to be a good indicator of the atmospheric residence time of a substance.

The elemental cycles encompass not only the natural components of the atmosphere but also the substances which are emitted by man, either deliberately as chimney or sewer emissions or inadvertently by leakage from other processes. The burning of coal and oil has generated CO_2 which has accumulated in the atmosphere to the extent of producing a ten percent rise in the atmospheric CO_2 concentration during the past seventy years. This now participates in the carbon cycle in a fashion which cannot be distinguished from the CO_2 of the natural atmosphere. Sulphur from the same fuels, emitted as SO_2, has not accumulated in the atmosphere for any SO_2, natural or man-made, is quite quickly removed from the atmosphere by one of several processes. That sulphur now participates in the natural sulphur cycle in

ways that have been variously assessed as favourable to the biosphere (Ross 1972, Johansson 1959) or damaging (Swedish case study, 1972). Since sulphur is one of several elements which in some places are in critically short supply for plant nutrition the man-made addition can improve crops and natural vegetation in some circumstances. Where the SO_2 is oxidized and hydrolyzed to produce sulphuric acid in quantities which cannot be neutralised by the local natural stocks of basic substances the acidification of waters and the direct deposition of acidic particles may be harmful.

The atmospheric branches of the various cycles range from those with the entire time spent in the gas phase, such as carbon dioxide, to those in which the entire time is spent as a solid particle, such as silicates. Nitrogen in nitrate or ammonium may have passed through the entire range of states from gaseous ammonia or NO_2 through solution in water droplets to existence as a solid particle of the salt of nitrate of ammonium. Thus there are some natural classifications under which the transport of trace substances may be discussed. Liss and Slater (1974) have considered the behaviour of soluble gases in a general form which allows the role of the sea as a source or sink to be determined from the relative concentrations in the air and in the water, taken together with some thermodynamic data. A number of workers have considered the uptake of sulphur dioxide by various surfaces so that the rate of removal from the atmosphere may be estimated from a knowledge of the chemical nature and the roughness of the surface, the concentration of SO_2 in the air some distance above the surface and the wind speed.

There is no general theory to describe the removal of particles from the air, although the role which is played by particles as condensation or ice nuclei in clouds is quite well understood. There has been little consideration of the different chemical and physical natures of real particles and how that might affect the mechanisms of removal from the air in rain and snow, the cloud physics studies being directed at ideal particles of sea salt, ammonium sulphate, silver iodide and so on. Sedimentation and impaction most effectively removes large particles close to their source and are believed to play only a minor part in removing small particles far from their source and particles which have been formed by chemical reactions between gases in the air, which are also small. At such distances the removal by rainout and by washout should be the most efficient mechanisms. In some studies the distinction between rainout, whereby the particles are incorporated in cloud droplets as they form, and washout, which is the capture of particles by falling raindrops or snowflakes, should be recognised but in the study of trace substances in rain which I will present it is not possible to distinguish between the two. The term "washout" will be used to cover the total effect of the two processes. Because of the efficiency of washout on small particles the long-range transport of particles and the part it plays in the elemental cycles is best studied by considering the chemical composition of rain and snow sampled where there are no strong local sources of the substances to dominate the sample. Some ions such as sulphate or nitrate may have entered the atmosphere in the form of their gaseous precursors. Others such as sodium or calcium must have entered the atmosphere as particles or solution droplets for they have no volatile forms. By selecting the species for study it is possible to embrace only particulate substances or else substances which have lead a varied existence in the air.

Table 1.1 Elements sampled by the European Air Chemistry Network

In precipitation		In air	
precipitation amount	millimetres/month		
sulphate (as sulphur)	mg/m^2.month	sulphate	μg/m^3
chloride	"	chloride	"
nitrate (as nitrogen)	"		
ammonium (as nitrogen)	"	ammonium	"
sodium	"	sodium	"
potassium	"	potassium	"
magnesium	"	magnesium	"
calcium	"	calcium	"
pH			
alkalinity	μequivalents/litre		
conductance	μmhos/cm		

Notes: 1 mm of rain on 1 m^2 is 1 litre of rain
1 mg/m^2 is 0.01 kg/hectare

This thesis describes a study of the chemistry of precipitation (rain and snow) samples collected throughout northwestern Europe and the islands of the northeastern Atlantic. Most of the stations are in the European Air Chemistry Network (EACN) which comprises a number of sub-sections each of which is based on an analytical laboratory. The EACN was established in 1955 to collect monthly precipitation samples and analyse them in a manner which was pioneered in the Stockholm laboratory of the International Meteorological Institute. This work was a continuation of work initiated by Professors Rossby and Egnér in 1948.

The EACN is unique in the geographical extent of its operations, the number of sites at which samples have been collected and the time for which sampling has been sustained. Other networks in the USSR, the USA and elsewhere have operated for shorter periods or covered smaller areas. In its fullest form the EACN sampling and analysis covered twenty properties of rain or air in each month and at each site. A full description of the routine may be found in the several papers published in the period 1955 - 58. The properties observed are listed in Table 1.1 .

Precipitation sampling is the simpler task, requiring only a monthly change of sample bottle in a cabinet which in cold climates includes a thermostatically controlled heater to melt snow and prevent freezing of the sample. The air sampling requires a pump to draw air as a constant rate through an absorbing solution which captures gases and particles. The electrical and mechanical equipment needed for pumping and to maintain the level of the absorbing solution has complicated the process to the extent that it has operated well only where good servicing facilities have been available. The air sampling data is consequently less extensive and more erratic in quality than data on precipitation. A recent study by Brownscombe, Porter and Goldsmith (1973) has given cause to believe that there are several fundamental problems with the present form of air sampler. In this thesis I use only the precipitation chemistry data. Appendix A records the time for which sampling has been carried out at the major EACN sites and identifies the laboratories in which the samples were analysed.

It is a common procedure to consider the relative quantities of the various elements which are sampled in air or in precipitation against their relative abundances in nearby natural reservoirs which may produce aerosols. The trace substances in precipitation at maritime sites, especially islands, may be considered in relation to their relative abundances in sea water. Because the sea is massive and well mixed it is expected that the aerosol produced by bubbles bursting at its surface contains the principal ions in the same ratio as in the sea. Peirson, Cawse and Cambray (1974) have suggested that the minor ions in sea water, and some substances with land or industrial sources, especially some of the heavy metals, may be concentrated in the maritime aerosol by processes which accumulate them at the surface of the sea. On land the chemical composition of precipitation is often related to the abundances of different elements in local soils but the validity of making this connection may be questioned if it is found that the larger part of that element in precipitation travels long distances in the atmosphere before being washed out. When South Pole snow has been analysed (e.g. by Zoller et al, 1974) the relative abundances of the elements have been compared with their crustal abundances for the aerosol is assumed to have been derived from land and sea surfaces throughout the southern hemisphere. It cannot have originated locally for, apart

Table 1.2 The abundances of some elements in the sea and in the Earth's continental crust.

	In sea water*	In continental crust
chlorine	19.353 g/kg	.013 %
sodium	10.76	2.36
sulphur	2.712 (as sulphate)	.026
magnesium	1.294	2.33
calcium	.413	4.15
potassium	.387	2.09
bicarbonate	.142	
bromine	.067	.00025
strontium	.008	.0375
boron	.004	.001
fluorine	.001	.0625

* at a salinity of 35 $^{o}/_{oo}$. pH of the sea is 8.1 ± 0.2

The sea water composition has been taken from Riley and Skirrow (1965)
The continental crust composition has been taken from Taylor (1964)

from recent settlements of sometimes dubious cleanliness, the surrounding terrain consists of clean snow and scoured rock for a distance of four thousand kilometres. Table 1.2 gives the relative abundances in sea water and in the earth's crust of some of the elements for which the European Air Chemistry Network precipitation samples are analysed.

A consideration of the ratio of two elements in air or in precipitation can tell much about either the sources of the two elements or about their comparitive behaviour since their generation at a common source. It has been pointed out by Eriksson (1970) that the trends with time of the concentrations, and the relative concentrations, of the various ions analysed in the EACN laboratories provide information on atmospheric chemistry which is pertinent to a number of problems of the atmospheric transport of trace substances and therefore of their cycles in nature. That approach has been taken in the studies of the calcium/magnesium ratio in Chapter 2 and the chlorine/sodium ratio in Chapter 5. From these it is concluded that these secular variations tell us as much about atmospheric chemists as they do about atmospheric chemistry.

The quality of the data which is recorded by the EACN and by similar networks has only recently been brought into question. The traditional check upon the nine ions for which precipitation is analysed is the requirement that the positive ions must balance the negative in total charge and that the measured conductivity should agree with that which is estimated from known ionic mobility and the ionic concentrations which are measured. Granat (private communication) reports that in the Stockholm laboratory the balance of positive and negative ions is generally found to within a few percent, as also is the conductivity.

The limitations of such controls are readily apparent. At island and coastal sites, where sea salt may comprise nine tenths of the weight of the sample, or more, there is no residual power in these tests to verify even the presence of other species. Even the balance of the two principal ions, chloride and sodium, may be incorrect to an extent which encourages misinterpretation of the data, as I describe in Chapter 5. In such a situation these tests give a check only on the order of magnitude of concentration of minor constituents of sea salt. At inland sites where the pH is low and the concentration of other ions is low the high mobility of the hydrogen ion and the coarseness of the pH scale when expressed in hydrogen ion concentration leads to a similar situation with almost no check on the minor ions in solution.

There has recently been commenced a programme of exchanging samples between laboratories. Such comparisons must improve our knowledge of the quality of data produced in the various laboratories. However, as all laboratories use similar techniques for some analyses there remains the possibility that the same interference is biasing all measurements. It would be desirable to check the reliability of analysis by manufacturing samples which contain realistic mixtures of the ions and distributing those for comparativeanalysis in all laboratories which participate in the EACN. Since we are concerned with the average quality of analysis, and not with the best that can be achieved, the usual precautions should be taken to have these quality control samples treated in a manner which is identical with the the samples of precipitation.

Past data cannot be verified in the way that current data may. If it is in error then the nature of the error may be made plain by the analysis of the data. Obvious errors such as those in precipitation amounts which Paterson and Scorer (T973a) reported might be corrected with the use of independently collected data from nearby meteorological stations. The more subtle errors such as those of chemical analysis which are discussed in Chapters 2 and 5 cannot be corrected later. As their existence can remain hidden until the data have been used several times, or might never be discovered, they are particularly expensive errors for they distort our understanding of the atmosphere. The simple fact of the existence of data, its quality unknown, tends to discourage others who might otherwise make similar measurements but of a higher quality. For this reason those people who would monitor the environment have a responsibility to do the job properly. Each successive fruitful analysis of data strengthens our belief in its correctness. In addition to a formal programme of quality control on all new data it is desirable that it should be used in substantial analyses as soon as possible so that it is fully tested. The more substantial initial analysis a body of data has undergone the more valuable it becomes as a validated record.

The positive results of this study which concern the broadscale distribution of aerosol from the land and from the sea do not rely upon very accurate chemical analysis. They seem also to be unaffected by intense local sources of aerosol except perhaps at Lerwick where the nearby coast is a prolific source of sea salt particles. Where accurate chemical analysis is necessary, such as for the verification of the Cauer hypothesis, it has been possible only to disprove the existence of a category of real deviations from a precise quantitative relationship, the ratio of chlorine to sodium in sea salt.

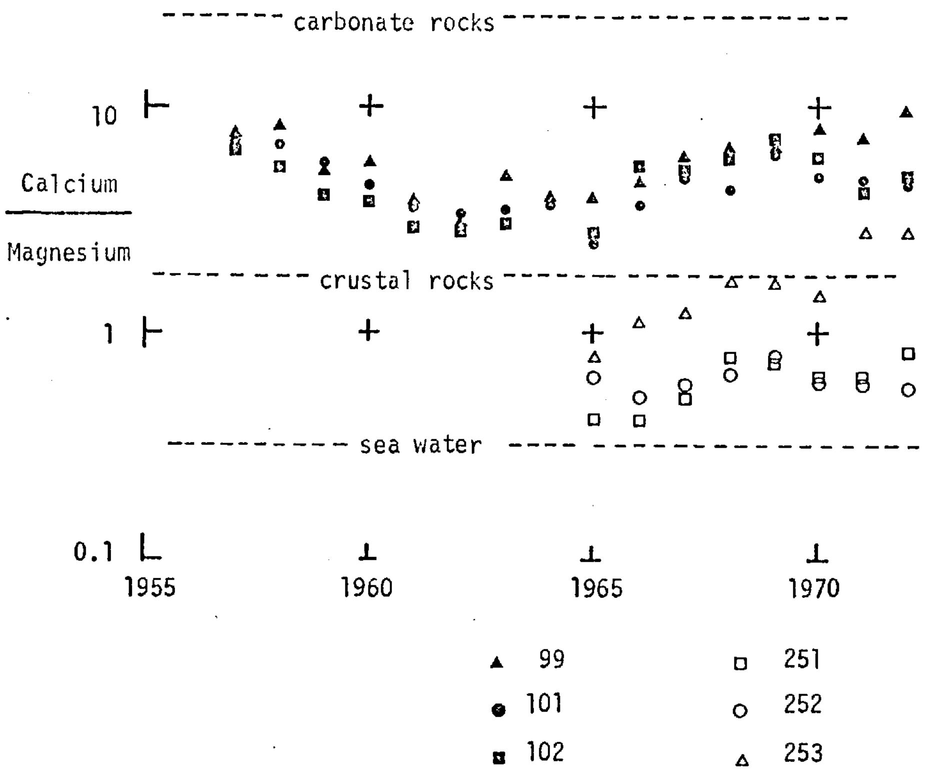


Figure 2.1 The run of annual ratios of calcium/magnesium in precipitation at three Austrian and three Irish stations. Ca/Mg is shown on a logarithmic scale. Dashed lines show the ratios of the two elements in sea water, crustal rocks and carbonate rocks. In each country all or most stations record the same trend.

Chapter 2. The ratio of calcium to magnesium.

In the investigation of the chlorine to sodium ratio which is described in Chapters 5 and 6 I will consider two species from one source - the sea. A variation in the ratio of these ions in precipitation could arise from chemical processes in the atmosphere or from additional sources of one or both ions. There is no reason to expect a similar close relationship between calcium and magnesium in precipitation for they may come from quite different sources. In this case the variation of the Ca/Mg ratio may convey information about these separate sources. The table below shows that the ratio of the two in three categories of source differs by an order of magnitude or more. It is worthy of note that the primary source of the two elements, the crustal rocks, has a ratio of Ca/Mg which falls between the two reservoirs, the sea and carbonate rocks, whose relative proportions of calcium and magnesium are a result of chemical fractionation due to the different solubilities of calcium and magnesium salts.

	In sea water	In crustal rocks	In carbonate rocks
Total weight of calcium	0.6 x 10^{21} g	100 x 10^{21} g	(2.5 x 10^{21} g)
Total weight of magnesium	1.9 x 10^{21} g	56 x 10^{21} g	(0.1 x 10^{21} g)
Ratio Ca/Mg	0.31	1.8	25

At maritime sites, where the sea is the main source of aerosol, the ratio Ca/Mg in precipitation should be considerably less than unity. At continental sites, far from the sea, the ratio should at least approach the crustal rocks value of 1.8 and may be as high as 25 or more for some carbonate rocks, in particular those of recent origin, have a Ca/Mg ratio as high as fifty (Degens, 1965). Figure 2.1 shows the annual ratios for four sites in Eire and three in Austria over a number of years. The Irish stations, dominated by the Atlantic Ocean, fall closer to the sea water ratio while the values recorded in Austria fall between the ratios characteristic of crustal and carbonate rocks.

One feature of the curves is the systematic variation of the annual Ca/Mg ratio at single stations. At Austrian stations the ratio declined to a minimum in 1962 and then rose again through the late sixties. At Irish stations the ratio has risen significantly since the commencement of analysis for magnesium in 1965. If they are real, such trends could indicate a variation in the amount of sea salt from the Atlantic which has been carried over western Europe. Alternatively it might be due to a change in the rate of production of mineral aerosol rich in calcium in the centre of Europe. Any such trend indicates that at least two sources of calcium and/or magnesium contribute to the aerosol over Austria and Eire. A change of the ratio by a factor of two or three, if it indicates a change in the

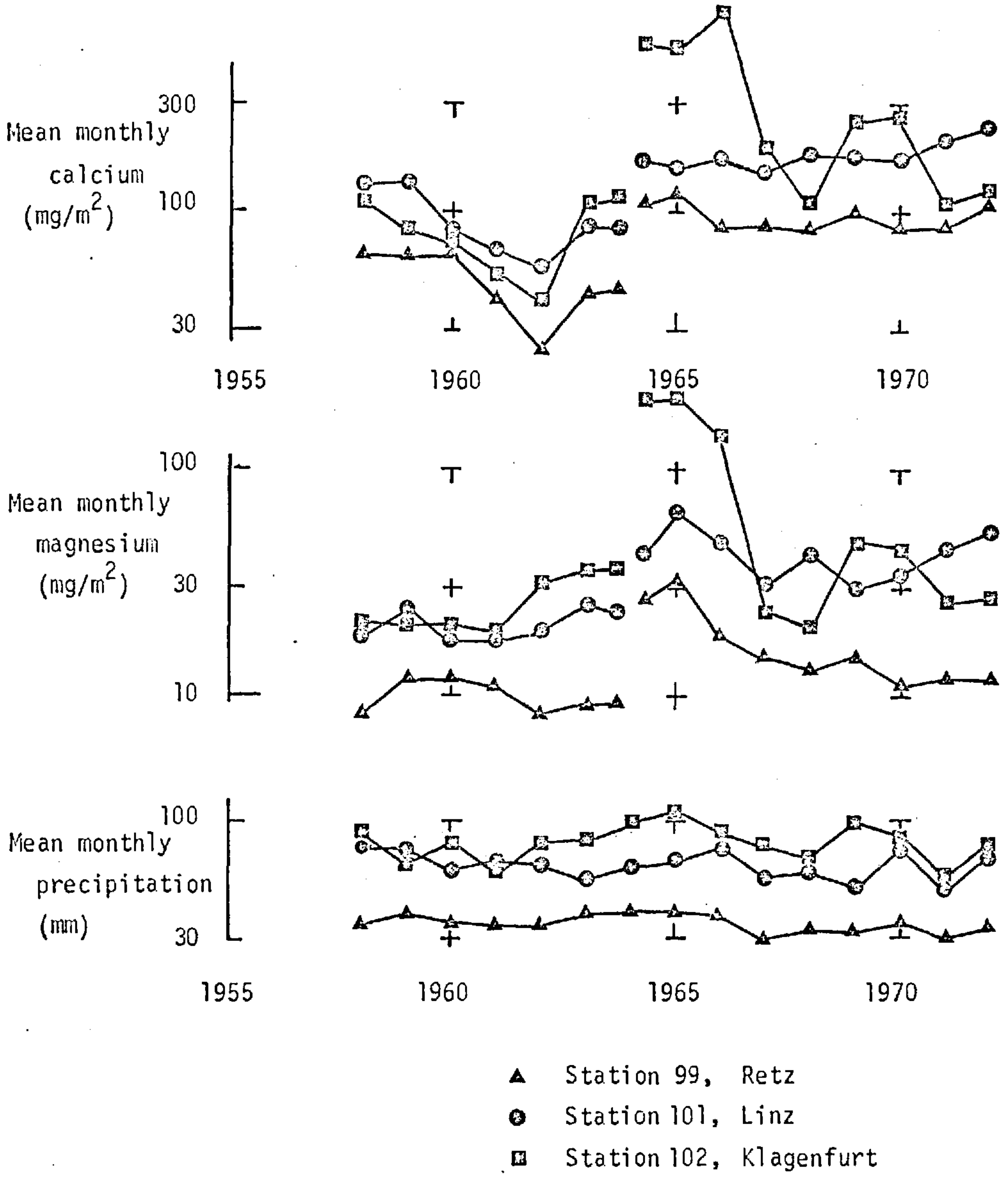


Figure 2.2 Mean monthly amounts of precipitation and of calcium and magnesium in precipitation at three Austrian stations between 1958 and 1972. Note the abrupt increase in the amounts of both calcium and magnesium in 1964.

maritime or continental nature of airmasses which produce precipitation, must be deemed a significant event in the weather of Europe. The continuity of the trend is notable. If there is such a variation in the atmospheric transport of natural particles there should be a parallel change in the transport of man-made air pollution. Schmidt (1971) has reported a trend in the air pollution in Rotterdam which is presumed to be generated by the influence of changing weather on pollutants from local sources.

To determine if the trend in the Ca/Mg ratio is principally due to change in amounts of calcium, presumed to come from the land, or change in the amount of magnesium, presumed to come from the sea, we consider separately the absolute amounts of the two elements. The mean monthly amounts for each year at each of three Austrian stations are shown in Figure 2.2 . Two values are given for the mean amounts of calcium and magnesium in 1964. Until April 1964 the Austrian samples were analysed in the German laboratory. After May 1964 they were sent to Stockholm for analysis. Figure 2.2 shows variations in the amounts of both calcium and magnesium so the change in the ratio cannot be attributed to just one element and one source. The most conspicuous variation is the approximately threefold increase of both calcium and magnesium between the end of German analysis and the commencement of Swedish analysis which occurred at all stations. There was no concomitant increase in the amount of precipitation.

For such variations to be produced by the mixing of two aerosols the major calcium contributor must have a Ca/Mg ratio higher than the highest ratio which is recorded for the mixture in precipitation. The major magnesium contributor must have a Ca/Mg ratio which is lower than the lowest recorded in precipitation. From the variations of Figure 2.1 we may conclude that the crustal rocks do not produce the greatest fractions of calcium and magnesium in the aerosol. The aerosol over Europe seems to be governed by the mixture of sea salt, the main magnesium contributor, and the weathered fragments of carbonate rocks which are the main calcium contributor.

The marked change in concentrations and absolute amounts of both calcium and magnesium between the end of German analysis and the start of Swedish analysis seems to imply an intensification of the sources of both sea salt and carbonate rock aerosol. It is surprising that this could occur to such a marked degree while the ratio remains constant. We cannot exclude the possibility that the changes are due to errors in the chemical analysis of the samples, either before or after the change in laboratory.

Paterson and Scorer (1973a) pointed out the discrepancy between annual Ca/Mg ratios in different European countries. In Figure 2.3(a) the ratios at stations from northern Germany to Austria, separated by distances up to nine hundred kilometres, are compared with stations of the French/Belgian/Dutch network to the west and the Danish network to the north. It is evident that one strong pattern of variation in the ratio is common to all stations in Germany/Austria. Yet it does not extend a short distance into Belgium and France or into Denmark. The factor which determines the ratio appears to be the laboratory in which the analysis is made and not the atmospheric transport of calcium for it is implausible that the atmsophere could impose one pattern of washout of calcium and magnesium aerosol over the whole of Germany and Austria and a different pattern just outside the borders of the region.

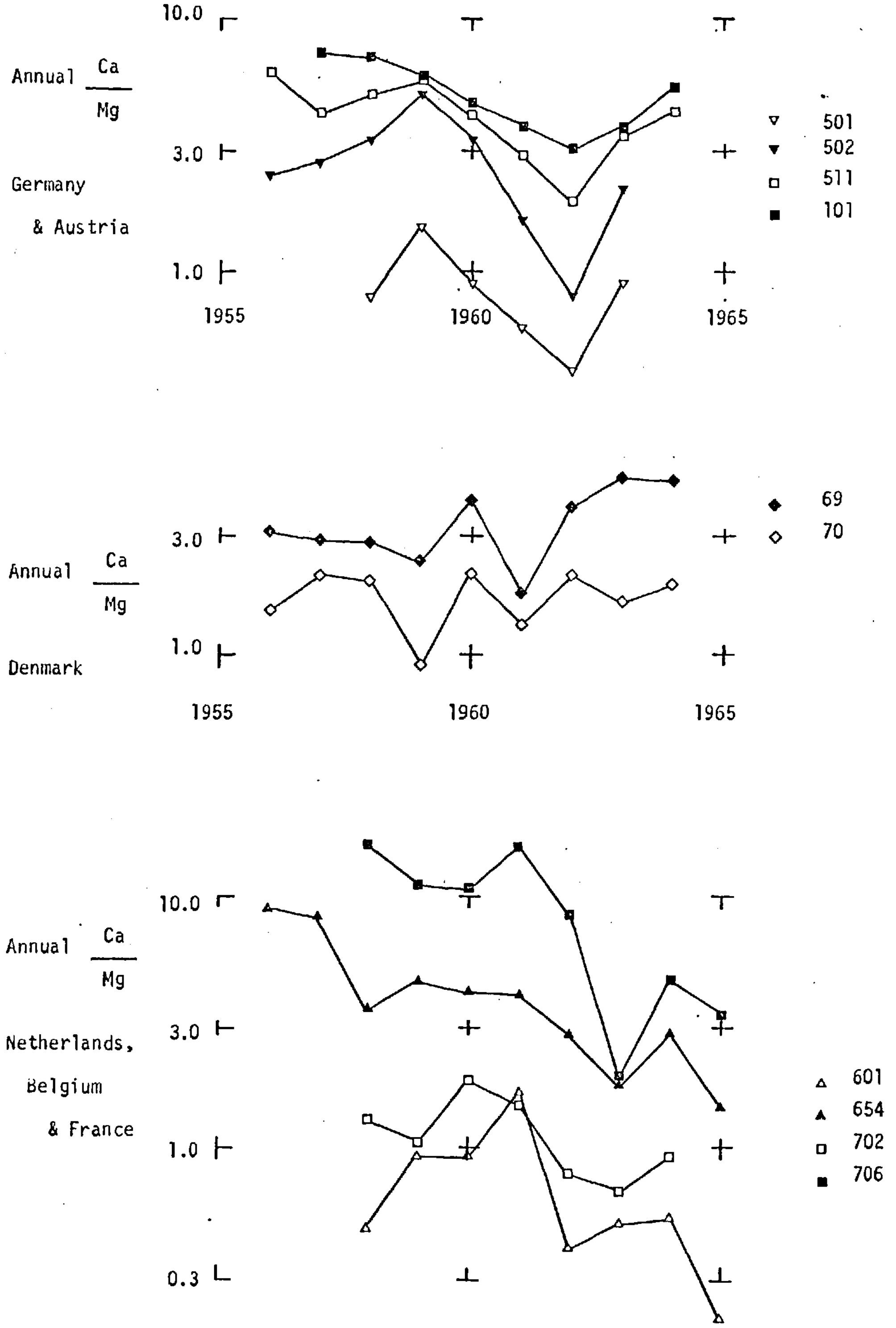


Figure 2.3 Trends in the Ca/Mg ratio at several stations in each of three sections of the European Air Chemistry Network. Samples from four German and Austrian stations, for which results are shown at the top, were analysed in Germany. Samples from the two Danish stations were analysed in Denmark and in Sweden at various times (see Appendix A). Dutch, Belgian and French samples were analysed in Belgium. Within each country there is a distinct pattern which is not found elsewhere.

In order to consider the relationship between a number of stations in a concise and quantitative way the correlation coefficients of least squares linear regressions of the annual Ca/Mg ratios at pairs of stations have been calculated. This procedure has been described in detail by Paterson and Scorer (1973b). By considering the ratio of Ca/Mg on a logarithmic scale variations in either element receive equal weight. The values of the correlation coefficients so determined will bear only a limited physical interpretation. In this context they should be considered to be primarily a diagnostic tool to be used in examining the data.

I will assess the results of these calculations on the basis of the following assumptions about the form of valid data. The only justification for the assumptions is that they seem reasonable.

1. There may be a significant positive correlation between stations which are separated by short distances for they are subject to similar precipitation in airmasses bearing particles from closely-related source regions.

2. For widely separated stations the correlation falls to zero.

3. The correlations between the administrative sub-sections of the EACN (each based on analysis of samples in a single laboratory) are similar to those within sub-sections over the same distance.

4. The presence of major watersheds or other geographical features between stations may lead to significant negative correlations.

The results of the analysis are shown in Figure 2.4 which gives the values of $r|r|$ as a function of inter-station distance. This function of the correlation coefficient, r, has been selected because it retains the sign of r and has the magnitude of r^2, which expresses the amount of the variance at one station which can be accounted for in terms of the variance at the other.

We are considering a network with some dozens of stations. It would be possible to calculate the correlation for each of $\frac{1}{2}n(n-1)$ station pairs where n is the number of stations. However it is not necessary to calculate $r|r|$ for each of the thousand-odd pairs because a clear pattern emerges from a few dozen values from station pairs selected to give a wide range of inter-station distance in each category.

Figure 2.4(a) shows that within the German/Austrian network the correlations between stations at all separations are high, there being no apparent decrease with distance. The magnitude of the correlations implies that even at distances of eight hundred kilometres, from the North Sea coast of Jutland to the Austrian mountains, six tenths of the variation at one station can be deduced from variations at the other. Figure 2.4(a) also shows low correlations with Belgian/French/Dutch stations at all inter-station distances. The German/Austrian results up to 1964, the period included in this calculation, must be considered invalid for they do not satisfy assumptions 2 and 3 above.

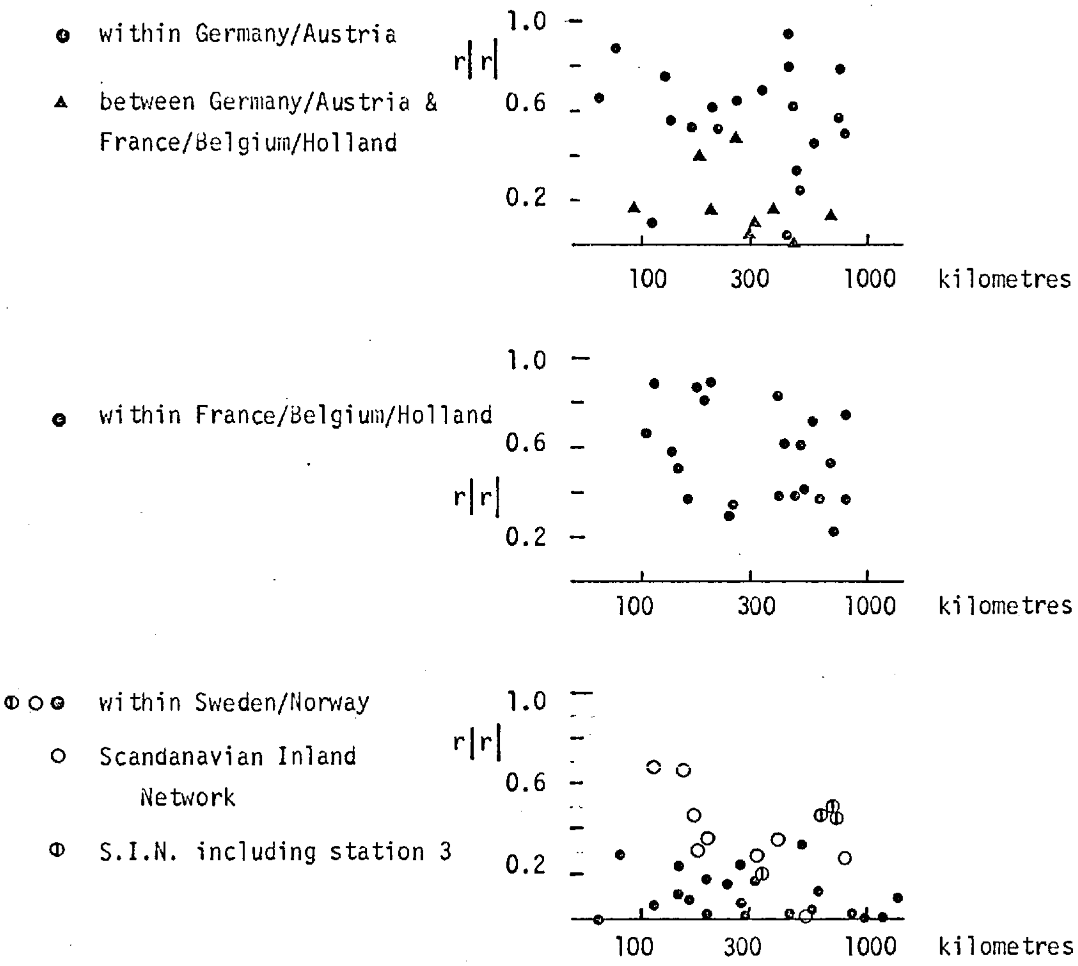


Figure 2.4 Correlations between annual Ca/Mg ratios at pairs of stations in regions as noted at left. Within each regional network of Germany/Austria and France/Belgium/Holland the ratios are highly correlated at all distances. Between the two regions the correlations are low, even for short distances between stations. In Sweden/Norway the ratios are poorly correlated except in the case of pairs of inland stations.

The Belgian/French/Dutch correlations shown in Figure 2.4(b) appear to decrease with increasing station separation, although the typical value of $r|r|$ at a separation of eight hundred kilometres is still so high that it is doubtful that it would fall to zero within the breadth of the continent. We can only judge whether such high correlations are realistic in the light of results from other regions, for these results may well be inconsistent with the second assumption above, that the correlation falls to zero for widely separated stations. It is not possible to apply the third criterion for we have already rejected the German results and the British results may be inapplicable for comparison as an adjacent neighbour due to the quite different island situation of the British stations.

In a compact country such as Denmark there can be no large inter-station distances. There is a further complication in this case in that the Danish samples have at times been analyzed in the Stockholm laboratory and at other times in Copenhagen. Figure 2.5 shows that there has been a considerable degree of correlation between the three main Danish stations, although their results differ from those of the German and Belgian laboratories in that there is no long-term trend evident. This could be a sign of healthy results if the long-term trends in Germany are due to slow drifts in laboratory performance and not to real geochemical phenomena, as seems to be the case.

The Swedish and Norwegian results should be treated as coming from a single network for all samples from this region have been analyzed in the Stockholm laboratory. The Finnish samples also were analyzed in Stockholm until 1961. Figure 2.4(c) shows the correlations as a function of distance for the Norwegian and Swedish stations. The calculated values are shown in two sets as an introduction to the next chapter of this thesis. The first set, shown by open circles, is for pairs of stations of which one or both are situated on a coast. The correlations between such pairs are generally low and positive. There is some slight evidence of decreasing correlation with increasing distance. The other set, shown by solid circles, is for inland pairs of stations. Within this set there is a clear a-sociation of correlation with distance. The correlation falls to near zero at distances in excess of eight hundred kilometres. The highest value, at a distance of one hundred kilometres, is 0.7 which is comparable with the higher correlations found within the German and Belgian networks. Station pairs which include station 3 have been specially identified and will be referred to in Chapter 3.

The Swedish and Norwegian results appear to conform to the criteria for valid data which are listed above. The subset of inland stations, which I will call the Inland Network, conforms to the criteria while showing a clear decrease in correlation with increasing station separation. The magnitude of the correlation in the Inland Network is generally much smaller than that found in the Belgian network which must lead us to suspect the validity of the high values observed in Belgium/France/Holland. The high correlation in those countries could arise, as in Germany, from variations in the performance of the laboratory.

It is not possible on the basis of this analysis to say whether the Finnish results are reasonable. The median correlation between Finnish stations is low and there is a wide scatter of results. Finnish stations are uncorrelated with Swedish stations but the next

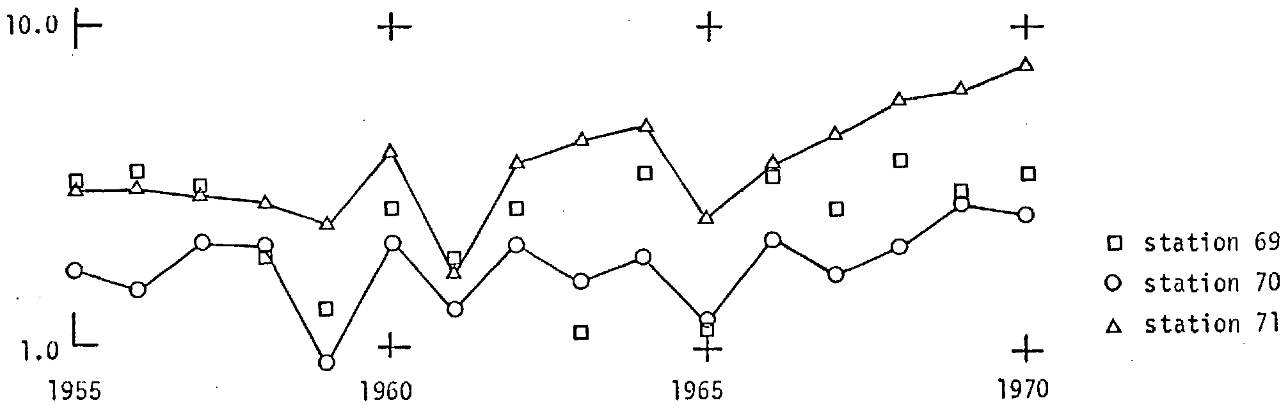


Figure 2.5 The annual calcium/magnesium ratio in precipitation at three Danish stations between 1955 and 1970.

two chapters will show that the correlations between the stations of the Inland Network in Sweden and Norway arise from their situation in a topographic feature of which Finland is not a part. In such circumstances we should not expect significant positive correlations between Finland and Sweden. The least that can be said for the Finnish results is that they do not suffer from the spurious high correlations which in southwestern Europe are evidence of some sort of laboratory malfunction.

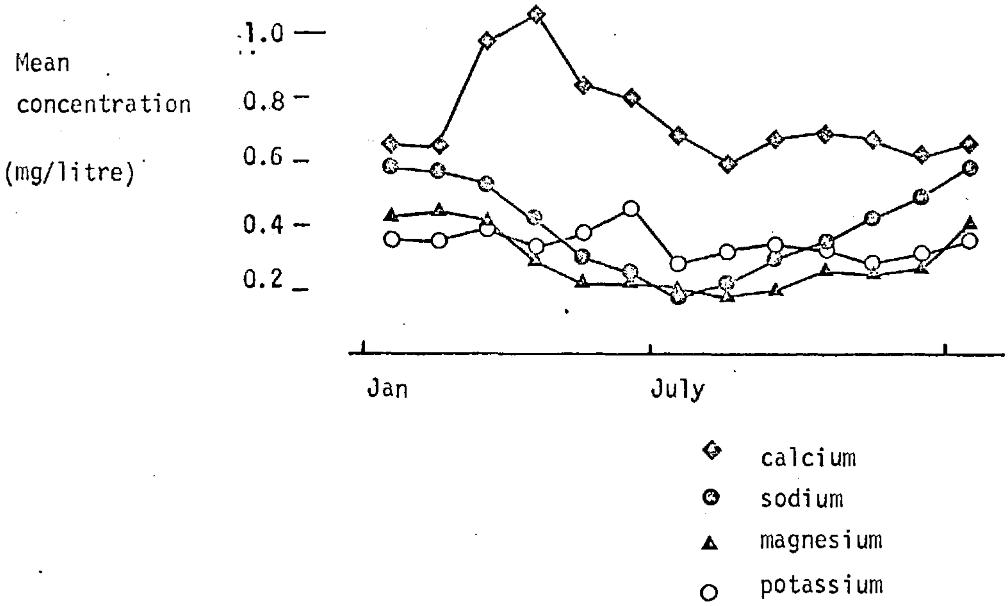


Figure 3.1 The average concentration in precipitation of four elements by month of year. The averages are estimated from ten years data at eight inland stations in Sweden and Norway. Note the peak in the concentration of calcium in spring and the summer minima in concentrations of each of the four elements, at the time of greatest precipitation. In precipitation magnesium is almost as abundant as sodium whereas in sea water there is eight times as much sodium as magnesium.

Chapter 3. The Inland Network - a pattern in precipitation chemistry.

In Chapter 2 I considered trends in the ratio of annual amounts of calcium and magnesium in precipitation. Such an analysis is sensitive to long term trends both in the transport of either element and in the calibration of the laboratory analysis for each. The analytical defects revealed in that chapter lead me to confine further work on calcium and magnesium to the geographical area of Scandanavia and the European islands. As the methods which were used to check continental data cannot be used for island data there remains a greater degree of uncertainty about its quality. However the island data is used only in analyses which are reasonably insensitive to errors of the type found on the continent.

In the analysis in Chapter 2 the single figure for each station for a year includes all of the magnesium and calcium from as many as one hundred days of precipitation. It is evident from Figure 3.1 that the chemical character of April precipitation differs on average from that of January. In this chapter I will consider the elements separately by month of the year. I am first concerned with the set of stations in Sweden and Norway which were identified in the last chapter as the Inland Network. I will demonstrate that there are consistent relationships between some of these stations, as evident in the monthly data as in the annual, which constitute a pattern in precipitation amounts and chemistry. Some inland stations in the region, which might be expected to fit into the pattern on the simplest geographical grounds, are demonstrated to differ from the pattern. This different behaviour is explained by the topography of the region.

In the next chapter the distribution of sodium and calcium in precipitation, in both time and space, is then considered. It is demonstrated that the stations of the Inland Network receive more sea salt during the Summer than during the Winter while the rest of Scandanavia receives more during the Winter. Calcium of land origin is precipitated in the largest amounts in the Summer, both over the land and over the sea. The relatively uniform distribution of such calcium, from Iceland to Finland and from Lappland to Jutland, indicates that the atmosphere carries it over long distances.

In Figure 3.1 is shown the monthly average concentration in precipitation of four metal ions for eight inland stations in Norway and Sweden. The average calcium concentration in January has been calculated as the average for eight stations of the median amount of calcium divided by the median amount of precipitation in January of ten years. The gaps in the data, indicated in Appendix 1, have made it impossible to use a standard set of years in the calculations. The same consideration applies to the calculation of correlations later in this chapter, a factor which has rendered the results both more difficult to obtain and of reduced power.

Of the four elements calcium deviates most conspicuously from a simple annual cycle. The calcium concentration reaches its peak value in March or April, a month after the continental rainfall minimum which is in February and March, as seen in Appendix C. A number of factors which might affect the production of aerosol from the ground, including snow cover, vegetation cover and soil moisture, are also changing quickly at this time of year. This makes it impossible to draw conclusions about the relationship between

precipitation amounts and the concentration of calcium. It should be noted that none of the other elements share this behaviour with calcium, from which we can infer that they do not come from the same source and travel with the calcium.

Both sodium and magnesium exhibit a Winter peak in concentration. Sodium occurs in the sea at eight times the concentration of magnesium. It is clear from Figure 3.1 then that less than one quarter of the magnesium in precipitation comes from the sea if there is no fractionation which enhances the concentration of magnesium in sea salt aerosol at the point of production. This possibility has been considered and dismissed by Bloch (1973) and others. The other three quarters of the magnesium evidently comes from the land.

The concentration of potassium varies little during the year. In view of the low concentration of potassium in sea water relative to sodium, 0.036 times sodium by weight, and the seasonal variation in precipitation amounts the same considerations apply as in the case of magnesium. The implication is that most of the potassium comes from the land and that the production of potassium aerosol is greater in the Summer than in the Winter.

If we consider the difference in amount of calcium (say) between one April and the next we may find an indication of the typical distance of transport of calcium by the atmosphere in April. The physical reasoning is as follows:

> Suppose that the principal source of calcium aerosol in April is the Sahara. In some years the wind in April may carry the Sahara aerosol to the north so that it most affects northwestern Europe. A high concentration of calcium may be found in the rain which falls on Dublin while Moscow receives relatively little calcium. Twelve months later the transport may be more to the northeast so that Moscow receives much calcium while Dublin receives little. In the case of two targets which are close together, such as Oslo and Stockholm, it is unlikely that calcium from such a large source at such a distance would hit one without hitting the other. An April which saw little calcium in precipitation on Oslo would see little at Stockholm. On the other hand, if calcium in Scandanavian precipitation were to come mainly from a nearby source, such as Copenhagen, then it is quite likely that Oslo would receive much calcium while Stockholm received little. In this case Stockholm and Uppsala would most likely receive similar amounts.

If we consider a succession of Aprils then one way of expressing such a relationship between two "targets" is through the correlation coefficient which is estimated in the course of a linear regression analysis. The details of the fitting of a straight line to a set of experimental points by the method of least squares is described fully in, for example, Kendall and Stewart (1967) and I will not dwell on the subject here. It is necessary to comment on the limits of the validity of the method in studies such as this.

For the regression analysis to be quite valid the variables must be distributed normally. Monthly amounts of precipitation and of ions in solution are not distributed normally but rather in a log-normal manner. It is desirable therefore in this type of analysis to use as the variable the logarithm of the amount of precipitation, magnesium, calcium etc.

JUNE	JULY	AUGUST	SEPTEMBER	OCTOBER	NOVEMBER	DECEMBER	JANUARY	FEBRUARY	MARCH	APRIL	MAY		
.66	.36	.49	.86	.58	.42	.69	.15	.00	.29	.53	.36	.45	59-60 99 km
.58	.14	.00	.26	.53	.45	.41	.80	.44	.14	.18	.49	.37	15-16 140 km
.81	.12	.04	.35	.66	.53	.76	.32	.00	.74	.26	.32	.41	15-59 152 km
.52	.17	.03	.32	.84	.76	.52	.61	.78	.11	.23	.11	.42	15-60 175 km
.59	.32	.19	.27	.71	.44	.74	.71	.49	.52	.37	.23	.46	16-21 180 km
.23	.13	.06	.38	.58	.34	.37	.38	.58	.22	.40	.02	.31	15-21 276 km
.80	.19	.36	.07	.56	.25	.41	.40	-.16	.40	.06	.02	.28	16-59 293 km
.48	.41	.13	.02	.71	.24	.21	.59	.21	.56	.03	.18	.31	16-60 308 km
.32	.14	-.01	.31	.74	.48	.36	.18	.20	.01	.01	.38	.26	21-60 392 km
.46	.00	-.01	.36	.38	.03	.45	.08	-.06	.22	.28	-.01	.18	21-59 418 km
.40	.16	.25	.08	.29	.26	.01	.02	-.01	.01	.52	.05	.17	3-59 594 km
.28	.06	.10	.07	.37	.29	.00	.17	.29	-.08	.40	.02	.16	3-60 684 km
.38	.01	.10	.40	.31	.13	.00	.25	.10	.15	.05	-.02	.15	3-15 685 km
.23	.00	.00	.64	.11	.04	-.02	.18	.01	.00	.00	.00	.10	3-16 772 km
.41	.21	-.03	.34	.22	.01	.00	.20	.19	.28	.08	.00	.16	3-21 948 km
.49	.16	.11	.32	.51	.31	.33	.34	.21	.24	.23	.14		

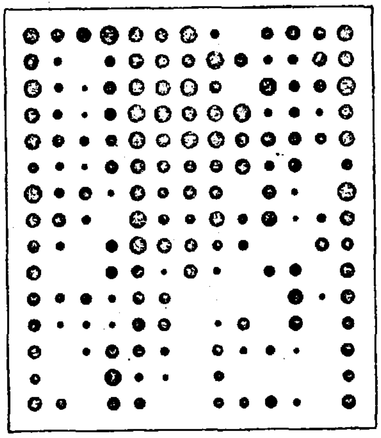


Table 3.1 Correlations between monthly precipitation amounts at pairs of stations of the Inland Network. Values of r|r| from the regression on seven to fifteen months are tabulated on the left. They are shown graphically on the right with areas proportional to r|r|. June is repeated.

.18	.36	.37	.88	.28	.37	.00	.36	.03	.05	.66	.44	.33	59-60 99 km
.48	-.04	.02	.53	.37	.52	.53	.27	.61	.00	-.12	-.02	.26	15-16 140 km
.32	-.01	.06	.46	.35	.26	.07	.07	.24	.31	-.08	.08	.18	15-59 152 km
.50	.00	.25	.48	.14	.17	.18	.62	.45	.02	-.04	.00	.23	15-60 175 km
.02	-.03	.59	.46	.59	.03	.19	.20	.30	.49	.00	.16	.25	16-21 180 km
-.15	-.28	.23	.45	.09	.05	.59	.07	.30	.01	.14	-.07	.12	15-21 276 km
.48	.11	.37	.50	.00	.04	.45	.19	.11	.53	.04	-.26	.21	16-59 293 km
.13	.00	.67	.37	.04	.34	.00	.19	.35	-.17	.00	.05	.16	16-60 308 km
-.01	.05	.67	.26	.04	.34	.30	.18	.29	-.14	-.05	.01	.16	21-60 392 km
.07	-.07	.10	.29	-.03	.36	-.07	.64	.14	.27	-.38	-.04	.11	21-59 418 km
.26	.01	.21	.22	.56	.66	.71	.56	.00	.00	.17	.16	.29	3-59 594 km
.35	.00	.04	.25	.14	.14	.00	.03	.31	.01	.04	.40	.14	3-60 684 km
.62	.58	.25	.26	.11	.26	.07	.07	.35	.00	.01	.27	.24	3-15 685 km
.42	-.08	.03	.10	.00	.04	.07	.62	.18	-.01	-.05	-.32	.08	3-16 772 km
-.01	-.56	.01	.12	.00	.32	-.15	.21	.18	.00	-.14	.01	.00	3-21 948 km
.24	.00	.26	.38	.17	.26	.20	.29	.26	.09	.01	.06		

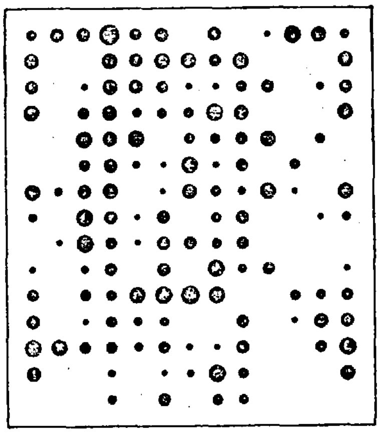


Table 3.2 Correlations between monthly magnesium amounts at pairs of stations of the Inland Network. Values of r|r| from the regression on seven to fifteen months are tabulated on the left. They are shown graphically on the right with areas proportional to r|r|. June is repeated.

.30	.38	.45	.65	.46	.13	.38	.29	.00	.17	.72	.00	.33	59-60 99 km
.64	.14	.01	.15	.41	.11	.03	.71	.49	.04	.66	.28	.31	15-16 140 km
.49	.50	.03	.02	.19	.38	.35	.49	-.05	.48	.20	.00	.26	15-59 152 km
.32	.21	.03	-.04	.26	.37	.09	.16	.00	.02	.24	.18	.15	15-60 175 km
.45	.14	.06	.00	.40	-.01	.17	.42	-.49	.15	.30	.00	.13	16-21 180 km
.64	.25	-.11	.07	.16	.11	.17	.34	-.11	.02	.58	-.04	.17	15-21 276 km
.50	.28	.12	-.03	.45	.12	.35	.38	.04	.06	.16	.09	.21	16-59 293 km
.40	.06	.24	.00	.32	.10	.13	.29	.00	-.02	.05	.20	.15	16-60 308 km
.14	.00	-.01	.00	.08	.03	-.02	.09	-.03	.05	.34	.25	.08	21-60 392 km
.31	.23	-.10	.00	.32	.10	.10	.24	.19	.14	.34	.07	.16	21-59 418 km
.29	.49	.10	-.06	.12	.53	.35	.06	-.05	.00	.23	.34	.20	3-59 594 km
.09	.49	.00	.00	.50	.18	.01	.25	.22	.01	.16	.02	.16	3-60 684 km
.21	.32	.20	-.02	.36	.21	.26	-.01	.00	.08	.05	.00	.14	3-15 685 km
.44	.27	.00	.08	.19	.31	.14	.03	-.11	-.05	.01	.14	.12	3-16 772 km
.36	.06	-.46	.02	.00	.05	.06	.00	.12	.03	.04	.00	.02	3-21 948 km
.37	.25	.04	-.06	.28	.18	.17	.25	.01	.08	.27	.10		

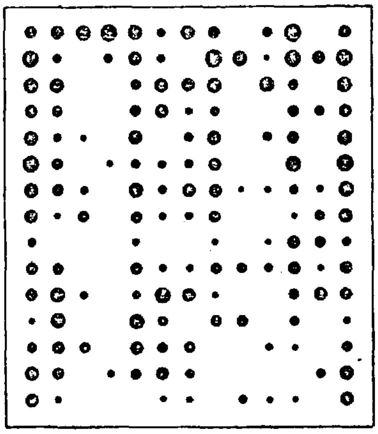


Table 3.3 Correlations between monthly calcium amounts at pairs of stations of the Inland Network. Values of r|r| from the regression on seven to fifteen months are tabulated. They are shown graphically on the right with areas proportional to r|r|. June is repeated.

The relationship is expressed in terms of a dependent variable, y, as a function of the independent variable, x. In this case there is no such relationship as the two variables are exactly equivalent.

For the correlation coefficient to be significantly different from zero at the 5% level of confidence with seven data points (five degrees of freedom) r must exceed 0.75 and with fifteen data points (thirteen degrees of freedom) r must exceed 0.51 . In this analysis it has been possible to use only between seven and fifteen data points for each value of r which is calculated.

I will now consider six stations which were identified in the last chapter as members of the Inland Network. For each calendar month and each of the fifteen possible pairs of stations the correlation coefficient of a linear regression on the logarithm of the precipitation amount, etc., has been calculated. These results have been arranged systematically in five tables, one for each of precipitation, sodium, potassium, magnesium and calcium. Each table has twelve columns, one for each month of the year, and fifteen rows, one for each station pair, which are arranged in order of increasing inter-station distance. This arrangement is suggested by the considerations above which lead us to expect higher correlations for smaller inter-station distances. It will be shown that this arrangement accounts for much of the variation in the table, leaving one very significant deviation to be accounted for.

The tabulated values are in fact a function of the correlation coefficient, $r|r|$, which retains the sign of r and has the magnitude of r^2 which is the fraction of the variance in one variable which can be accounted for in terms of the variance of the other. The tables are presented in two forms, one numerical and one graphical, side by side. On the left are the tables of numerical values with the averages across the rows and down the columns. The tables on the right are presented as solid circles which are proportional in area to the values of $r|r|$ where these are positive.

In view of the many qualifications stated already it seems that there would be doubtful validity in any further manipulation of the numbers in the tables or quantitative interpretation of them. This is further supported by the relatively low values of the correlation coefficients, most of which fall individually below that which is significant at the five percent level of confidence. For these reasons I consider that the arguments cannot be carried beyond this point. However, the information in the tables as they stand does merit a discussion.

Consider first the correlation between precipitation amounts, shown in Table 3.1. One significant feature of the table, and of the tables for calcium and to a lesser extent for magnesium, is the occurrence of high correlations between all pairs of stations in June. In this respect the June column stands out in all three tables for no other month has such high values while those for the month before, and in some cases also the month after, are low. There is a factor which leads to large (or small) amounts of precipitation at all stations of the Inland Network in June. The June rainfall phenomenon is discussed further in Appendix C . Because June is a singular month in this respect it is appropriate to take it as the starting columns of the tables.

JUNE	JULY	AUGUST	SEPTEMBER	OCTOBER	NOVEMBER	DECEMBER	JANUARY	FEBRUARY	MARCH	APRIL	MAY			
.16	.67	.20	.35	.45	.66	.03	.07	.02	.08	.64	.62	.33	59-60	99 km
.08	.00	.00	.05	.59	.41	.45	.01	.58	.11	.35	.14	.23	15-16	140 km
.22	.44	.15	.41	.59	.28	.23	.50	.00	.22	.10	.10	.27	15-59	152 km
.58	.12	.31	.53	.24	.64	.23	.00	-.01	.00	.02	.02	.22	15-60	175 km
.01	.17	.02	.29	.26	.31	.01	.28	.23	.15	.41	.48	.22	16-21	180 km
.34	.48	.41	.08	.08	.18	.36	.30	.17	.20	.14	.14	.24	15-21	276 km
.02	.12	.04	.14	.50	.25	.49	.03	-.08	.78	.07	.21	.21	16-59	293 km
.19	.01	.01	-.03	.29	.35	.01	.69	.00	.00	.00	.14	.14	16-60	308 km
.37	.46	.28	.00	.01	.00	.07	.21	.04	.02	.05	.11	.13	21-60	392 km
.00	.64	.26	.00	-.14	.07	.23	.21	-.27	.26	.00	.01	.11	21-59	418 km
.07	.34	.19	-.04	.05	.48	.02	.01	.12	.04	-.02	.00	.10	3-59	594 km
.27	.35	-.04	-.02	-.02	.34	.08	.01	.01	.31	-.03	.16	.12	3-60	684 km
.37	.12	.11	-.01	.01	.12	.22	-.01	.04	.04	.06	.01	.09	3-15	685 km
-.01	.00	.12	.22	.01	.03	.14	.00	.01	-.08	.01	.12	.05	3-16	772 km
.21	.11	-.01	.19	-.17	.08	.18	.10	.00	-.01	.03	.32	.09	3-21	948 km
.19	.27	.14	.14	.18	.28	.18	.16	.06	.14	.12	.17			

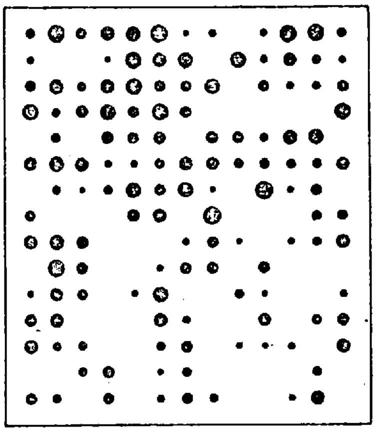


Table 3.4 Correlations between monthly sodium amounts at pairs of stations of the Inland Network. Values of $r|r|$ from the regression on seven to fifteen months are tabulated on the left. They are shown graphically on the right with areas proportional to $r|r|$. June is repeated.

-.26	.24	.35	.15	.49	.50	-.38	-.07	.14	.11	.55	.00	.15	59-60	99 km
.17	-.02	.07	.04	.04	.00	.48	.41	.01	.12	.00	.32	.14	15-16	140 km
.07	.08	-.02	.00	-.11	.03	.28	.08	.02	.03	.04	.00	.04	15-59	152 km
.02	-.03	-.03	.05	-.08	.14	-.01	-.01	.02	.31	.40	.09	.07	15-60	175 km
.00	.05	.16	.02	.27	.02	.05	.27	-.03	.31	.07	.17	.11	16-21	180 km
.62	.06	.05	.19	-.05	.00	.11	.03	.11	.48	.17	.12	.16	15-21	276 km
.04	.27	.00	.14	.56	.05	.67	.16	.02	.03	.00	.06	.17	16-59	293 km
-.11	.21	.00	.02	.38	.28	-.12	.13	.08	.44	.01	.31	.14	16-60	308 km
.06	.15	.00	-.08	.10	.18	-.06	.01	.00	.49	.16	.01	.09	21-60	392 km
.23	.11	-.10	.01	.01	.03	.00	.61	.03	.17	.01	-.07	.09	21-59	418 km
.07	.03	.06	.03	.19	.29	.29	.12	.15	.39	.19	.00	.15	3-59	594 km
.02	.11	.03	-.10	.06	.27	-.05	.08	.08	.20	.23	.01	.08	3-60	684 km
.11	.04	.01	-.08	.06	-.01	.20	.01	.01	.04	.01	-.01	.03	3-15	685 km
.40	.00	.05	.23	.04	.05	.53	.09	.09	.02	.04	.03	.13	3-16	772 km
.14	.00	.00	.01	-.10	.14	.00	.14	-.07	.04	.05	-.09	.02	3-21	948 km
.11	.08	.05	.05	.13	.13	.13	.14	.04	.21	.13	.06	.10		

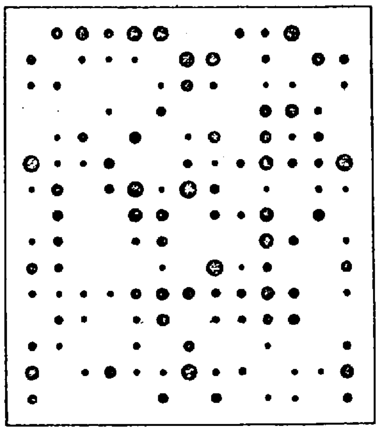


Table 3.5 Correlations between monthly potassium amounts at pairs of stations of the Inland Network. Values of $r|r|$ from the regression on seven to fifteen months are tabulated on the left. They are shown graphically on the right with areas proportional to $r|r|$. June is repeated.

The higher correlations in Table 3.1 are clustered toward the top of the table, which indicates that the closer stations are better correlated with each other. They are also clustered in the Autumn and Winter months. Only in October does the average correlation over the whole network match that in June but as September and November also have moderately high correlations this appears to be more a characteristic of the season than of a short period of only a few weeks. In May, July and August the correlations are generally low. This behaviour may be a consequence of the convection which produces Spring and Summer rain. Such convection, which occurs in cells of small horizontal extent, may produce heavy rain at one station while other stations tens or hundreds of kilometres distant have no rain. Again it should be noted that the monthly sample consists of the sum of rain from as many as fifteen rain days. As shown in Figure 3.2, not only does the average amount of rain per rain day increase steadily with time during this season but so also does the average number of rain days per month. This makes the singularity of the high June correlations the harder to explain.

Table 3.2, of similar form to 3.1, shows the correlations between the amounts of magnesium. Again the higher correlations are clustered toward the top of the table and in the Autumn and Winter months. After low correlations in July the correlations increase through August while correlations in precipitation are still low. The highest correlations in magnesium occur in September, well before the correlations in precipitation have reached their peak. It is evident that the pattern of correlation in magnesium during the Summer is not simply a reflection of that in precipitation amounts as it might be if the quantity of precipitation were the dominant factor and not the concentration of magnesium in any month. The Spring is a time of consistently low correlations in magnesium amounts.

Table 3.3 shows the correlations between the amounts of calcium. Once again the higher correlations are clustered toward the top of the table, for shorter inter-station distance. Between October and January the correlations at all distances are moderate or high. However, this pattern of high correlations of calcium amounts in the Winter differs from the others in that it starts two months after the high correlations for magnesium and one month after those for precipitation. In April, which we saw in Figure 3.1 to be a peak month in the concentration of calcium, there is also a moderate or high correlation between stations at all separations. July is also a month of moderate or high correlations in calcium while seeing a lower correlation in rain amounts and no correlation in magnesium. If the earlier discussion of Figure 3.1 left any doubt that calcium and magnesium aerosols enter the atmosphere from different sources, or through different processes, such doubt should be dispelled by the dissimilarity of the patterns of correlation in the removal of calcium and magnesium.

Table 3.4 shows the correlations between the amounts of sodium, the only element in this set which is believed to come principally from the sea. Once again the higher correlations are clustered toward the top of the table, for shorter inter-station distances. The occurrence of months of high correlations at all distances is less evident here than in the previous tables. There is no June maximum with sodium, which suggests that the phenomenon which produces the high June correlations in precipitation, magnesium and calcium does not greatly influence the transport and washout of salt aerosol from the sea. Rather than

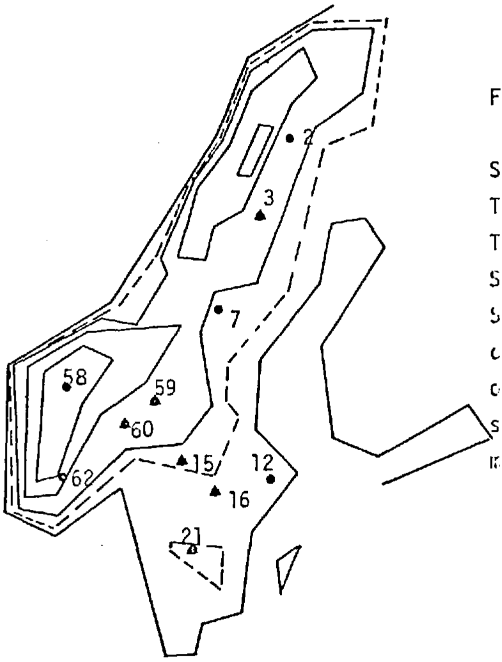


Figure 3.2

Simplified contour map of Norway and Sweden. The contours are drawn at intervals of 500 metres. The 250 metre contour is shown as a broken line. Stations of the Inland Network are shown by stars. Several other inland stations are shown by solid circles. Note that the saddle region, at a height of less than 1000 metres, lies between northern and southern highland regions which reach over 1500 metres.

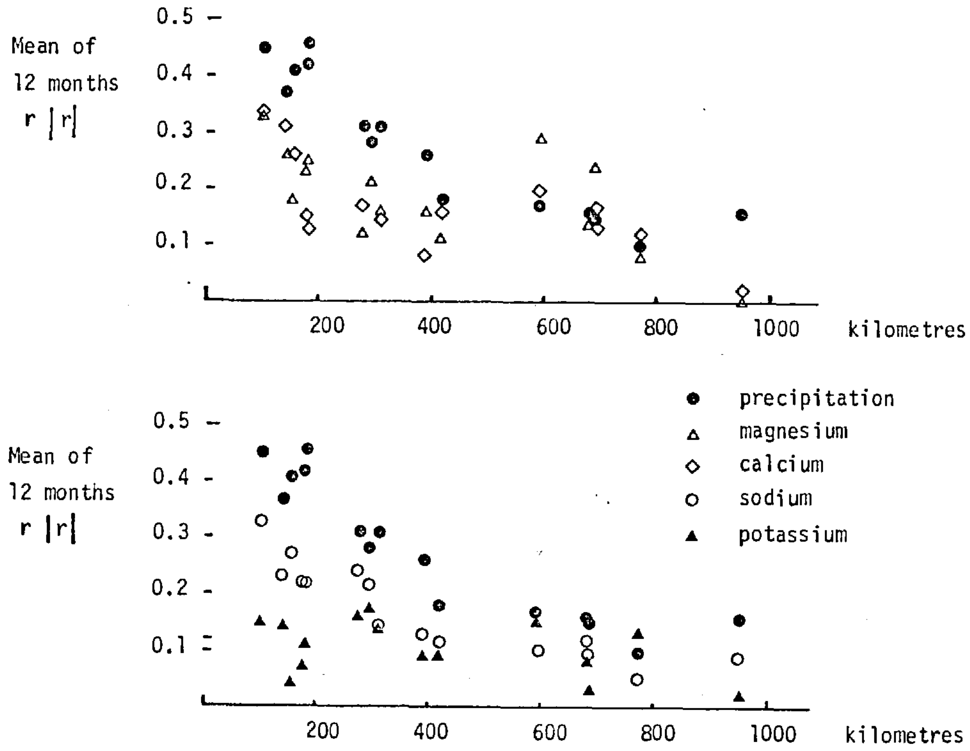


Figure 3.3 Mean correlations between pairs of Inland Network stations, from the final columns of Tables 3.1 to 3.5 . The average correlation decrease with increasing distance except in the case of potassium, for which it is low at all distances. The five most distant pairs all include station 3 which is situated on the southeast slope of the northern highlands.

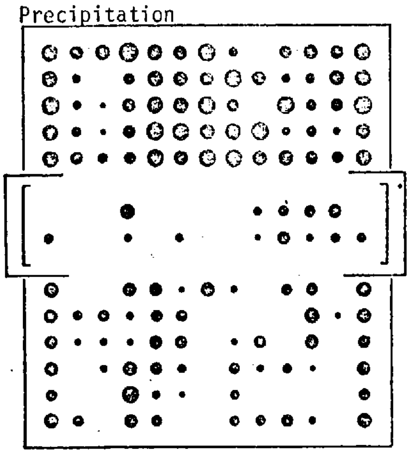
having a Summer minimum in correlations as do precipitation, magnesium and calcium there seems to be a slight Summer maximum of correlations in sodium. This includes station 3 as well as the southern stations. Note the low correlations in June, July and August for all station pairs which include station 16. November and December appear to be months of higher correlations.

Table 3.5 shows the correlations between amounts of potassion and is interesting for its lack of structure comparable with the other tables. There are few high correlations between amounts of potassium. The moderate correlations are scattered about the table in a manner which appears to be almost random. This implies that the closer pairs of stations are no more in harmony in their receipt of potassium than are the more distant and that there are no major factors of specific calendar months which cause the delivery or non-delivery of potassium to all or most of the Inland Network stations. This type of behaviour is to be expected of an element the sources of which are local and random in their rate of production. If we assume that potassium is such an element then the tendency for positive correlations which may be seen in Table 3.5 could be taken as typical of that generated by biases in chemical analysis and the many other minor factors in the system which might tend to generate positive correlations. These same factors must also have influenced the data on the other elements, in which case they will have served to degrade any patterns which are generated by systematic features of the production, transport and removal of those aerosols. In other terms Table 3.5 is an indication of the noise which is generated in such a system of precipitation collection and analysis while Tables 3.1 to 3.4 show the strength of signal which may remain in the presence of such noise. Table 3.5 may in fact contain a signal also but the signal-to-noise ratio is so low that we should be loath to comment on the form of the signal.

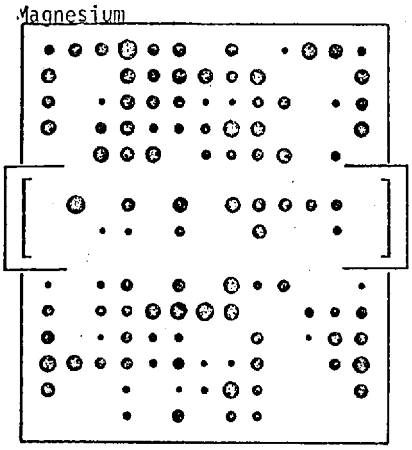
So far I have treated the correlation as if it should be a simple function of distance, decreasing monotonically with increasing distance between stations. Such an approach would be valid if the data were for an array of stations on a large level plain. Where the topography influences the patterns of precipitation we cannot expect two stations which are on opposite sides of a major watershed to be related to each other in the same way as a pair of stations at the same separation within the watershed. And similar effects may arise in more subtle ways. The evidence to support this view may be found in the results which have been presented already. I will discuss that in the last section of this chapter after a brief consideration of the large-scale topography of Scandanavia.

Figure 3.2 shows a map of Scandanavia with the simplified principal contours at intervals of 500 metres. The contour at 250 metres above mean sea level appears as a broken line. The high ground in Norway and Sweden is in two regions, in the north and in the south, each of them having an appreciable area above one thousand metres. Between these is a saddle region at a height between 500 and 1000 metres. Thirteen inland stations of the EACN are marked, the six stations which have already been identified as members of the Inland Network being distinguished from the others. These six are all to the east of the highlands. Five of them are shielded from the ocean by the southern highlands and one, station 3, by the northern highlands. All are on the slope which faces southeast across the Baltic and into the continental interior.

Precipitation



Magnesium



Calcium

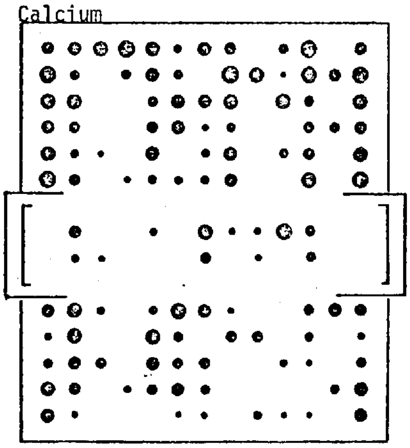
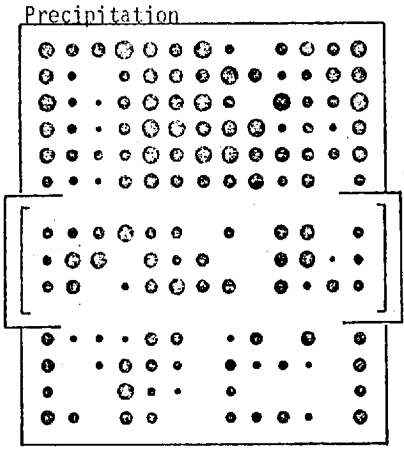


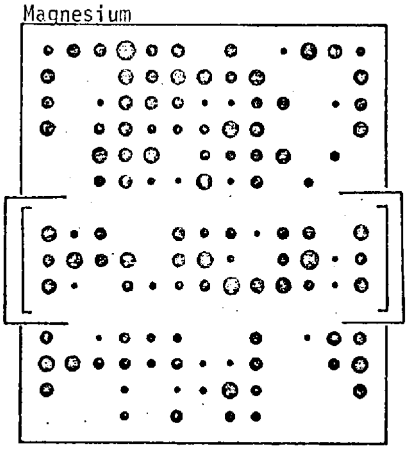
Table 3.6

Correlations between Station 58 and 2 stations of the Inland Network for precipitation, magnesium and calcium compared with the Inland Network correlations, reproduced from Tables 3.1, 3.2 and 3.3 .

Precipitation



Magnesium



Calcium

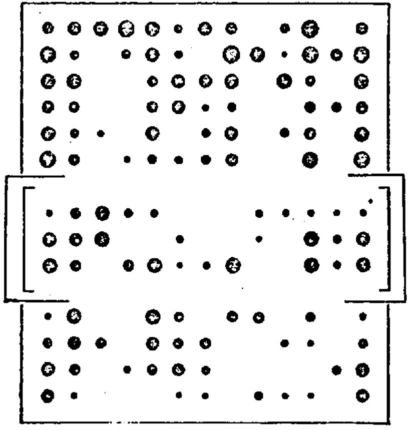


Table 3.7

Correlations between Station 7 and 3 stations of the Inland Network for precipitation, magnesium and calcium compared with the Inland Network correlations, reproduced from Tables 3.1, 3.2 and 3.3 .

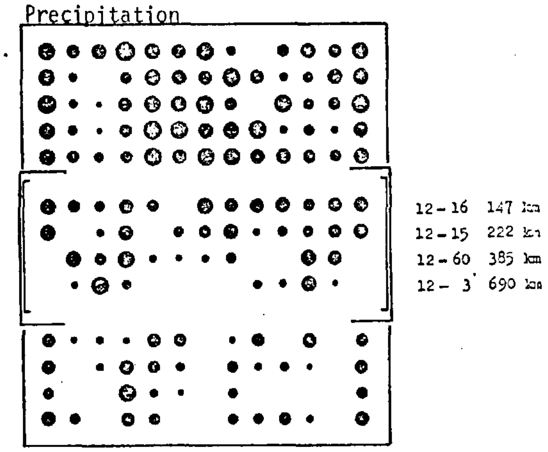
If the distance were the only factor determining correlations between stations then station 3 would be less correlated with the other five than are they with one another. The greatest distance between members of the southern group of five is between stations 21 and 59, a distance of 418 km while the shortest distance between station 3 and one of the southern group is 594 km to station 59. But as seen in Figure 3.3, the correlations between station 3 and the southern group are much higher than would be expected from an extrapolation of the results from the southern five. This Figure shows the data from the last columns of Tables 3.1, 3.2 and 3.3 plotted against the distance between stations. On this evidence station 3 is much more clearly a member of the Inland Network than is station 21. Looking back to Figure 2.4(c) we can see that this situation was already evident in the analysis of the ratio of annual amounts of calcium and magnesium.

We have now identified a pattern in precipitation amounts and chemistry which characterize what I have chosen to call the (Scandanavian) Inland Network. Further stations might be identified as conforming to this pattern, in which case they would be recognized as also belonging to the Inland Network. Its recognized extent would be broadened in this way. Other stations which do not conform to the pattern, and therefore lie outside the Inland Network, would help to identify its boundaries.

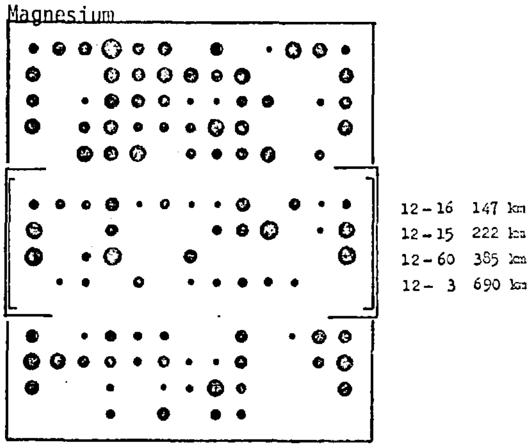
Consider station 58 which is close to the southern region of the Inland Network. The correlations between station 58 and stations 60 and 15 for precipitation, magnesium and calcium are superimposed upon the pictorial form of Tables 3.1, 3.2 and 3.3 and presented as Table 3.6 . Consideration of just two stations is sufficient to disprove station 58's conformity to the pattern of the Inland Network for it differs in two respects in all three elements. The high correlations in June are totally absent in all three tables. The high correlations in the winter, which are distributed slightly differently in each of the tables, are not in general found in the station pairs 58-60 and 58-15 although in the spring the correlations across the watershed become comparable with those within the Baltic catchment. Station 58, a short distance to the west of the watershed, does not conform to the pattern of the Inland Network which, as far as we know, lies entirely on the east slope.

Station 7 lies on the east slope between station 3, the single northern station which is definitely a member of the Inland Network for it has high correlations in the appropriate months at distances between six hundred and a thousand kilometres, and the most northerly of the southern stations. For all three elements the magnitudes of the correlations between station 7 and the three nearest Inland Network stations are comparable with those within the Inland Network. However, their distribution between months is in some ways significantly different. The June correlations in all three elements are consistent with station 7 being a member of the Inland Network but whereas the Inland Network has low correlations in one or two summer months in each element the correlations of station 7 with its nearest neighbours are generally high. And in the winter the fit of the station 7 correlations with the pattern of the Inland Network is poor. In the spring months the correlations fit the Inland Network pattern a little better.

Precipitation



Magnesium



Calcium

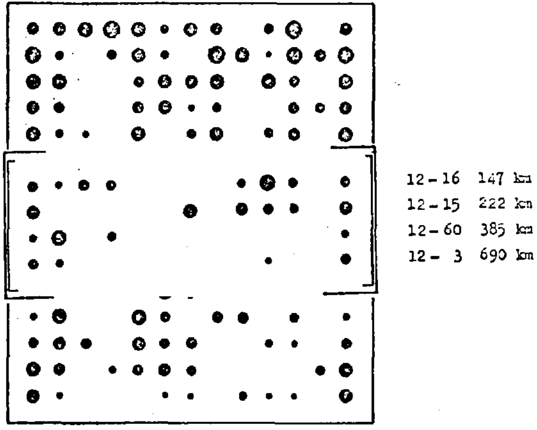


Table 3.8

Correlations between Station 12 and 4 stations of the Inland Network for precipitation, magnesium and calcium compared with the Inland Network correlations, reproduced from Tables 3.1, 3.2 and 3.3 .

We may thus conclude that although station 7 has some features in common with the Inland Network it is not a full member. Figure 4.3 and Appendix C show that in seasonal distribution of amounts of precipitation station 7 is typical of east slope stations from Karesuando in the extreme north of Sweden to Jonkoping in the south. The summer precipitation at station 7 is well correlated with that on the east slope to north and south of the saddle region while the pattern within the southern region is fragmented, especially in August. If the Inland Network pattern did not so clearly include station 3 we should be tempted to consider it a phenomenon confined to the southern set of five stations. The fact that the Inland Network pattern is significantly weaker in the saddle region and is re-established on the east slope of the northern highlands suggests that it is the result of large scale air movements and transport of particles over long distances. The topography on a scale of hundreds of kilometres also plays a part in generating the pattern.

The "signal" of the Inland Network is only of moderate strength. It is not very much greater than the noise level which was indicated by Table 3.5 . This factor makes it difficult to identify its boundaries. The German and Belgian data must be rejected for use in an analysis such as this for the modest strength of the signal to be expected of the atmosphere would be swamped by the spurious signal of varying standard of laboratory analysis which was indicated in Chapter 2.

Station 12 lies low on the east slope of the southern highlands. It fits the Inland Network pattern of correlations in June, as shown in Table 3.8, but in other respects the fit is quite poor. (The nature of the June phenomenon of high correlations is considered further, but inconclusively, in Appendix C.) The fit of the calcium correlations in winter is especially poor. It seems that the southern region of the Inland Network does not extend right to the foot of the slope, although it does extend down as far as station 16. The geographical extent of the Inland Network remains undetermined and it seems likely that the basic nature of the phenomenon precludes its strict delineation. We can say that it is an extensive pattern for which there are plausible explanations. In the next chapter I present a more robust analysis of the chemical character of precipitation at stations along east-west and north-south cross-sections through the Inland Network and far out into the North Atlantic in order to elucidate other aspects of the washout of sea salt and soil aerosols by precipitation.

Chapter 4. Aerosol from the land and from the sea.

In the previous chapter I have presented evidence for broad scale patterns in the amounts of precipitation, calcium, magnesium and sodium. Our consideration of these patterns in conjunction with the topography of Scandanavia has given us cause to believe that they are generated by the influence of topography on the amounts of precipitation from, and the aerosol content of, different airmasses. We must hold one strong reservation about the validity of such evidence for it may be strongly influenced by either one of two types of error which have been shown elsewhere in this thesis to occur in the data of the European Air Chemistry Network.

The errors in Belgian and German analyses of calcium and/or magnesium which were discussed in Chapter 2 persisted in much the same form for a year or more before changing from a consistent underestimate of the amount of calcium (say) at all stations to a consistent overestimate in the following year or years. Such an error will affect all calendar months equally. It will also affect the correlation of station pairs at all separations equally, producing spuriously high correlations throughout a table such as Table 3.3 . For this reason it has been considered inadvisable to us Belgian and German data for analyses such as those seen in Chapter 2. The errors in Swedish sodium or chloride analysis which are discussed in Chapter 5 affect the patterns of correlations in a different way. These errors have been shown to occur in data for a number of stations, or perhaps for all stations, in the network during one month. They might occur during two successive months on some occasions but do not, on the evidence of the analysis in Chapter 5, persist for longer than that. Such errors will enhance the correlation at all inter-station distances for a single calendar month but will not contribute equally to correlations in all calendar months. It is possible that the large amounts of magnesium recorded for the Inland Network in August and September 1965 reflect such an error. This would spuriously raise the correlations shown for those months in Table 3.2 . It would not affect the variation of correlation with distance to the same extent.

In this chapter I will present analysis of the monthly amounts of sodium and calcium, which I have selected as principal elements from the sea and land respectively, which does not involve the calculation of correlations between stations. The findings of the previous chapter are used to guide the analysis and it is demonstrated that the principal results of that chapter concerning topography and washout of different elements are confirmed by this second and more robust analysis.

Wind and waves, which generate sea salt aerosol, reach their maximum intensity on the mid-latitude oceans during the Winter, as is seen in Appendix B. It is therefore to be expected that the quantity of sea salt in precipitation also reaches a maximum during the Winter, at least at maritime stations. We should expect that the same is true of the quantity of sea salt which is carried across the coast and over the continent but its subsequent fate at increasing distances inland is not clear. I will now consider this question, taking sodium as the measure of the amount of sea salt. I will also consider the amount of calcium in precipitation over both the land and the sea, having selected this

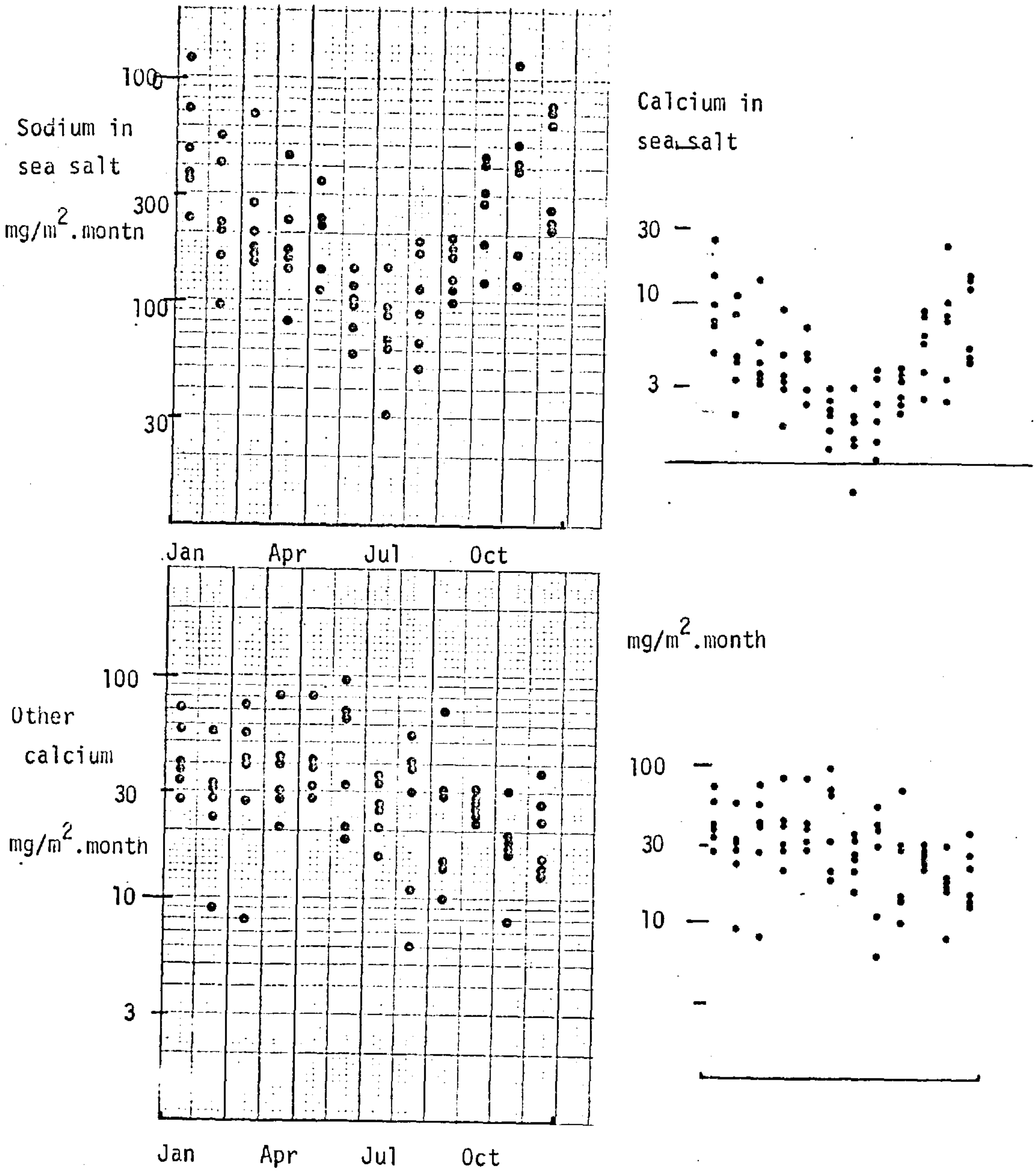


Figure 4.1 Method of estimating the amount of calcium from the sea, derived from the amount of sodium, and calcium from the land. Data for EACN station 253, Clones in Eire.

element as a characteristic constituent of the land-origin aerosol. Where maritime stations are studied the amount of calcium coming from the land will be considered to be the total amount of calcium less the amount estimated to have come from the sea, assuming this to be in strict proportion to sodium in the relative amounts which are found in sea water.

In this analysis I present the basic data on sodium and on calcium in a diagram of a standard form. This is quite unlike the analysis of the previous chapter in which a derived statistic - the correlation coefficient - was calculated in order to portray a subtle characteristic of the basic data. In that analysis the possible effects of a small group of systematically erroneous values could not be distinguished in the final results from some effects of the real atmosphere. In this analysis we keep the great advantage of the eye's ability simultaneously to discern patterns and reject anomalies in data when it is presented in a suitable form. This allows discrimination which is of far greater sophistication than is possible with a formal group of derived statistics.

The standard diagram, which is seen in Figure 4.1, shows the monthly amounts of calcium from the sea and calcium from the land at one precipitation station of the EACN over six years. The calcium from the sea is estimated as 0.038 times the amount of sodium. Thus the quantity shown in the diagram is one twenty sixth of the amount of sodium and one ninetieth of the total amount of sea salt. All January amounts are plotted on one vertical line as are all February amounts and so on. The amounts are given on a logarithmic scale in milligrammes per square metre per month. The entire period's results are adjusted to the quantity assuming the same overall average concentration and an overall average precipitation amount of 1000 mm per annum. Where possible the years from 1960 to 1965 have been used.

Before we consider a set of such diagrams which describe a number of stations along a band of latitude let us look at some of the features of this single diagram for Clones in central Ireland which is station 253 of the EACN. On the left is the diagram which has been plotted directly from the tabulated data. On the right is the final form with the scale on the upper part of the diagram shifted up by a factor of 26.3 to indicate the amount of calcium assumed to have come in the sea salt and then shifted down by a factor of 0.982 to allow for the average annual precipitation over the six years from 1961 to 1966 being 982 mm rather than the 1000 mm to which these diagrams are standardized. The lower part of the diagram on the right has been shifted only by this second factor.

Figure 4.1 shows the very strong annual cycle in the amount of sea salt. The typical summer amounts are only one fifth of the typical winter amounts. In any named month the amounts in six years fall within a twofold to fivefold range and the distribution within that range is reasonably symmetrical on the logarithmic scale. While the amounts of sodium in the upper left diagram exceed the amounts of calcium in the lower left diagram in all months the amounts of calcium from the sea, in the upper right diagram, are less than the amounts of calcium from the land, in the lower right diagram, in all months. The annual cycle in amounts of calcium from the land does not have the smooth variation which sea salt calcium shows, being simply a reduction from a typical value of forty milligrammes per square metre per month during the first half of the year to a typical twenty milligrammes per square metre per month during the second half.

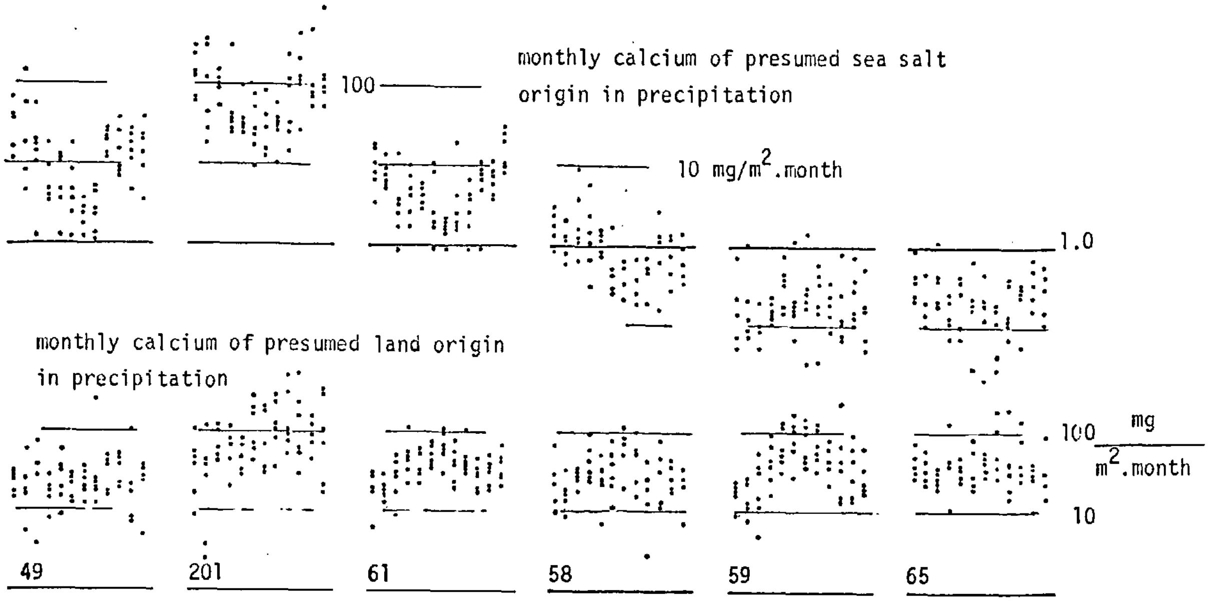


Figure 4.2

Monthly amounts of calcium from the sea and calcium of presumed land origin at six stations as shown on the map at right. The data are for the years 1960 - 65.

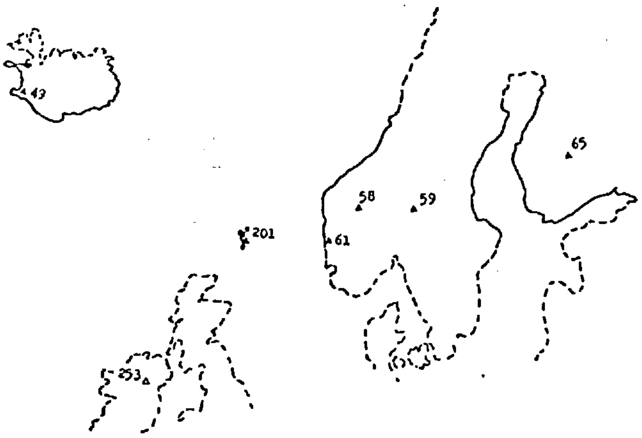


Figure 4.2 consists of six diagrams of the same form as Figure 4.1, describing a chain of stations which stretches from Iceland to Finland. The stations, which are shown on the inset map, belong to three different subsections of the EACN. Samples from stations 49, 61, 58 and 59 are analyzed in Stockholm while those from station 201 are analyzed in London and those from station 65 have been analyzed in Helsinki since 1961. Stations 49 and 201 are on islands, Iceland having an area of 1.0 x 10^5 km^2 and the Shetlands an area of 1.4 x 10^3 km^2.

Considering first the amounts of sea salt, there is a strong trend to lower amounts in going from the Shetlands to Finland, decreasing steadily with distance from the coast. Between stations 201 and 65 the amount of sea salt decreases by a factor of three hundred. The factor of four between the amounts at stations 49 and 201 may be due to the closer proximity to the coast of the station in the Shetlands. It may be due in part to the overestimate of the amounts of sodium at British stations which has been discussed in Chapter 8. With the one exception of station 59 all stations experience an Autumn and Winter maximum in sea salt amounts. This starts one month earlier at the island stations than at the mainland stations. The abrupt change between August and September in Iceland is conspicuous. I will defer consideration of the anomalous results at Station 59 until later in this chapter when it will be demonstrated that those results are an integral part of the Inland Network phenomenon.

There is a striking similarity between the patterns and amounts at stations 49 and 61 in Figure .2 and station 253 in Figure 4.1 . I suggest that this represents the characteristic pattern of sea salt concentration in rain at maritime sites around the northeast Atlantic where there is no strong local source due to waves breaking on nearby coasts. At Lerwick the windward coast is only five kilometres away and oriented across the prevailing wind and Atlantic swell. This may be the source of the additional salt at station 201.

Junge (1963) has suggested, from the observation of sea salt in North America and elsewhere, that the concentration in the air, and consequently in the rain, reaches a constant "plateau" value after traversing sufficiently far from the coast and that this is representative of large areas of the interior of the continents. It seems likely that the same is true of the maritime regions when the contribution of the large particles which have a very short atmospheric lifetime is excluded. This may be done by taking island stations a modest distance inland, or platforms at sea which are sufficiently high above the waves. One attempt to do this over the North Sea is described in Appendix B. If station 65, more than one thousand kilometres from the Atlantic ocean, is representative of the continental plateau while stations 49, 61 and 253 are representative of the maritime plateau the mean annual values of the two plateaux differ by a factor of about fifty. The factor is slightly lower than this - perhaps thirty five - in the summer and slightly higher - perhaps seventy - in the winter. This difference is not consistent with Junge's belief that the change in concentration of sea salt in air with distance inland is due more to dispersion upward than to washout for dispersion and dilution is greater in the summer than in the winter. However, it is possible that during the summer a larger fraction of the sodium in Finnish precipitation comes from the land and not from the sea.

If the washout of sea salt aerosol is everywhere a maximum in the winter then the production must also be at its greatest rate in the winter. We had already deduced this from a knowledge of wind and waves. Now we can estimate the magnitude of the winter excess of production on the north Atlantic for on both land and sea the amount of sodium in winter precipitation exceeds that in summer by a factor of between four and ten. It is clear that local differences in the distribution of precipitation through the year must render this an imprecise number but we can be confident that the estimated order of magnitude of difference is correct for it is repeated at island, coastal and inland stations along a belt of latitude two and a half thousand kilometres long. The same pattern has been reproduced in four laboratories which operate independently of each other.

Consider now the calcium from the land in precipitation at the same set of stations. This is shown in the lower half of Figure 4.2 . At the two island stations the amount of calcium from the sea in winter equals the amount from the land. At these stations during the summer, and at other stations throughout the year, the calcium from the land is in considerable excess. Thus it is only at the island stations during the winter that the amount of calcium from the land differs significantly from the total amount which is measured. The adjustment for sea salt is otherwise small or negligible and uncertainties about the amount of sea salt due to poor sodium analyses are of no significance. They might be significant for island sites during the winter.

Although I have referred to this calcium in excess of the quantity in sea salt as "calcium from the land" it is yet to be demonstrated that it does come from the land and not from some secondary oceanic source. Such a source might be the organic surface-active material which accumulates at the sea surface. When this film is in a compressed state it damps capillary ripples, giving the water surface the streaky appearance known as slicks. It is conceivable that such a compressed film could hold fragments of detritus from plankton which may be rich in calcium, thereby enhancing the calcium content of any aerosol generated by the bursting of bubbles at the surface. It is to be expected that the higher organic productivity and calmer conditions of the ocean in summer produce extensive areas of such surface films more often than do winter conditions. If this mechanism were to contribute an appreciable amount of calcium to the aerosol over the oceans we should expect to see its greatest effect during the summer. In this respect it may not be distinguishable from a land source which we might expect to also reach maximum aerosol production in the summer. Appendix B gives the results of analysis of aerosol and precipitation collected above the North Sea which suggest that there is some enrichment of calcium in sea salt but too little to account for the summertime enrichment of a factor of eight in Iceland and five in the Shetlands. For simplicity I will continue to refer to "calcium from the land" while recognizing that some of it may be an enriched fraction in sea salt aerosol.

The similarity of the calcium amounts at all stations shown in Figure 4.2 is noteworthy. Iceland receives slightly less, and the Shetlands slightly more than the mainland stations but when compared with the variation in amounts of sea salt these differences are very small. It is possible that the high values in the Shetland arise from the chemical analysis being in error or from a nearby exceptional source such as a road. Otherwise, the constancy of amount from a thousand kilometres out to sea to a thousand kilometres into the continent indicates that either there is a strong and equal local land source of calcium around each

of the six stations or that the calcium aerosol is distributed fairly evenly in the air along this band of latitude. The former possibility seems most unlikely for it requires that the few kilometres of land upwind of the Shetlands station contribute as much calcium aerosol to the station's precipitation as a few tens of kilometres in Iceland, a hundred kilometres in Ireland and a thousand kilometres in Finland. And this would have to persist at the Scandanavian stations even through the three months of the winter during which they are under snow, for the supply of calcium to those stations is scarcely abated during the winter. It is much more likely that the calcium aerosol is well mixed in the lower troposphere and that which is brought down in precipitation in Iceland, the Shetlands and Ireland has its origins in diffuse land sources distributed across the continents. In view of the westerly winds which are characteristic of these latitudes the calcium in Iceland's precipitation is more likely to come from North America than from Europe. Thus there seems to be a plateau in the concentration of calcium of land origin which extends across the north Atlantic and well into Scandanavia. There appear to be no intense sources of calcium within this region as there were local sources of sea salt at the coast of the Shetlands. Presumably there are such sources somewhere but as the distribution of particle sizes among the calcium aerosol at its point of production is likely to be quite different from that of sea salt the subsequent behaviour should also be different.

There is one very important factor which distinguishes the atmospheric cycle of land calcium from that of sea salt. The sea salt aerosol is generated in a region in which water is being actively evaporated into the air. The larger sea water droplets fall back into the sea but lose some of their water by evaporation before doing so. The remaining salt particles from the smaller droplets, which remain suspended in the air, are then associated with air which has become moist by the evaporation both from droplets and from the sea surface. Calcium aerosol is generated from a land surface which is dry and its production is probably favoured by the passage of dry air so that it is thereafter associated with dry airmasses which are less likely to produce rain or snow. Whereas the sea salt and moist air from the sea is likely to produce rain within a short time after its passage inland the calcium aerosol and dry air is unlikely to produce rain. This difference between the two aerosols may account for the two plateaux in sea salt amounts, the higher representing a steady state in the source region while the lower represents a diluted sink region, and the one plateau in amounts of calcium from the land which is unaffected by major coastlines even though they constitute a boundary to the source region. The longer atmospheric lifetime of the calcium aerosol which is inherent in this situation leads to it being better mixed in both the air and in the rain than is the shorter-lived sea salt aerosol.

I will now consider the seasonal variation in amounts of calcium. We have seen that the winter maximum in production of sea salt aerosol is reflected in the amount of sodium in rain over the ocean and the continent. The evidence on calcium from the land is less clear cut than this. Whereas stations 58, 59 and 61 in Norway show a clear summer maximum in calcium there is little seasonal variation at station 65 in Finland. Neither do the island stations exhibit a distinct summer maximum. We will see later that a number of Norwegian, Swedish and Danish stations do have a summer maximum in calcium but unless it can be shown that the amount in rain, integrated over a very large area on the scale of the North Atlantic and Europe, is at its maximum during the summer we cannot deduce that the summer is the time of greatest production of calcium aerosol.

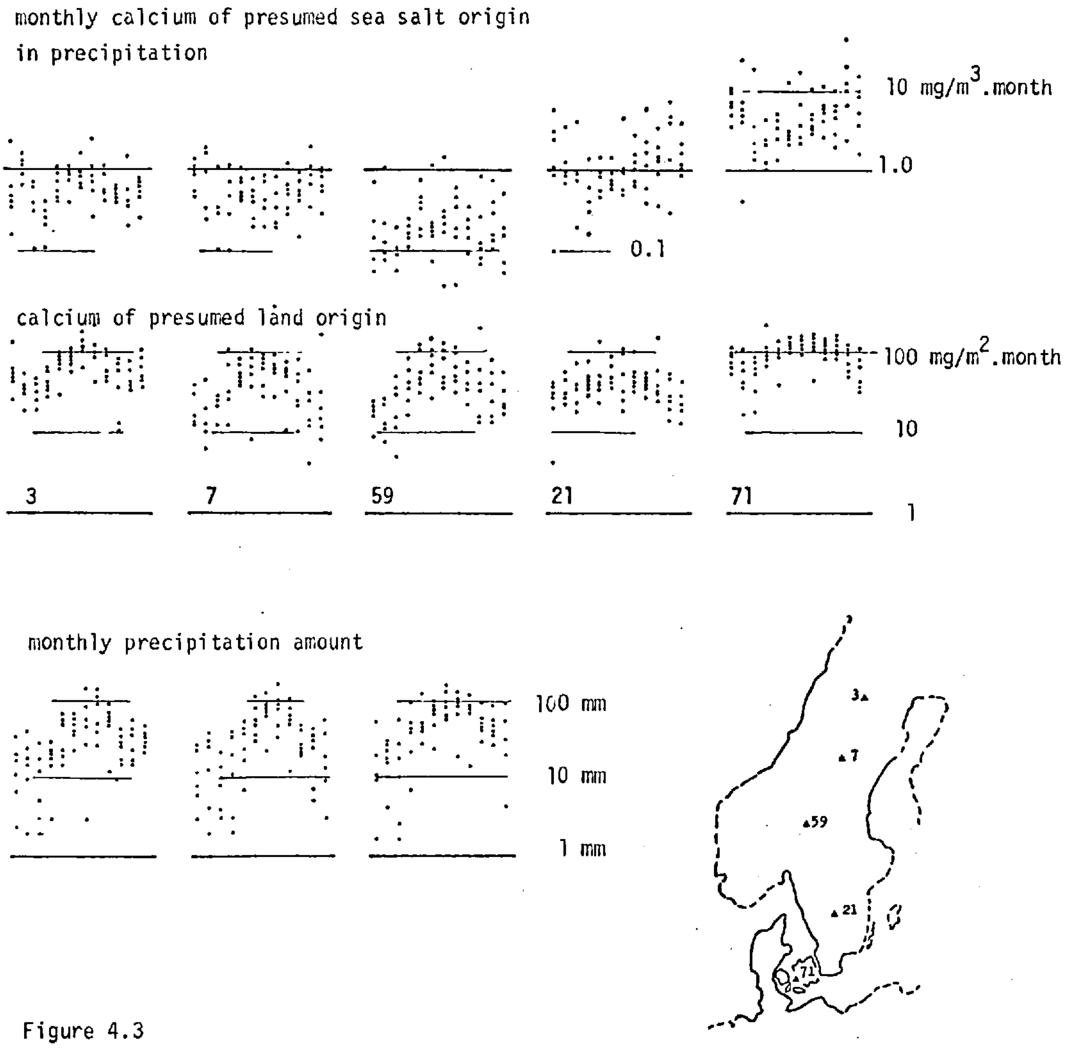


Figure 4.3

Monthly calcium in precipitation at five stations as shown on the inset map. Stations 3, 59 and 21 are of the Inland Network. Precipitation amounts also are shown for the three northernmost stations.

The atmospheric lifetime of calcium must be longer than that of sea salt to produce the better mixing which is evident. However, the difference is possibly only a factor of two or three, a week or two compared with a few days. This would not smooth out a seasonal variation in source strength by varying the amount of calcium which is stored in the atmosphere. If some land areas which are sources of calcium aerosol contribute only in the summer, then either their contribution is of little significance on the hemispheric scale or there are other sources which have a comparable contribution to make in the winter. It is reasonable to assume that continuous snow cover on the sub-polar continent prevents the production of calcium aerosol from the underlying land. Thus there must be a poleward transport of calcium from tropical or temperate regions during the winter.

Before leaving Figure 4.2 two features which distinguish station 59 from the other five should be noted. At this station, which is situated on the eastern side of the southern highlands, the greatest amounts of sea salt come in the summer. Also, the spring and summer peak in calcium amounts is more pronounced here than elsewhere. In the consideration of some characteristics of Scandanavian precipitation in Chapter 10 I will demonstrate that this peak is not due solely to the difference in precipitation amounts. These two characteristics will now be shown to be a fundamental part of the properties of the Inland Network.

Figure 4.3 shows the annual pattern of sea salt and calcium in precipitation at five stations in a longitudinal belt inland of the Scandanavian highlands. Stations 3, 59 and 21 are members of the Inland Network. Station 7 has been assessed as a possible member of the Inland Network but found to differ from the pattern of correlations between stations which was described in Chapter 3. Station 71, which is in Denmark and for which the samples were analyzed in Stockholm during this period, has not been assessed as a possible member of the Inland Network.

It is evident that station 59 receives significantly less sea salt than any of the other stations, an amount which we saw in Figure 4.2 to be commensurate with that found in precipitation in central Finland. Station 71 is an island station in the Baltic and it is therefore not possible from this analysis to say whether the considerable amount of sea salt which it receives is of local origin or has been borne there by the wind from the North Sea. Stations 7 and 71 show the winter maximum of sea salt which was characteristic of five of the six stations represented in Figure 4.2 . In this respect their receipt of sea salt is in accord with the rate of production at sea. However, stations 3 and 59 show a clear summer maximum in sea salt amounts which is out of step with the rate of production. This characteristic of their precipitation chemistry must be imposed by a selective mechanism of transport which prevents sea salt reaching these stations during the winter. This mechanism does not prevent sea salt reaching station 7 at the same time.

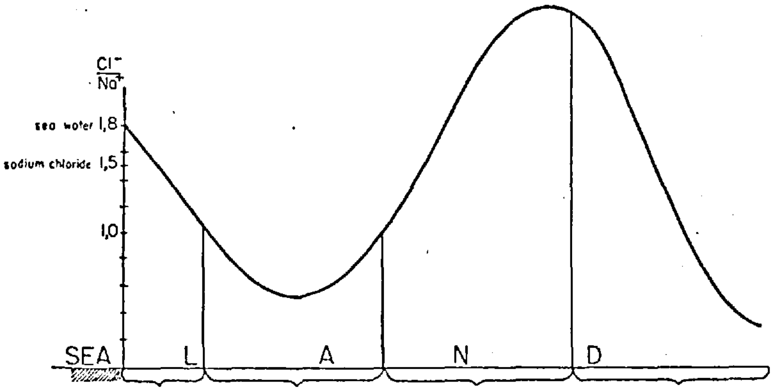
The annual pattern of sea salt at station 21 has less in common with the Inland Network stations than with the others. In five of the six years shown in Figure 4.3 the winter amounts exceeded the amounts typical of the summer. However, in the other year, not necessarily the same year for each month, the October to March amounts of sea salt fell well below the typical summer value, in the range which is characteristic of other Inland Network

stations. We expect such behaviour of stations in the boundary region between the Inland Network and the surrounding area.

Taken in conjunction with the topography of Norway and Sweden the patterns of sea salt at the ten stations shown in Figures 4.2 and 4.3 suggest that the southern and northern highlands effectively shield large areas from sea salt during the winter. The saddle area in central Norway does not greatly impede the flow of maritime air during the Winter. The southern boundary of the area which is shielded by the southern highlands is in the vicinity of station 21 and fluctuates with time. During the summer the maritime air containing sea salt penetrates into these regions either by passing directly over the highlands or by turning after entering Scandanavia across the central saddle and through the Skaggerak region. In Chapter 3 we noted the higher correlations of sodium amounts for stations of the Inland Network at all separations during the summer. This implies that the invasion of the Inland Network by sea salt during the summer tends to occur over the entire length of the Network at the same time. The failure of station 16 alone of the six Inland Network stations to fit this pattern is not readily explained in terms of long range transport and should perhaps be sought in local sources of contamination by sodium salts.

The annual pattern of calcium at each station in Figure 4.3 has the common feature of a summer maximum. This feature is shared with the Norwegian stations 58 and 61 on the western side of the mountains. However, as noted previously, there is no summer maximum either at the island stations or in Finland. Stations 3, 7 and 59 have more pronounced summer peaks than do stations 21 and 71 to the south which perhaps indicates that summer precipitation on the eastern slopes favours the washout of calcium particles. Stations 58 and 61 have rather less pronounced summer peaks. The generally higher concentrations of calcium at station 71, and their limited variation during the year, suggest that that station is closer to a source of calcium, perhaps to be found in the soil of central Europe.

It now appears that the region of the Inland Network is in fact two distinct areas with dimensions of some hundreds of kilometres and containing about six stations of the EACN. They are separated by a region of similar magnitude which contains fewer EACN stations. The land slopes up to the WNW to a ridge at a height of between one thousand and fifteen hundred metres. Where the slope is less or the height of the ridge is less the characteristics of the Inland Network are found no more. The height of the ridge is evidently the critical factor for sea salt transport but the slope may play a greater part in determining calcium characteristics. The Inland Network is shielded from maritime surface air during the winter. During the summer it receives a greater concentration of calcium in precipitation than does either a west-facing slope of the same mountain range or the more level ground of Finland. This may be a consequence of the formation of orographic clouds and precipitation in calcium-rich air from the south and east. The high correlations between station 3 in the northern sector and the stations of the southern section indicate that the air over a front of many hundreds of kilometres has similar amounts of calcium which may be washed out in precipitation. The same may be true of magnesium. Such homogeneity implies large source regions and long distances of travel, a characteristic of calcium aerosol which was inferred earlier on other grounds.



Condensation nuclei consist of NaCl and some other sodium salts.

Rains over the oceans and near coast.

Relatively small amounts of NaCl left for precipitation but other sodium salts still serve as condensation nuclei.

Showers and rains in maritime air some distance from coast.

Minute droplets of HCl or possibly certain chlorides such as H_4NCl, $CaCl_2$, $MgCl_2$, now serve as condensation nuclei.

Rains on the periphery of stagnant warm anticyclones or in modified maritime air masses arriving by way of central or even southeastern Europe.

Practically all HCl has disappeared. Small amounts of sodium added along continental trajectory, resulting in very low Cl/Na ratio and quite low salt content.

Precipitation from polar continental air masses.

Fig. 1. Schematic representation of the variations in the weight ratio of chloride to sodium in precipitation from an air mass moving in over the continent.

Figure 5.1 Rossby and Egner (1955) schematic representation of the action of the Cauer process in the dissociation of sea salt aerosol and the separated washout of sodium and chlorine.

Chapter 5. Sea salt sodium and chloride in precipitation

In Chapter 2 I considered the relative amounts of calcium and magnesium in precipitation. As these two elements occur in different proportions in the different reservoirs from which aerosol may be drawn, in particular from the sea and from carbonate rocks, the ratio of the two indicates the relative contributions of the various reservoirs to aerosol washed out of the air in precipitation. The consideration in this chapter of the ratio of chloride to sodium is prompted by a different interest. The sea is believed to be overwhelmingly the principal source of both of these ions in aerosol and therefore also in precipitation. Since both of them are well mixed in the ocean, their principal salts are very soluble and neither is adsorbed at the air/water interface it is to be expected that sea salt aerosol contain the two ions in the same ratio as they occur in sea water. The weight ratio of Cl/Na in sea water is 1.80, which I will signify by R_s. The ratio of Cl/Na observed in precipitation will be signified by R.

If the weight ratio in aerosol brought down in precipitation differs from R_s then either chlorine or sodium from another source has been added to the sample, chlorine or sodium originally present in the sea salt has been removed or the analysis is wrong. The contribution of sodium from the land, and chlorine from the soil or from coal, which may be of some local significance, will be considered in Chapter 6. In this chapter I will consider the evidence for the dissociation of sea salt aerosol and preferential washout of one component, a process which was first proposed by Cauer (1949) and which remains controversial to this day. I will re-evaluate the data from the fore-runner of the EACN which Rossby and Egnér (1955) believed was in support of the Cauer hypothesis but which appears to be incorrect in the light of more recent data. I will consider sufficient of the recent data to cast light on the effect, if any, which the Cauer process would have upon the chemical composition of precipitation. Finally I will consider the reality of the Cauer process.

Rossby and Egnér studied the distribution of sodium and chlorine in precipitation which fell on Sweden in each of the twenty four months between October 1948 and September 1950. Their principal concern in the paper of 1955 was to relate the amounts of those and other ions to the mean atmospheric circulation in each month. Figure 1 of that paper, which the authors considered to be a reasonable summary of their results, is reproduced here as Figure 5.1 for reference, with the caution that this and the next chapter will not support that form of relationship. I will discuss another aspect of their results which pertains to occasions represented by the left side of the diagram for occasions when precipitation falls from air which has just left the ocean. These occasions contribute the bulk of sodium and chlorine in the year's precipitation. I shall consider that if the analytical results on such occasions are shown to be grossly incorrect then we should not accept the details of the situations when the concentrations of sodium and chloride are much lower and more liable to errors of measurement. The data which I use here are the annual amounts of sodium and chloride during 1948 - 50 in the form in which they were published by Emanuelsson, Eriksson and Egnér (1954).

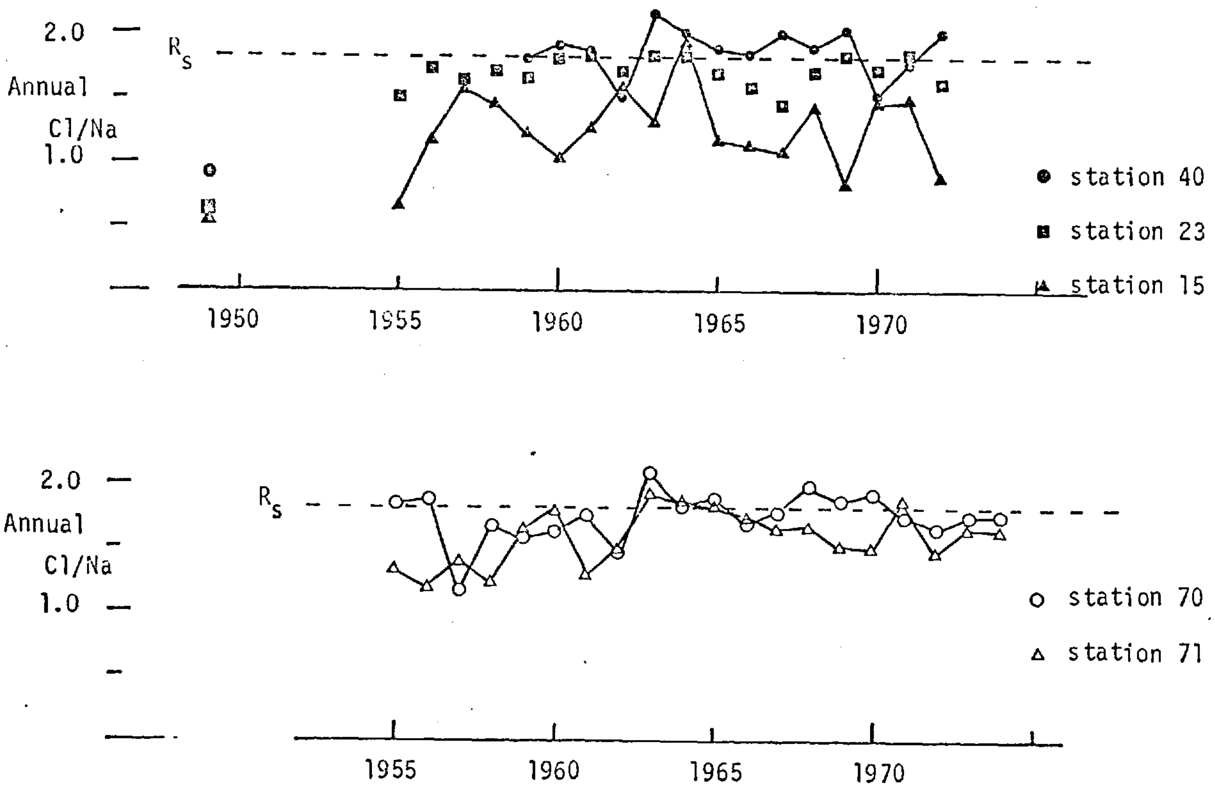


Figure 5.2 The variation at three Swedish stations and two Danish stations of the annual chlorine/sodium ratio in precipitation from 1955 to 1972. Rossby and Egners' results for three stations in 1948 - 50 are also shown. The sea salt ratio of chlorine/sodium is 1.80, denoted by R_s.

The results of Rossby and Egnér suggested that along the southwest coast of Sweden the sea salt brought down in precipitation has lost about one half of its chlorine in regions where between twenty and sixty kilogrammes of chlorine per hectare per year would be expected if it arrived in strict proportion to sodium. Futher inland, where seven to ten kg./ha.year would be expected the amount observed was only three or four kg/ha.year. Rossby and Egnér assumed that the chlorine which had failed to rain out on the coastal strip would be washed out further downwind, producing in that region an excess of chloride. This might be far inland or near the coast or even out to sea, depending on the trajectory of the air which carried it. As the mechanism is capable of producing regions near the coast where a net excess of sodium is rained out over the year there must also be areas where a net excess of chlorine is rained out during the year.

Eriksson (1960) refined the theory, allowing for the excess chlorine being lost from the air while it is yet over the sea. He assumed that the chlorine which departs from decomposing sea salt is transformed to gaseous Cl_2 or HCl. When this happens over the sea the gas diffuses toward the water surface which acts as a sink for either of these gases. An interesting alternative hypothesis is that some of it is transported to the stratosphere where it plays a part in keeping the ozone layer in balance. The process of absorption by the sea allows a coastal excess of sodium without there being necessarily an excess of chlorine in precipitation elsewhere on land. Realisation of this situation would make rather special demands on the life of the sea salt aerosol. It would have to be exposed for some time to the dissociating influence of ozone, sulphur dioxide or ultra-violet radiation and then carried close enough to the sea surface to lose a significant amount of its gaseous chlorine component by diffusion to the water surface.

Figure 5.2 shows the reason for doubting the validity of Rossby and Egnér's experimental results. The Cl/Na ratio at three sites in southern and central Sweden are given for the 24-month period in 1948-50 and for twelve-month periods at the same or nearby sites for years after 1955. Where the 1948-50 data indicated some 25 kg/ha.year deficit of chlorine the average of fourteen years from 1959 is an excess of 5 kg/ha.year at EACN station 40. At EACN station 5 the 1948-50 results show a chlorine deficit of three kg/ha.year, an amount which has not been equalled in any year since 1955. The average deficit for eighteen years from 1955 is 1 kg/ha.year. This quantity could equally well be expressed as a sodium excess of 0.5 kg/ha.year. For reasons which have been more fully discussed by Paterson and Scorer (1975b) it must be concluded either that the period 1948-50 was exceptional in this respect, and thus inappropriate for use in establishing a theory about the chemistry of sea salt aerosol, or that there was present in the system of precipitation collection and analysis an error which lead to a great overestimate of the amount of sodium in precipitation. It is not possible that the early results were correct and all subsequent results in error for results equivalent to the more recent set have been obtained by researchers in other parts of Europe and the USA.

A brief glance at the EACN data on sodium and chlorine in precipitation shows that there are considerable deviations from the sea salt ratio, R_s, many of which will be examined in this and the next chapter. As doubt has been cast on the principal traditional explanation of these results we should reconsider the nature of the deviations. In this chapter I will

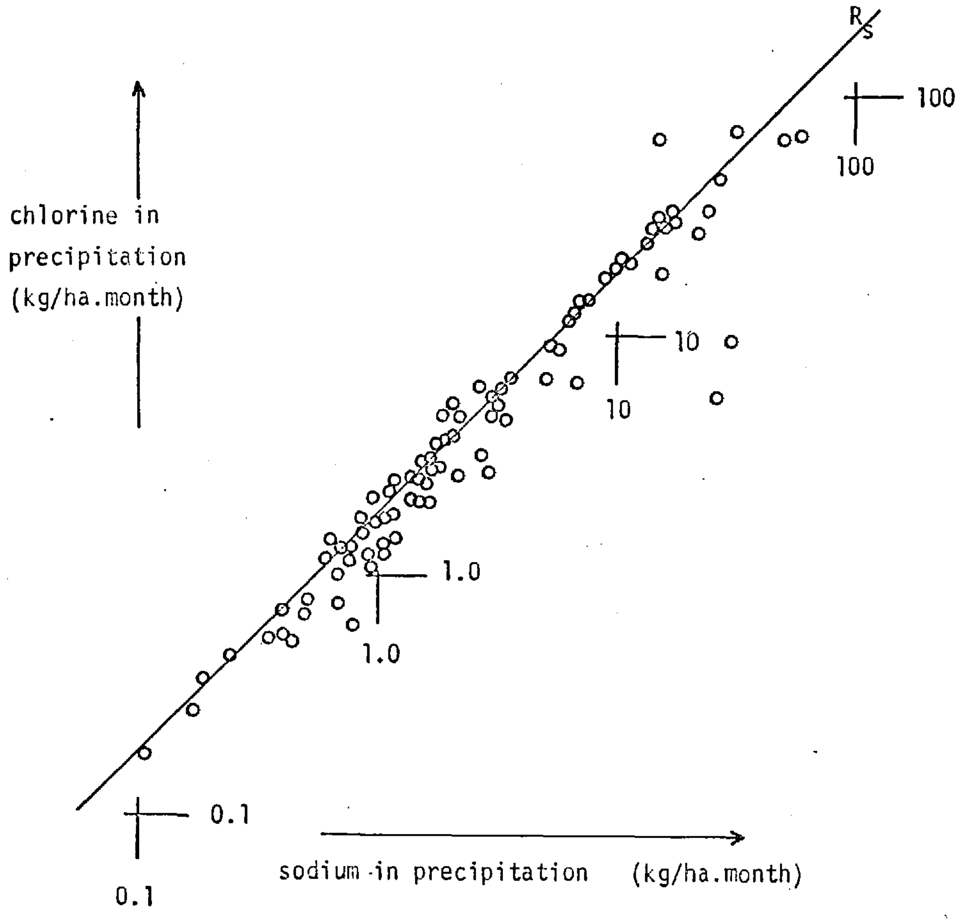


Figure 5.3 Monthly amounts of chlorine and sodium in precipitation at several coastal stations in southern Sweden in 1960 - 61. Note that deviations above and below R_s are evenly distributed among months with large and small amounts of salt in precipitation.

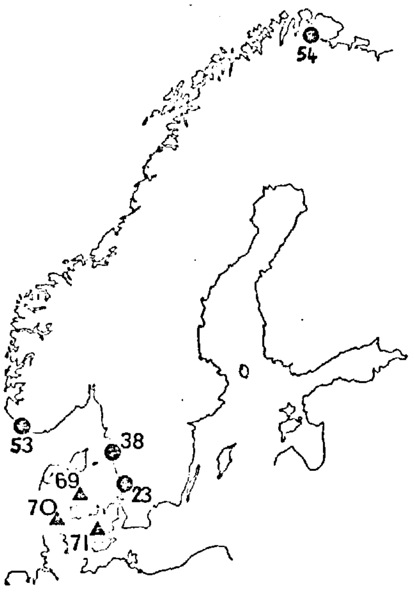


Figure 5.4

Seven stations for which monthly values of the chlorine/sodium ratio, denoted by R, are analysed in Tables 5.1 to 5.3 .

not seek to account for the month by month data as has been done by Munn and Rodhe (1971) for two Swedish stations. The following analysis is intended to establish the limits of confidence in the EACN data and the view which should be taken of precipitation analyses in which R is found to deviate from R_s.

Figure 5.3 shows, for three years, the monthly amounts of sodium and chloride at several coastal stations in Norway and Sweden. It should be noted that most of the observations fall very close to the R_s line over the range which covers almost three orders of magnitude of salt amounts. Deviations from R_s, both above and below the value, are equally distributed among months of large and small amounts of salt. In now considering the statistics of the deviations from R_s I will disregard the absolute amount of salt and treat only the values of R, the ratio of chlorine to sodium. We will consider the statistical distribution of deviations in time and determine whether the distribution which is observed could arise from geochemical phenomena or from laboratory factors.

Where deviations from R_s result from phenomena which modify the sea salt while it is suspended as an aerosol we expect that the same phenomena might affect samples at adjacent stations in the same month. Considering the stations shown on the map in Figure 5.4 it would be likely that a high value at station 38 is matched by a high value at station 23. High values might be expected also at stations 69 and 71 in the Danish network. It is possible that high values would be found also at the more maritime station, 53 in southern Norway and 70 in Denmark. It does seem likely that station 54, thirteen hundred kilometres away in northern Norway, would be reasonably independent of the six southern stations. Of course, similar considerations hold for low values of R. We expect some degree of coincidence between the southern stations and a greater degree of independence of station 54.

We might also find high or low values of R at single stations caused by intermittent local sources of sodium or chlorine. With a station spacing in the southern region of the order of two hundred kilometres it is to be expected that such sources must exist within one hundred kilometres of the station or they will make their effect felt at more than one station. Any such source should result in the nearby station exceeding R_s or falling below R_s, depending on whether it is a source of chlorine or of sodium, more often than do other stations in the group.

We should now consider the analysis of the samples. The samples are returned to the laboratory for chemical analysis and are usually analysed within the next month. Fresh bottles are sent out each month. Thus, a laboratory cause for deviation of the ratio from R_s could be either the dispatch of a set of bottles which already contain either sodium or chloride, or the deviation from correct calibration of the methods of either sodium or chloride analysis. By such means a set of high R values in March (say) could be caused by

(1) the dispatch of a set of bottles in February which are contaminated with chloride

(2) a genuine washout of excess chloride from the air over Scandanavia in March

(3) a deviation in the analysis during April toward either overestimating chloride or underestimating sodium.

	Norway & Sweden				Denmark		
	23	38	53	54	69	70	71
1959	•	•	•	•	•	•	•
	•	•	+	•	•	•	•
	•	•	+	+	•	+	-
	•	-	•	•	•	-	•
	•	•	•	-	•	•	•
	-	-	•	-	•	•	•
	-	•	-	•	•	-	•
	•	•	•	•	•	•	•
	•	•	•	+	•	•	•
	•	•	•	-	-	-	-
	•	•	+	-	+	•	•
1960	•	•	•	•	•	•	•
	•	•	•	•	•	-	-
	-	-	•	-	•	•	-
	•	•	•	-	-	•	•
	+	•	•	•	•	-	-
	•	-	-	-	•	+	+
	•	•	•	•	-	-	-
	•	•	•	-	•	•	+
1961	•	•	•	•	•	+	+
	•	•	•	•	•	-	-
	•	•	•	•	•	•	-
	-	-	•	•	•	•	•
	+	+	•	+	+	•	+
	+	•	-	•	+	•	-
	-	•	-	-	•	-	-
1962	-	-	-	•	-	-	-
	•	•	-	•	•	•	•
	•	•	•	•	•	•	•
	•	-	-	•	-	-	•
	-	-	-	-	-	-	•
	+	•	+	+	+	•	•
	•	•	•	•	•	•	•
	•	-	•	-	•	•	•
	•	•	•	•	•	•	•
1963	-	-	-	-	•	•	-
	•	•	•	•	•	•	•
	•	-	+	-	•	•	•
	•	-	•	•	•	o	-
	•	-	•	•	•	•	•
	•	-	-	•	•	•	•
	•	•	+	•	•	•	•
	+	+	+	•	+	+	+
	+	+	+	•	•	+	+

Table 5.1 This table shows the simultaneous occurrence of values of R at seven Scandanavian stations of the EACN during forty four months in five years.

- indicates the occurrence of R (defined as Cl/Na) less than 1.50

. indicates the occurrence of R between 1.50 and 2.16

\+ indicates the occurrence of R greater than 2.16

If (1) or (3) were to occur occasionally then it might affect some or all of one month's results at one laboratory. It is unlikely to coincide with a similar event at another laboratory. If (2) were to occur occasionally then we expect to find it in the same months in an adjacent set of stations for which samples are analyzed at another laboratory. I have selected the period 1959-63 for analysis because, for the first half of that time the Danish samples were analysed in Copenhagen with samples from twelve other Danish stations. The Norwegian and Swedish samples were analysed in Stockholm. The Danish analysis was discontinued in May 1961. After August 1961 the samples from Danish stations 69, 70 and 71 wer analysed in the Stockholm laboratory with the samples from about thirty Norwegian and Swedish stations. We can thus compare, for the same set of stations, the degree of coincidence of high or low values of R when analysed in one laboratory or in two.

Table 5.1 shows the occurrence of values of R less than 1.50 and greater than 2.16 during the sixty month period. Samples were collected at each of the seven stations in forty four months, during which time the Danish samples were analysed in Copenhagen for the first twenty one months. The results are expressed in the contingency tables, Table 5.2, which give the number of occasions on which none, one, two, three or four of the Swedish and Norwegian stations experienced low (or high) values of R tabulated against the simultaneous occurrence of low (or high) values of R at none, one, two or three Danish stations. The upper pair of tables covers the 21 months during which two laboratories operated. The lower pair covers the period when all samples were analysed in Stockholm.

The tables show that the two laboratories produce low (and high) values of R at different times. In the first period, when the analysis was carried out in separate laboratories, on none of the three occasions on which three or more of the Stockholm results fell below 1.50 did more than one Danish result fall below 1.50 . From the same table, 5.2(a)i, we see that of the five occasions on which two or three of the Danish stations recorded low results, on none of these did more than one Swedish/Norwegian station record a low result. Similarly with the occurrence of high values, in Table 5.2(a)ii, although the situation is less clear in this as only thirteen high values were recorded at the seven stations in twenty one months.

In the second period, when all samples were analysed in Stockholm, there appeared a clear association between low (or high) values in Denmark and low (or high) values in Sweden and Norway. Table 5.2(b)i shows that on four occasions were low values recorded for two or more stations in each section of the network. And Table 5.2(b)ii shows that on three occasions were high values recorcded at at least two stations in each section of the network.

Let us consider what this tells us about the records of the network. There is a factor, unrelated to the chemistry of sea salt aerosol or precipitation, which leads occasionally to the finding of Cl/Na ratios in precipitation which deviate significantly from the sea salt ratio. If we may take the simultaneous presence of three or four deviant values out of four possible as evidence of its occurrence then the results of most of the Norwegian and Swedish stations are affected by it on one month in four. It should be remembered that thirty other samples are analysed in the laboratory each month in addition to those considered in this statistical analysis. It is possible that in the months for which only one or two deviant values are recorded in Table 1 there were also smaller groups of precipitation analyses affected by the factor.

(a) Between January 1959 and April 1961, with Danish samples analysed in Copenhagen:

Low values
(R l.t. 1.50) 3 Danish

4 Swedish & Norwegian

	0	1	2	3	
0	6	1	3	1	11
1	3	2		1	6
2		1			1
3	2	1			3
4					0
	11	5	3	2	21

High values
(R g.t. 2.16) 3 Danish

4 Swedish & Norwegian

	0	1	2	3	
0	13	1	2		16
1	3	1			4
2		1			1
3					0
4					0
	16	3	2	0	21

(b) Between August 1961 and December 1963, Danish samples analysed in Stockholm:

Low values
(R l.t. 1.50) 3 Danish

4 Swedish & Norwegian

	0	1	2	3	
0	9	1			10
1	2	2			4
2	4		1		5
3			1	1	2
4		1	1		2
	15	4	3	1	23

High values
(R g.t. 2.16) 3 Danish

4 Swedish & Norwegian

	0	1	2	3	
0	16				16
1	2	1			3
2					0
3		1	2	1	4
4					0
	18	2	2	1	23

Table 5.2 Derived from Table 5.1 this set of tables shows the degree of coincidence of high and low values of the Cl/Na ratio at a group of stations in Denmark and a group in Norway and Sweden when the samples are analysed in two laboratories or in one laboratory.

In assessing the significance of the factor to the records of the EACN we must consider not the number of occasions on which it occurred but the number of observations which have been changed by the factor. The occurrence of three low values of R in Denmark and three in Norway and Sweden in one month, counted as one occurrence of the factor, will affect the records as much a single occurrence of R less than 1.50 on six different months. Seen in this light the tables 5.2(b)i and (b)ii indicate the following score for seven stations during twenty three calendar months:

	Number	Percentage
Total number of observations	161	
Observations of R between 1.50 and 2.16	96	60
Low values attributable to the factor	21	13
Low values not necessarily attributable	20	12
High values attributable to the factor	16	10
High values not necessarily attributable	8	5

If this interpretation is accepted then it appears that at least twenty three percent of the coastal sample analyses deviate significantly from R_s because of the factor, which we must presume to arise in the laboratory. No more than seventeen percent deviate from R_s due to other causes. In these circumstances it is not possible to find strong evidence for a deviation from the sea salt ratio due to natural causes such as were proposed by Rossby and Egner and by Eriksson. If any such deviation does occur at coastal stations then it is so subtle as to be masked by an artefact of the network.

One further item in Table 5.1 is to be considered. This is the degree of coincidence between high (or low) values at the northern station, 54, and high (or low) values at the other three Swedish and Norwegian stations. We express this in a pair of contingency tables which covers all forty four months. The observed number of occurrences of each possible combination is set beside the number which is predicted on the null hypothesis that high (or low) values of R occur independently of high (or low) values at the other three stations.

The results are given in Table 5.3 . The sample is too small to allow us to reach firm conclusions about the degree of association of high or low values at station 54 with high or low values at the three southern stations. However, all deviations of the observed values from the predicted values support the belief that any such association is a positive one, of high with high and low with low.

Scandanavia is not the only region in the European Air Chemistry Network for which evidence of the Cauer process has been claimed. Oddie (1960) considered that the results of precipitation sampling at Lerwick, which revealed a repeated tendency for R to fall below R_s in the summer, could be explained only by a process such as that proposed by Cauer. He argued that at such a strongly maritime site as Lerwick the amounts of sea salt were so great that values of R less than unity could result only from some influence acting on the

Table 5.3 The degree of association of low (or high) values of R at station 54 in northern Norway with low (or high) values at three southern stations, 23 and 38 in Sweden and 53 in Norway. The tables of observed frequencies have been constructed from the data of Table 5.1, covering 44 months between January 1959 and December 1963. The tables of predict frequencies have been calculated on the null hypothesis that low (or high) values of R at station 54 occur independently of low (or high) values of R at the southern stations. All samples were analysed in Stockholm.

Low values (R l.t. 1.50)

Observed

Stations 23, 38 & 53	Station 54: 0	1	
0	21	5	26
1	5	2	7
2	4	4	8
3	1	2	3
	31	13	44

Predicted

	Station 54: 0	1	
0	18.3	7.7	26
1	4.9	2.1	7
2	5.6	2.4	8
3	2.1	0.9	3
	30.9	13.1	44

High values (R g.t. 2.16)

Observed

Stations 23, 38 & 53	Station 54: 0	1	
0	32	1	33
1	6	1	7
2		2	2
3	2		2
	40	4	44

Predicted

	Station 54: 0	1	
0	30.0	3.0	33
1	6.4	0.6	7
2	1.8	0.2	2
2	1.8	0.2	2
	40	4	44

sodium or chlorine of the sea salt and not by the addition of sodium from some other source. Brownscombe and Porter (private communication) point out that the phenomenon to which Oddie referred has recurred in some but not all of the later years and that it does not occur in all of the three rain gauges now operating at Lerwick. I will consider its recurrence in 1971 at both Lerwick and Eskdalemuir. The evidence suggests that it might have arisen in the laboratory.

Precipitation sampling of the EACN form has been carried out in Britain since 1957 with the samples being collected by the Meteorological Office and sent for analysis to the Laboratory of the Government Chemist. The data has been published occasionally by the Stockholm laboratory. The most complete analysis of the British data yet published was that by Stevenson (1967). The samples have been analyzed by the methods which were agreed upon at the establishment of the EACN. Changes of techniques which have been introduced in the Stockholm laboratory from time to time without consultation with, or notification to, the other participants in the EACN have not been introduced in Britain.

A second programme of precipitation sampling in Britain has been established more recently by the Atomic Energy Research Establishment (AERE) Division of Health Physics. The AERE uses neutron activation, X-ray fluorescence and other analytical techniques which differ from those of the EACN, being more suited to the simultaneous measurement of a wide range of metals. The AERE results which I quote here have been taken from AERE Report R 7134 by Cawse and Peirson (1972) which describes precipitation and air sampling at Wraymires, in Cumbria. That station and the two Meteorological Office stations, at Eskdalemuir and at Lerwick, are shown in Figure 5.5 .

The AERE monthly results for precipitation at Wraymires are plotted in Figure 5.6(a). In all months R falls close to R_s. When the excess chlorine, or sodium, is estimated for each month the total of each for the year is a three percent excess of chlorine and a five percent excess of sodium. These excesses are scarcely greater than the experimental error in a single determination. It is most reasonable to assume that at Wraymires salt from the sea, unmodified by any process at the point of production or during its life as an aerosol, is the only significant contributor of sodium or chlorine to precipitation. At the EACN station at Eskdalemuir, EACN No 205, for which the monthly amounts of chlorine and sodium are shown in Figure 5.6(b), there were no months with excess chlorine. The excess sodium amounted to 97% of the sodium from a presumed sea source. It would not be unreasonable to assume that at Eskdalemuir, 110 kilometres north of Wraymires, there is a land source which, through the year, contributes as much sodium to the precipitation as does the sea. However, such an assumption is not borne out by an examination of the Lerwick results from the same period.

At Lerwick, which is a maritime site receiving ten times as much sea salt as Eskdalemuir, there is also a great excess of sodium, as seen in Figure 5.6(b). Could this come from a local land source? The excess amounts to 25% of the sea salt sodium over the year and in total quantity is two and a half times the excess at Eskdalemuir. It would require a very strong land source of sodium in the Shetlands to produce such results. But also, as seen in Figure 5.7, if there were a Shetlands source of sodium it would have to operate in sympathy with that near Eskdalemuir because the two stations experience high - and low-values of R in the same months.

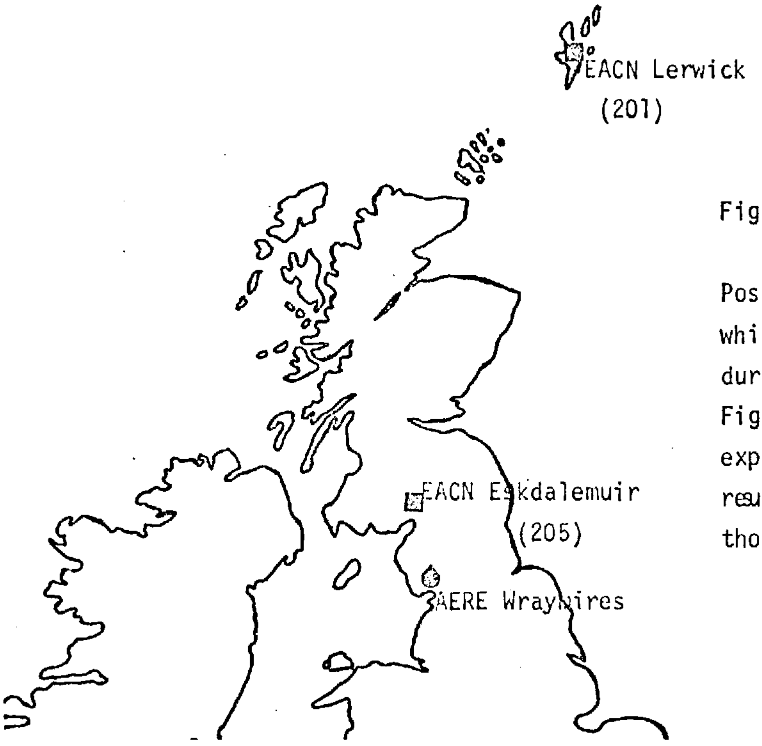


Figure 5.5

Positions of three stations for which monthly values of Cl/Na during 1971 are compared in Figure 5.6 . Despite their similar exposure Wraymires and Eskdalemuir results have less in common than do those for Eskdalemuir and Lerwick.

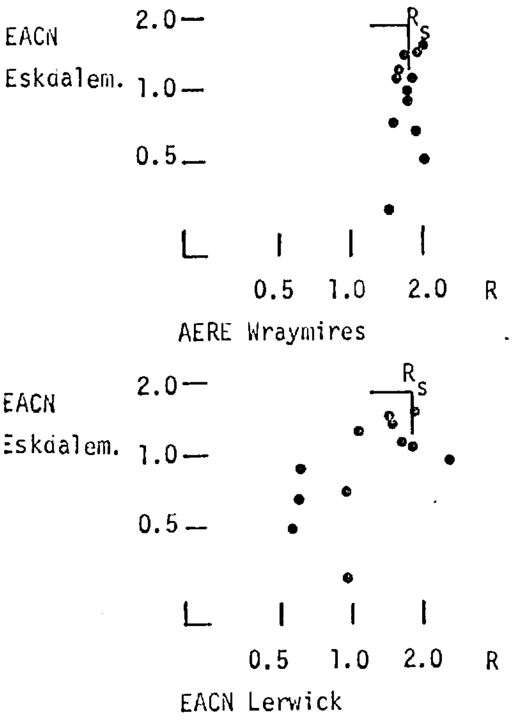


Figure 5.6

Simultaneous values of R (Cl/Na) at pairs of stations as noted during 1971. Despite the similarity of simultaneous values of R Lerwick received about ten times as much salt as did Eskdalemuir.

It is most unlikely that so many common factors relate the chemistry of precipitation at Lerwick and at Eskdalemuir, which are 550 kilometres apart and very differently exposed to sea and land sources, while Eskdalemuir and Wraymires, which are 110 kilometres apart and very similarly exposed to land and sea, have little in common if all of the data is to be believed. The significant factor relating Lerwick and Eskdalemuir is that samples from both are analyzed in the one laboratory. Yet it is the Wraymires results, from a different laboratory using quite different analytical methods, which conform to the most reasonable expectation about the chemistry of precipitation. This is that the predominant source of both chlorine and sodium is the sea, and that these two ions remain associated during their transport on the wind in just the way they are associated in sea water. It seems that the system which produces the British EACN results should be examined to discover the cause of the incorrect sodium or chlorine analyses. Brownscombe and Porter (private communication) suggest that the analysis is correct and the deviation results from sea salt which is deposited on the ground, chemically modified in some way and then carried again into the air to be redeposited in the rain gauge. Such a process could equally well explain the observations.

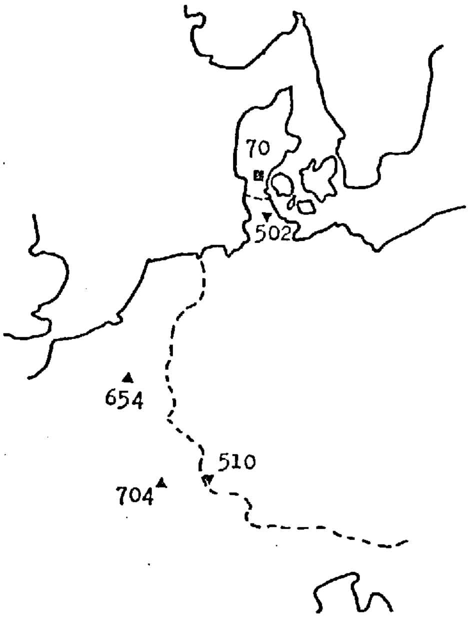


Figure 6.1

Five stations of the EACN for which the chlorine/sodium ratio is considered in Chapter 6.

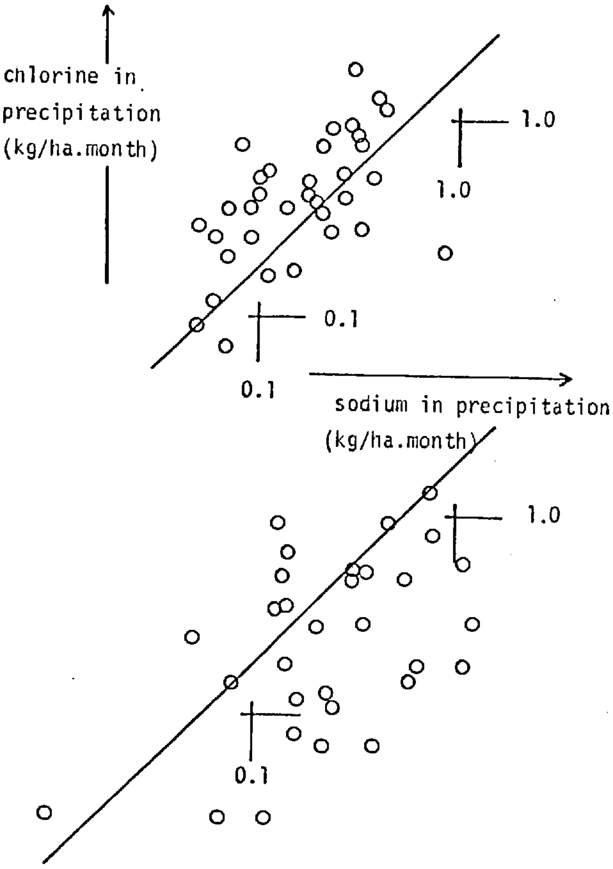


Figure 6.2

Monthly amounts of chlorine and sodium in precipitation during 1960 - 62 at station 510 in Germany (upper) and at station 704 in France (lower). Note the tendency toward excess chlorine at the German station and excess sodium at the French station.

Chapter 6. Sodium and chlorine in continental precipitation

If there are significant sources of sodium and chloride other than the sea they should be most easily identified in continental precipitation far from the coast where the sea salt concentration is low. Various workers have identified possible sources. Hutton and Leslie (1958) suggested that the prevalence of chloride among the soluble components of soils should lead to high chloride concentrations in soil-derived aerosol. Junge and Werby (1958) considered that the lower values of R which they found in precipitation in the centre of North America were a consequence of sodium from the soil being added as an aerosol to air which already contained sea salt. Such a result implies that the ratio of chlorine to sodium in the soil is less than R_s, which is not consistent with the belief of Hutton and Leslie. I will show later in this chapter that Hutton and Leslie's observations tend to support the view of Junge and Werby rather than their own. Before doing so I will consider the principal man-made component which has been suggested by Gorham (1958) and others - chloride from coal.

Skipsey (1974) has demonstrated that, at least for British coals, there is a strong relationship between the chlorine content of coals and their rank. Below a carbon content of 85% dmmf coals may have as much as 1% chlorine adsorbed, although 0.5% is more common. At carbon contents greater than 87% it is most uncommon to find more than 0.2% adsorbed chlorine. This is believed to be a consequence of the variation of the ultrafine structure of coal, for the surface area of internal capillaries decreases markedly with increasing carbon content, reducing the area available to adsorb chloride. The coalfields of the Ruhr and the Saar are noted for their coking coals which probably have carbon contents of 85% to 90% and low chloride contents. Mielecki (1948) has reported that the chlorine content of Polish coals in few cases exceeds 0.1% . Information on the chlorine content of continental coals is very sparse, however, and any estimate of total chlorine emissions from coal burning must be considered uncertain. If we assume that the chlorine content of continental coals averages 0.1%, and that upon combustion this is all emitted into the air then the table below gives the typical total annual emissions during the 1960's for several European countries. If all of the chlorine is then deposited within the borders of that country, either in precipitation or by dry deposition, then the areal density of the deposited is given by the last column. I do not suggest that this in fact occurs but will use this consideration in later discussion.

Country	Area	Cl from coal (0.1% of coal)	Coal Cl deposit (kg/ha.year)
Austria	8×10^6 ha	7×10^6 kg/year	0.9
Belgium	3×10^6 ha	22×10^6 " "	7
France	53×10^6 ha	70×10^6 " "	1.3
Italy	29×10^6 ha	10×10^6 " "	0.4
West Germany	24×10^6 ha	140×10^6 " "	6

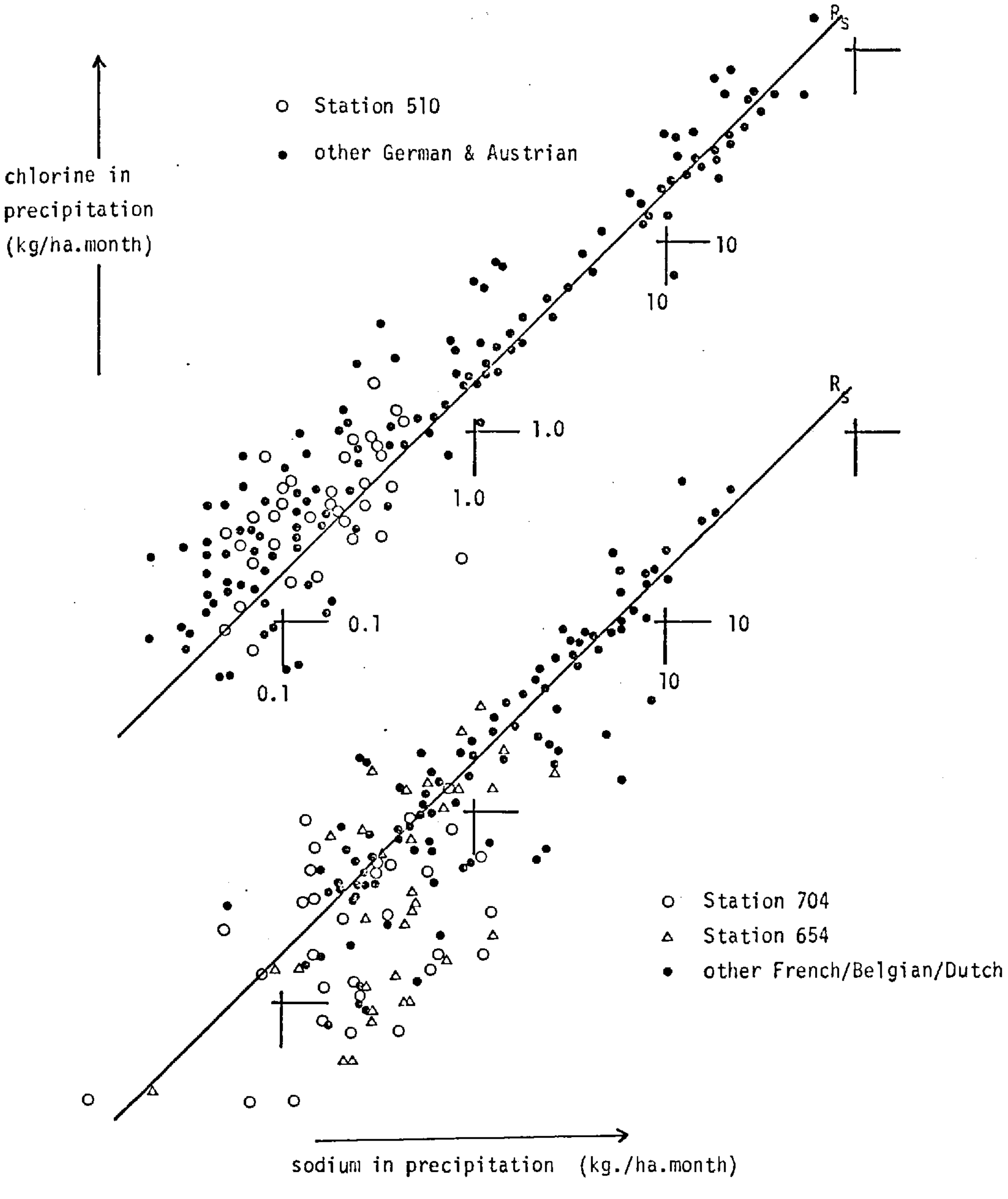


Figure 6.3 Monthly amounts of chlorine and sodium at stations 510 and 704 compared with results from other stations of the same networks. The excess chlorine at 510 is commensurate with that at stations in northern Germany and in Austria and is of the order of 0.2 to 0.5 kg/ha.month. German emissions of chlorine from coal were estimated at the start of the Chapter to be about 0.6 kg/ha.month. The amount of excess sodium at station 704 is consistent with that at other stations in the network, including station 654 which is in a region of high coal consumption.

We should recognise that the true rate of emission of chlorine from coal burning, now to be referred to as "excess" chlorine, could be half or double these values and that the difference between the five countries may be affected by, say, a systematic variation in the chemistry of coal from one side of Europe to the other. However, we can distinguish between two extreme possibilities for the removal of chlorine from the air which would produce clear differences in the distribution of chlorine in precipitation. If the chlorine comes to earth very close to the source the geographical pattern of emissions matches that of deposition but if the chlorine has a long atmospheric life it is deposited all over Europe and beyond. If the former is the case then Austrian precipitation should contain amounts of excess chlorine which are comparable with those in French precipitation and roughly an order of magnitude less than in West German precipitation. Belgian precipitation should contain an order of magnitude more excess chlorine than French precipitation. If the removal from the air is by dry deposition from the gas phase and not by washout by precipitation then the excess chlorine will not be found in precipitation in Belgium and Germany, or in Italy, Austria and France but rather on the absorbing surfaces of soil and vegetation. If the latter is the case, with the transport of the excess chlorine over long ranges, then it will be removed from the air to a greater extent by washout and will be found in precipitation over a much wider area. In such circumstances the German and Belgian emissions will be found in France and Austria as well as in all other European countries and the geographical pattern of deposition of excess chlorine cannot have strong gradients due to the local concentrations of coal-burning towns and industries.

I will now consider the EACN data on sodium and chlorine in precipitation in these countries. It will be seen that with increasing distance from the sea the observed monthly values of R, the chlorine to sodium ratio, deviate increasingly from R_s but in a fashion which is not consistent with the Cauer hypothesis. Neither is this deviation of a form which could result from excess chlorine from coal burning, although in Germany it is of the same order of magnitude as predicted in the table on the previous page. There are notable features of the patterns of chlorine deposition for which an explanation is yet to be found. Once again a major conclusion is that there have been significant and consistent distortions of the results by laboratory effects.

Consider first the comparison between the German and French networks at their point of closest approach. Figure 6.1 shows the positions of stations discussed here. Figure 6.2 shows monthly amounts of chlorine and sodium at two of these stations.. Station 510 in Germany is 120 kilometres from station 704 in France and should be exposed to similar conditions of rain and air chemistry. Treating the sea salt ratio of chlorine to sodium as a balanced quantity of each of these ions it is evident that at station 510 there was a tendency in 1960 - 62 toward excess chlorine while at station 704 there was a tendency toward excess sodium. In some months these excesses were greater than the quantities presumed to be from sea salt. We could make the assumptions of additional sources of sodium in eastern France and chlorine in western Germany but when further stations of each network are considered we find these assumptions to be untenable.

Figure 6.3 shows the results which were obtained at the same time at other stations of each network. It is evident that stations 510 and 704 are quite consistent with other stations

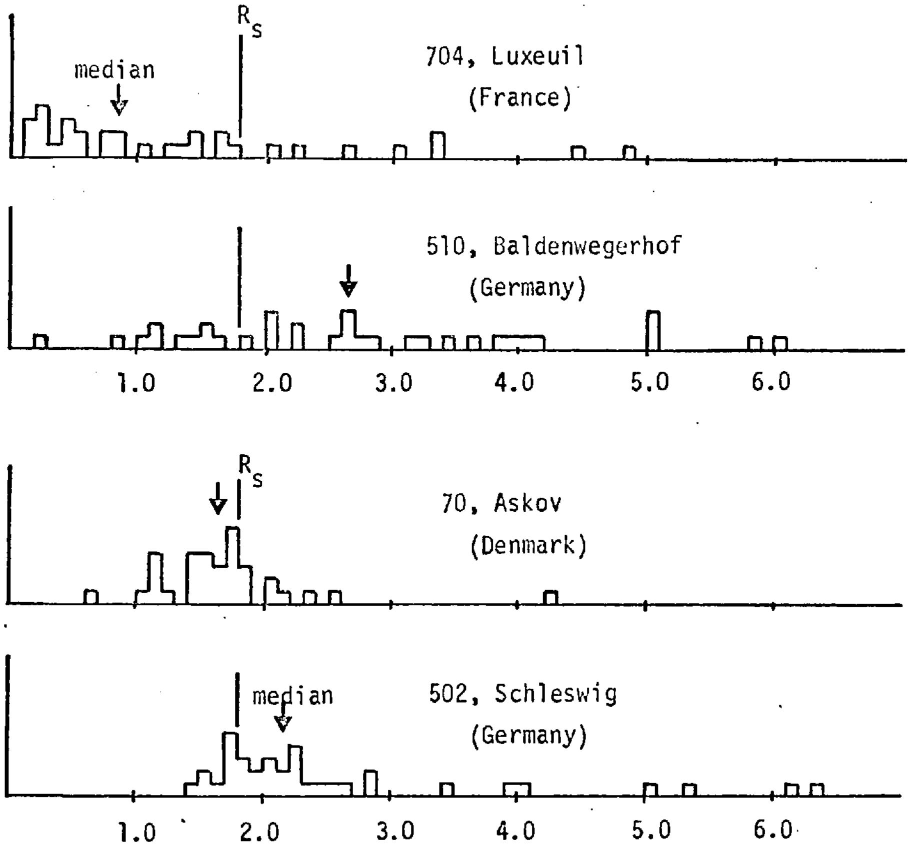


Figure 6.4 A comparison of Cl/Na ratios in monthly precipitation samples across two borders, for the period 1960 - 62. While the Danish and French stations found a tendency toward excess sodium nearby German stations in both cases tended toward excess chlorine. Samples from station 70 were analysed at first in Copenhagen and later in Stockholm. During both periods the tendency toward excess sodium was evident.

in their respective networks in their tendency to deviate above or below R_s. In the German network all months with small amounts of salt in rain tended to deviate toward high values of R while the opposite is true of the French network.

I will now consider the possibility that the excess chlorine in Germany comes from burning coal. It was estimated above that German emissions of chlorine from this source are of the order of sixty mg/m^2.month, which is of the same order as the amount of excess chlorine in precipitation. The amounts of excess chlorine in Austrian precipitation are comparable with those in southern Germany, although they are higher in proportion to the total chlorine for the chlorine of presumed sea origin is less in Austria than in Germany. If the excess chlorine in German precipitation comes from coal, from where does the excess in Austria come? The table at the beginning of this chapter indicates that the chlorine emissions per unit area in Austria are an order of magnitude less than those in Germany. Perhaps the chlorine in Austria is carried in on the wind, not from Italy where little coal is burnt, but from Germany. That cannot be correct for such a phenomenon would reduce the amount of chlorine of coal origin in German precipitation to an amount well below that which is observed, and would imply that German chlorine is carried also into France, at least as far as station 704. Furthermore, if all German and Austrian stations receive a large excess of chlorine why does not the Belgian station, 654, which is in the heart of the Belgian and German coal-burning areas? Figure 6.3 shows that that station, in keeping with all of the others in France, Belgium and Holland, records an excess of sodium.

Eriksson (1960) found that "the geographical pattern (of excess sodium in European precipitation) is puzzling and should be studied more in detail on monthly maps much in the same way Rossby and Egner did." However, in general he considered that the pattern was as predicted from Rossby and Egner's interpretation of the Cauer process. One of the puzzling features of the geographical pattern is the line along the German and Austrian borders which marks the change from a surplus of sodium in France and Yugoslavia to a deficit in Germany and Austria. Our experience suggests that in this work a physical map may be of less value than an administrative map.

We have achieved a result for sodium and chlorine which is similar to that for calcium and magnesium in Chapter 2. The results of the chemical analysis in different parts of the EACN are not compatible with one another and the difference cannot be explained in terms of atmospheric phenomena. In Chapter 2 this conclusion was reached by analysing the year by year variation of the calcium/magnesium ratio, while in this case we compared the deviations of the chlorine/sodium ratio from that in sea salt. It is clear that at least one network has produced erroneous results in 1960 - 62. It is quite possible that both networks were doing so. Figure 6.4 shows that there was also an inconsistency between the German station 502 at Schleswig and the nearest Danish station, 70, in 1960 - 62, at a time when Danish samples were analyzed at first in Denmark and later in Sweden. Both before and after the change of laboratory the Danish ratios tended to fall below R_s while the German ratios were were higher than R_s, although the deviations were smaller than those found further inland.

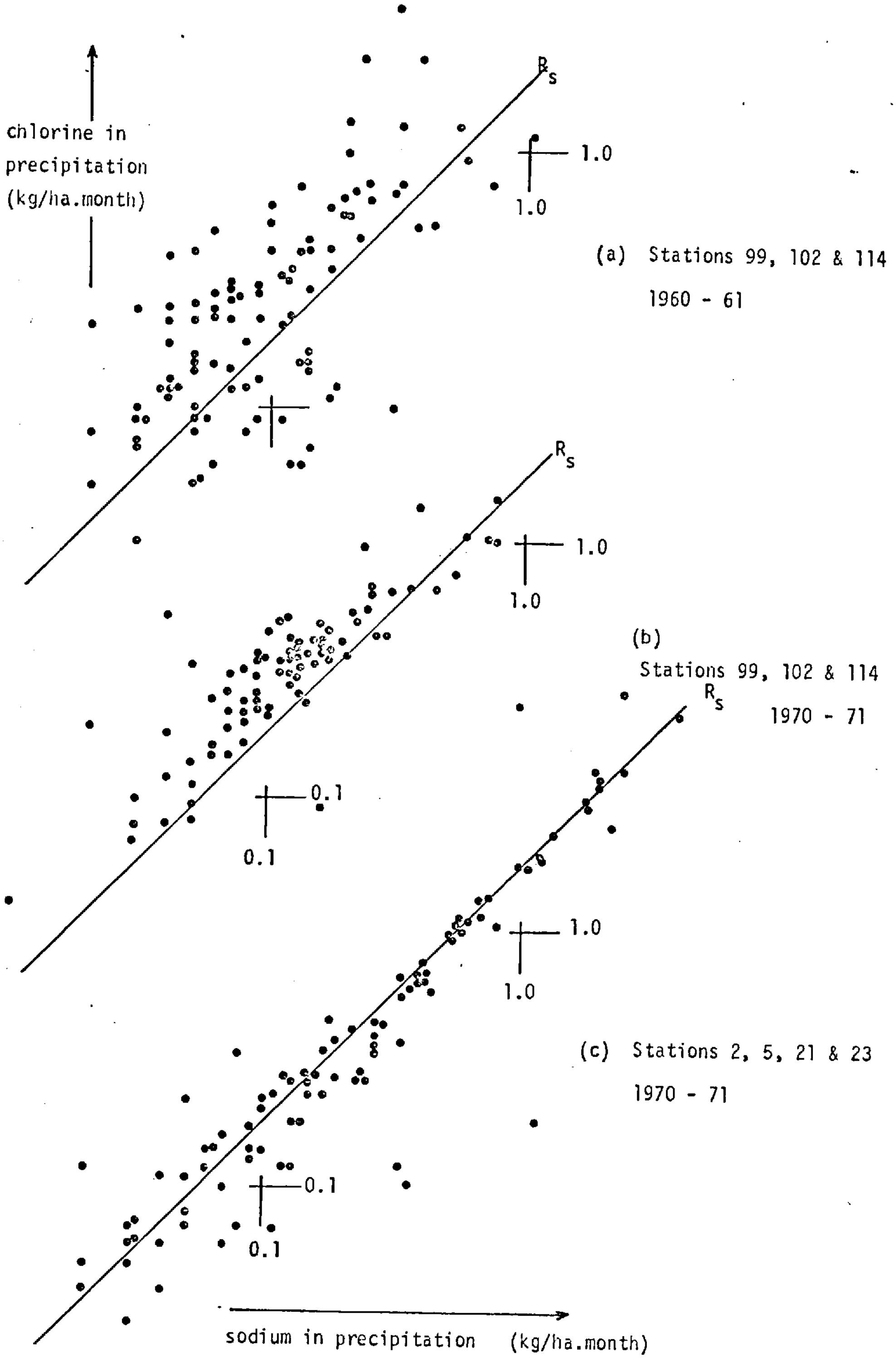


Figure 6.5 Amounts of chlorine and sodium in precipitation in Austria (a) with analysis in Germany and (b) ten years later for the same stations with analysis in Sweden. (c) shows simultaneous results for samples collected in Sweden. In the second period a clear excess of chlorine was found in Austria while in Sweden there was a slight tendency toward an excess of sodium. The difference cannot be simply due to instrumental calibration.

One other change of laboratory allows us a little more insight into the German results. The German sampling was discontinued early in 1964 and from May 1964 the four Austrian stations and one German station, 114 at Hohenpeissenberg in southern Bavaria, were reopened to send samples for analysis in Stockholm. Figure 6.5 compares results for those stations in 1960 - 61, before the change of laboratory, with results after the change, in 1970 - 71. In both periods there was a tendency toward excess chlorine. In the first period the scatter was much greater and one quarter of the samples were recorded as having a clear excess of sodium. Figure 6.5(c) suggests that the excess chlorine in the second period was not simply due to laboratory overestimates of chlorine in samples which were in fact dilute solutions of sea salt. This shows the results obtained in the same laboratory at the same time for samples collected at four Swedish stations. Allowing for some scatter, the Swedish precipitation appears to contain only sea salt. There is a slight tendency toward excess sodium, especially with smaller total amounts of salt, but this is similar to the deviations in an earlier period which we have seen in Chapter 5 to be artefacts of the system. It appears that German and Austrian precipitation does contain chlorine in excess. Whether this comes from coal is not clear. The apparent absence of excess chlorine in Belgian and French precipitation may be attributed to faulty chemical analysis but its absence in southern Denmark, as determined by both the Copenhagen and Stockholm laboratories, is less easy to explain.

Hutton and Leslie (1958) and Hutton (1958), whose results for rainfall in southeastern Australia have been incorporated in studies and surveys by Eriksson (1960) and Junge (1963), found characteristics of sodium and chloride which are similar to those found in various parts of the EACN. Figure 6.6 shows the ratio of annual amounts of sodium and chlorine in rain at stations between two kilometres and three hundred kilometres from the coast. The solid triangles give the results for the year to August 1955 and the open triangles give the results for the following year. The increasing fractional excess of sodium at lower total amounts of salt is characteristic of results in Sweden, Eire and Belgium also, where it was attributed to the action of the Cauer process. I have already discussed that matter. In Australia the excess of sodium was almost three kg/ha.year in 1955 and one kg/ha.year in 1956. This difference between successive years is worth noting for it occurred at all stations.

Bonython (1956) placed the problem of salt transport in an interesting context by considering the salt budget of Lake Eyre, the great salt pan in South Australia. Although the lake has an area of about a million hectares the salt has been found to be no more than fifty centimetres deep. It does not have the composition of sea salt, but is greatly enriched in the less soluble components of which the most notable is calcium sulphate. If fresh sea salt were brought down in rain in the catchment, an area of one hundred million hectares, at the rate of one kg/ha.year then the sodium chloride which is present could have accumulated in a few thousand years while the calcium sulphate would have taken half a million years if it is assumed that it has all been washed into the lake. It appears that the sodium chloride content has reached a steady state in the catchment while calcium sulphate is probably still accumulating. Bonython considered the possibility of salt being adsorbed onto dust and then carried away by the wind but thought that it would certainly return to earth well before leaving the catchment. As the strata under the lake are very dry it appears that brine is not lost by seepage. It cannot be lost by surface drainage for the lake bed lies about sixteen metres below sea level.

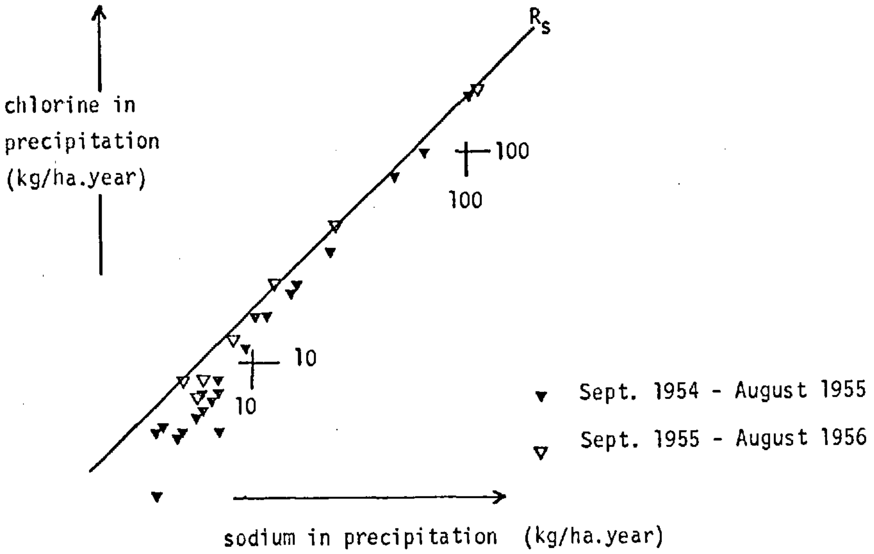


Figure 6.6 Annual amounts of chlorine and sodium in precipitation at stations in SE Australia, collected and analysed by Hutton and Leslie. In 1954 - 55 the excess sodium at all stations was about 2 kg/ha.year. In the following year the excess was 0.5 kg/ha.year.

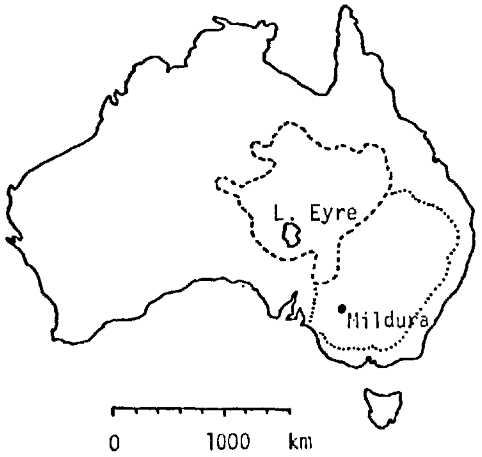


Figure 6.7

The closed Lake Eyre catchment and the Murray/Darling catchment which drains into the sea. The results of analysis of rain samples from Mildura by Hutton and Leslie are discussed in this chapter.

In describing the forms of salt deposits Bonython several times mentioned pure white feathery growths of efflorescent salt at the edges of slabs of gypsum and at cracks in even surfaces. This was found to be composed of 99.5% sodium chloride, which has a Cl/Na ratio of 1.54 . It is possible that this form of fine crystalline salt is broken up by the wind and carried away. The saltation of sand and dust particles in strong winds may occasionally break up the efflorescent salt which has accumulated over a period of days or weeks. It is not essential that the efflorescent salt attach itself to other particles in order to be carried away. If sodium chloride is carried away from the lake surface only and not from the sand and rock of the much larger catchment then in order to maintain a steady state the average rate of removal must be about 0.3 kg/ha.day which is about ten times the rate of deposition of salt at Mildura, one of the furthest inland of the stations at which Hutton and Leslie sampled the rain. Alternatively the steady state could be maintained by a process such as that suggested by Twomey (1960) which would concentrate the salt near the soil surface in fragile crusts which are then broken up by thermal expansion and contraction. A rate of removal of only 0.003 kg/ha.day over the catchment would then be sufficient to maintain the steady state. Figure 6.7 shows the position of Mildura in relation to the ocean, Lake Eyre and the Lake Eyre catchment. It is situated in the catchment of the Murray and Darling Rivers which drain into the sea at the South Australian coast. I will now consider the evidence for the salt which is deposited at Mildura being from the land rather than from the ocean.

Sea salt aerosol which reaches an inland station such as Mildura may be brought down efficiently in precipitation but will not be deposited in a dry form at an appreciable rate. Its association with moist maritime air favours washout. A land salt aerosol, and especially one from the dry centre of Australia, is unlikely to be washed out by rain. From this we may deduce that it is long-lived in the atmosphere, mixed well and travels over long ranges in much the same way as was deduced in Chapter 4 to be the case for northern hemisphere calcium aerosol of land origin. The air at Mildura may contain land salt aerosol from the Lake Eyre catchment and from other inland areas with salt pans. Some of the aerosol may arise from local soils as has been suggested by Hutton (1958). While the collection of such an aerosol by a rain sampler may be relatively inefficient due to the small size of the particles it would be a fairly constant process due to the predominance of dry days in all months. If the aerosol were generated at the local soil surface then a drought could result in an increased rate of production and consequently greater collection in the rain sampler. I will consider the shape of the distribution of concentration in rain as a function of monthly amounts of rain for each of these cases as this is the form of the data which has been presented by Hutton (1958).

> If greater precipitation in some months is a consequence of air being brought from the ocean, and that air is richer in sea salt, then the slope of a line fitting experimental data should be positive as shown in Figure 6.8(a). This situation is found for sodium and chlorine in Eire.
>
> If the precipitation is of constant composition the experimental points will fall on a horizontal line as shown in Figure 6.8(b).
>
> If the aerosol arrives independently of the rain the experimental points will fall on a line with a reverse slope of 45° as in Figure 6.8(c).

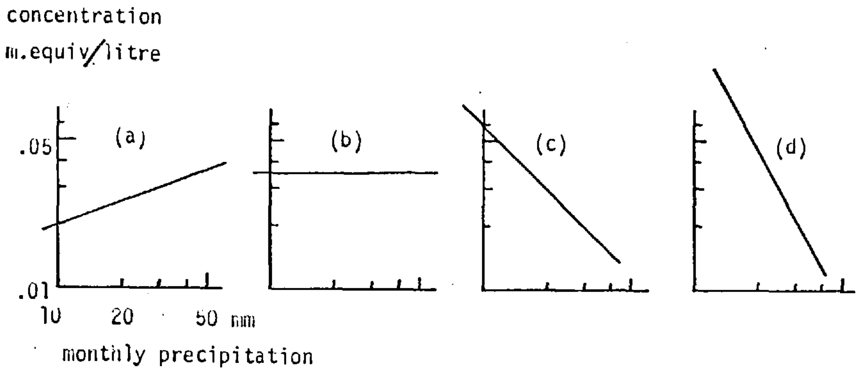


Figure 6.8 Schematic relationships between the amount of precipitation and the concentration of a substance given various assumptions about the form in which it reaches the rain gauge.

(a) source of substance coincides with greatest moisture source
(b) substance well mixed in the atmosphere and removed by rain.
(c) substance arrives as a dry aerosol independently from the rain
(d) substance preferentially raised from nearby surface in times of drought.

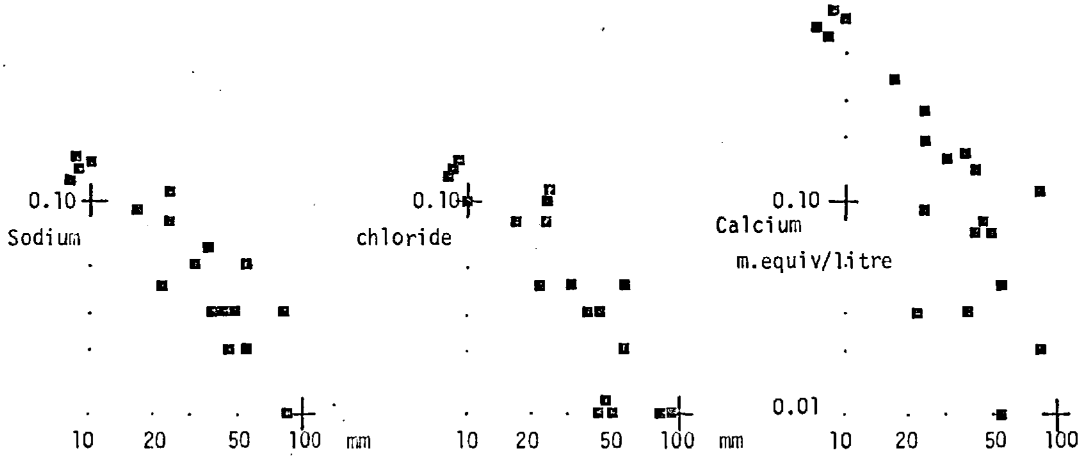


Figure 6.9 At Mildura, 1954 - 56, the relationships for sodium, chloride and calcium in rain between concentration and the amount of rain. From the considerations in Figure 6.8 it appears that sodium and chloride arrive in the rain gauge independently of the rain, in similar amounts expressed in equivalents, while calcium is preferentially mobilised from the local surface in times of drought.

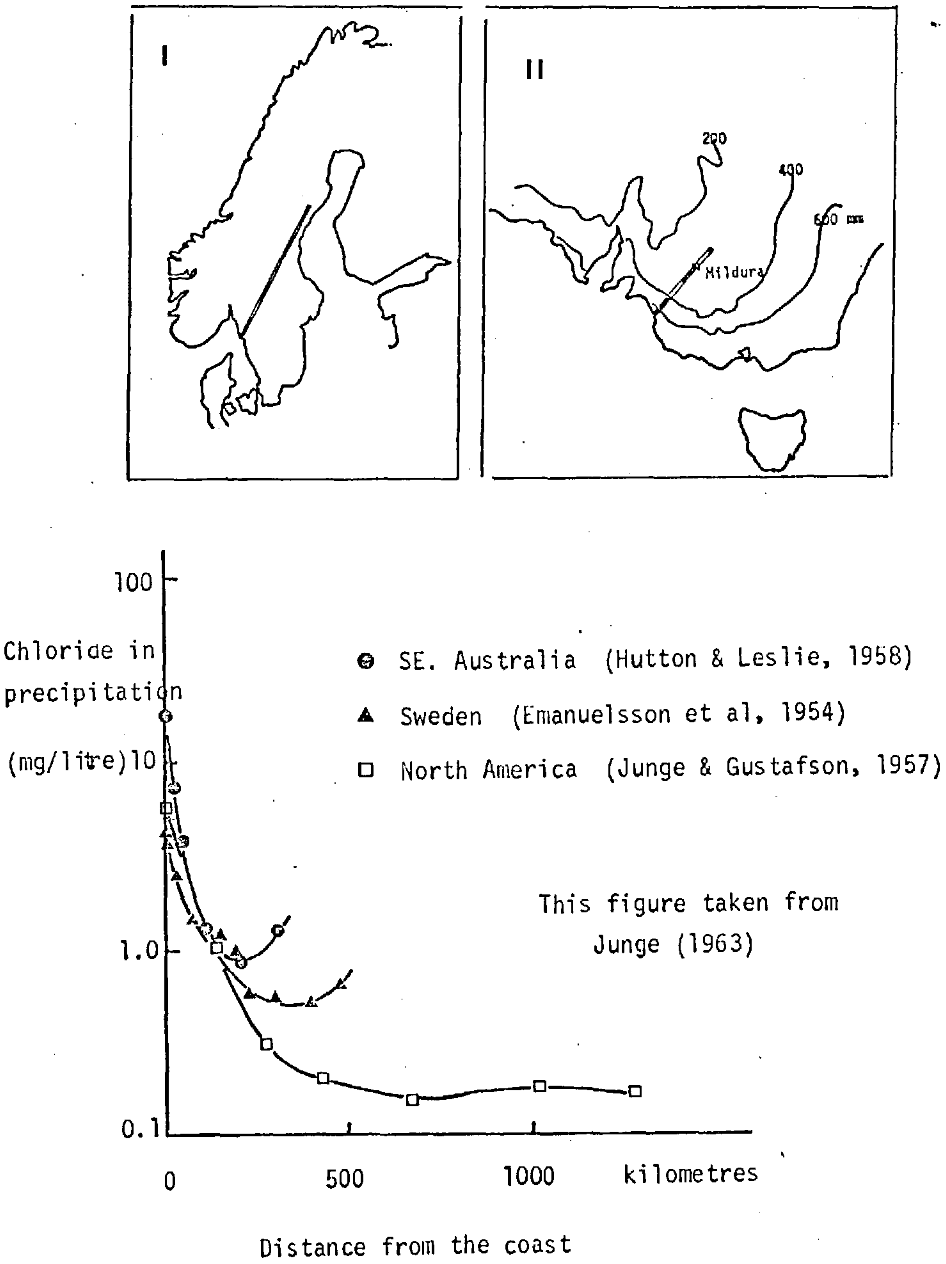
If very dry periods allow more dust to be raised from the ground and the rain does not bring significant amounts of the substance the points will be scattered about a line with a reverse slope which is greater than 45^0 as in Figure 6.8(d).

Figure 6.9 shows the distribution of monthly concentrations of sodium, chlorine and calcium in precipitation at Mildura between 1954 and 1956. The sodium and chlorine characteristics are clearly those of an aerosol which has little to do with the rain, quite likely a land salt aerosol such as may be produced over large areas of the continent. The calcium distribution is characteristic of an aerosol which is produced at the local soil surface and especially in times of drought. It seems that at Mildura most of the salt which falls out is land salt. The calcium also comes from the land but not from the same source as the chlorine and sodium. It is possible that the chlorine/sodium ratio of the land salt is 1 lower than that of sea salt.

Hutton and Leslie's (1958) suggestion, repeated by Junge (1963), that the soil contributes chlorine to the aerosol which is brought down in rain appears to be both deficient and incorrect. The soil in the arid centre of Australia, either directly or through the salt pans which have formed in the closed catchments, contributes as much sodium as chlorine to an aerosol which returns to earth more by sedimentation than by washout. At Mildura the total amount from the soil considerably outweighs that from the sea. There is little merit in Junge's suggestion that the vital information which we lack is the vertical profile of sea salt over the Pacific Ocean. That data is relevant only to Junge's theory that the decrease in sea salt aerosol concentration with increasing distance inland is due to the increase in mixing depth of the atmosphere. While that theory may be applicable to the number concentration of small sea salt particles it is not true of the ratio of concentrations by weight in the maritime "plateau" and the continental "floor" in sea salt aerosol concentrations. Such theories are of little value where there is a strong land source of salt aerosol.

Bonython's observation that the accumulation of salt in Lake Eyre has reached a steady state implies that over a period of centuries the transport of land salt aerosol out of the catchment equals the transport of sea salt into it. Areas situated downwind of the catchment experience sea salt aerosol concentrations such as are found at the upwind edge of the catchment, although the spectrum of particle sizes will be different due to the different mechanism by which they are produced and by the removal by sedimentation within the catchment of the larger particles. The catchment is simply a temporary reservoir of salt, holding its contents for some thousands of years before they move on. This reservoir may have profound effects on the land downwind in changing the seasonal and annual average concentrations of salt aerosol. Whereas the summer is the time of least production of sea salt aerosol it may be the time of greatest production of land salt aerosol. And a run of dry years may lead to a reduction in the amount of salt stored in the reservoir, increasing the amount of salt aerosol to which downwind areas are subjected.

Hutton (1958, 1965) deduced from the salt balance of a small seasonal lagoon in South Australia and from other studies that there is a cycle of the most soluble elements in a soil profile up to the surface, into the atmosphere and back again to the soil when rain falls



This figure taken from Junge (1963)

Figure 6.10 Part of Figure 74 from Junge (1963) showing the variation in concentration of chloride in precipitation with distance from the ocean on three continents. The European and Australian profiles were taken along the lines shown in insets 1 and 11.

through the atmosphere. From the interpretation of data on precipitation at Mildura, which I have presented above, it appears that the soil-derived aerosol is deposited more by sedimentation than by washout.

Let us reconsider the data of Figure 6.6 . The stations with the greatest amounts of sodium and chlorine are coastal stations, at which almost all of the salt is straight from the sea. At the stations furthest inland most of the salt has spent some time, perhaps some thousands of years, on the land since it first arrived from the sea. The ratio of chlorine to sodium at these stations is not unlike that at inland stations in Eire, among other places, where it is presumed to have arrived straight from the sea. There is no reason in this evidence to believe that the chlorine/sodium ratio of the land salt in Australia differs from that of sea salt, which is the same the whole world over. If the excess sodium in the Australian samples is real, and not an artefact of the chemical analysis, then its presence supports the belief of Junge and Werby (1958) that land areas contribute sodium in excess to the aerosol and not excess chlorine as was suggested by Hutton and Leslie (1958).

The effect which salt aerosol has on inland waters and on agriculture does not depend on its origin in the sea. Salt from a prolific land source has the same impact as a nearby ocean. We might consider the cycle of salt in inland Australia for its effect on inland waters. It was estimated earlier that, given Bonython's assumption of a rate of arrival of fresh salt from the sea of one kg/ha.year, it takes some thousands of years for the salt to re-emerge at the downwind side of the Lake Eyre catchment. If it must enter the atmosphere from the surface of the dry salt in the lake rather than from the diffuse source among the sand and rock of the desert then the aerosol which succeeds in leaving the catchment must be carried at least two hundred and more often five hundred kilometres by the wind. Much the same is true of salt picked up from the extensive sand and rock surface. For each kilogramme of salt which leaves the catchment several kilogrammes will have fallen short, to be dissolved and washed back into Lake Eyre during some later rainfall or "wet". On average then the salt may become airborne several times in ten thousand years before reaching a catchment area which returns in to the sea. The salt content of inland waters will then be considerably higher than is the case for a continent in which all rivers drain into the sea. Those rivers which drain into the dry lakes in central Australia, of which Lake Eyre is the largest, carry the salt several times before it leaves the closed catchements. Those on the perimeter of the continent which drain to the sea eventually carry not only the fresh sea salt which falls in their own catchments but also the bulk of that which falls in the closed catchments, all save that which is carried out to sea on the wind. The Murray/Darling river system, in which Mildura is situated, drains the western slopes of the Great Dividing Range of eastern Australia and must collect much of the salt from the Lake Eyre catchment. In this way the climatic fluctuations which produce for short periods a net increase or net decrease in the amount of salt in Lake Eyre will affect the salinity of the Murray/Darling waters. If a time of net removal of salt from Lake Eyre corresponds to a time of reduced rain in the Murray/Darling catchment then any increase in the salinity of those rivers is accentuated.

We may now consider the data on chlorine concentration in precipitation on several continents which was assembled by Junge (1963) as Figure 74, reproduced here as Figure 6.10. From this data Junge deduced the existence of different "plateau" values in sea salt concentrations in the interiors of different continents. I have considered the character of the data yielding two of the three curves in sufficient detail to support a comment on them.

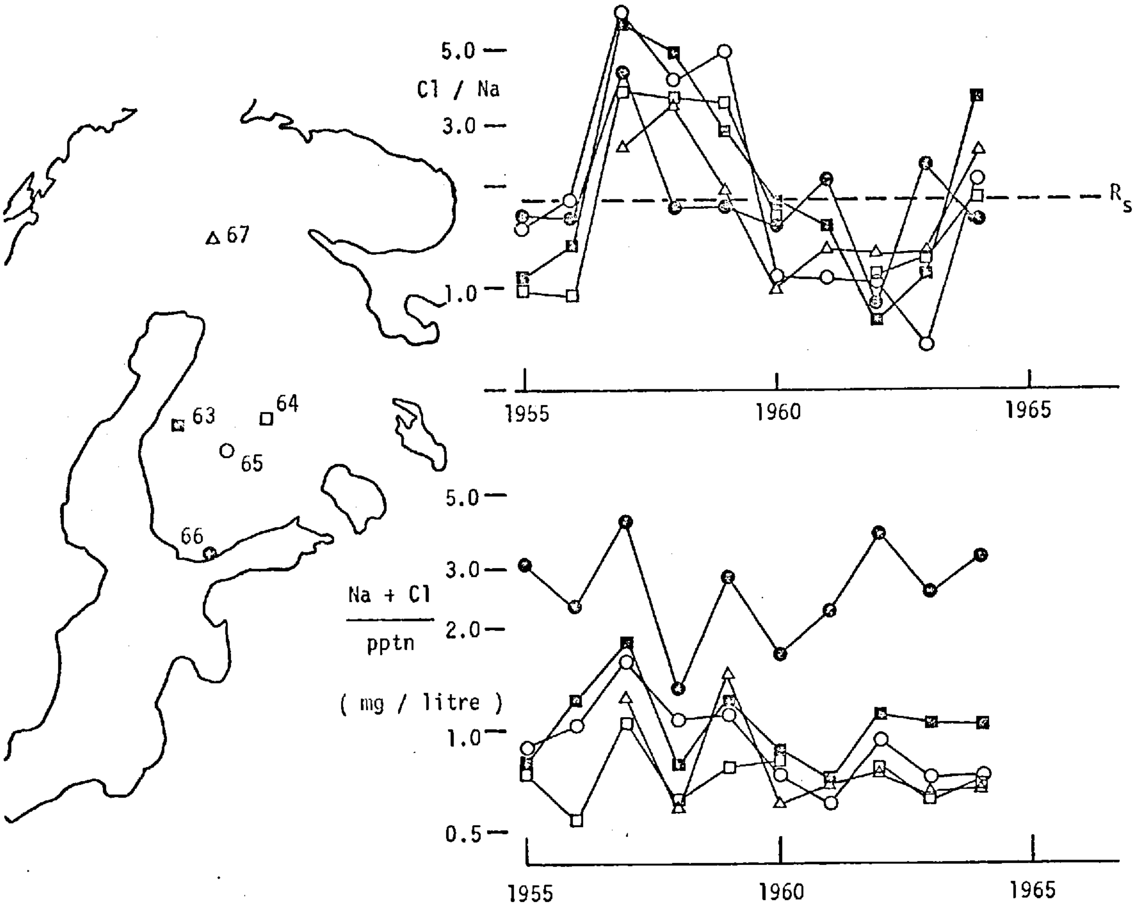


Figure 6.11 The variation with time of the Cl/Na ratio and concentration of sodium and chloride in precipitation at five Finnish stations. At all stations an excess of chloride in 1957 was followed in 1962 by an excess of sodium. The lower graph suggests that at station 66 most of the salt comes from the adjacent Baltic Sea.

Curve (i) gives the concentration of chlorine in Sweden along a line which is shown in Inset I. Junge regarded this as a line toward the centre of the continent from the continental coast near Goteborg. It is evident that the line is in fact parallel to the west coast of Norway and, after traversing the southern region of the Inland Network which is shielded from the sea in winter, it emerges into the saddle region through which sea salt aerosol is borne by the wind throughout the year. This could account for the upturn of the curve at four to five hundred kilometres from Goteborg. Junge attributed the upturn to the effect of the Baltic. It can hardly be described as identifying a continental plateau in concentration of sea salt. Curve (ii) is the data of Hutton and Leslie (1958) which was discussed earlier in this chapter. In this case the upturn is due not to a second sea source but to the dissolution of a relatively constant quantity of dry salt aerosol from the land in amounts of rain which decrease steadily with distance from the coast. That decrease is shown in Inset II which is reproduced from the Bulletin No. 1 of the Commonwealth Bureau of Meteorology. Junge's failure to comment on that upturn might be taken to imply that he did not regard it as a real feature. Thus it is seen that neither of these level regions in chlorine concentration curves represent a continental plateau. Whether the remaining curve, for North America, is sufficient to support a general theory of such continental plateaux is rather doubtful.

Other factors concerned with sodium and chlorine in aerosol and precipitation, such as the ratio of the ions in Finnish precipitation, merit some consideration. Figure 6.11 shows that there has been a marked secular variation which was similar at several stations. All stations recorded excess chlorine in 1957 and excess sodium in 1962. The higher concentration of salt at stations 63 and 66 suggest that the Baltic is a significant but not dominant source of sea salt at those two stations which nonetheless enjoy secular variations in R which are similar to those at inland stations. Are both of these observations consistent with the data being valid? If not, how can this be demonstrated?

There is very little discussion of these matters in the literature or at the meetings of the participants in the EACN. The consideration of EACN and other data on sodium and chlorine which I have presented in these three chapters raises doubts about some of the major topics, discussed at length by Eriksson (1959, 1960) and by Junge (1963), in the atmospheric chemistry of sodium and chlorine. It is right to be prejudiced against data in which the ratio of chlorine to sodium differs from the sea salt ratio. The entertainment of the Cauer hypothesis has weakened that prejudice for twenty years or more, for which we have paid the price in reduced quality of the data. It is time now for the data collected in the past twenty years to be examined critically and that which is of doubtful quality to be thrown away.

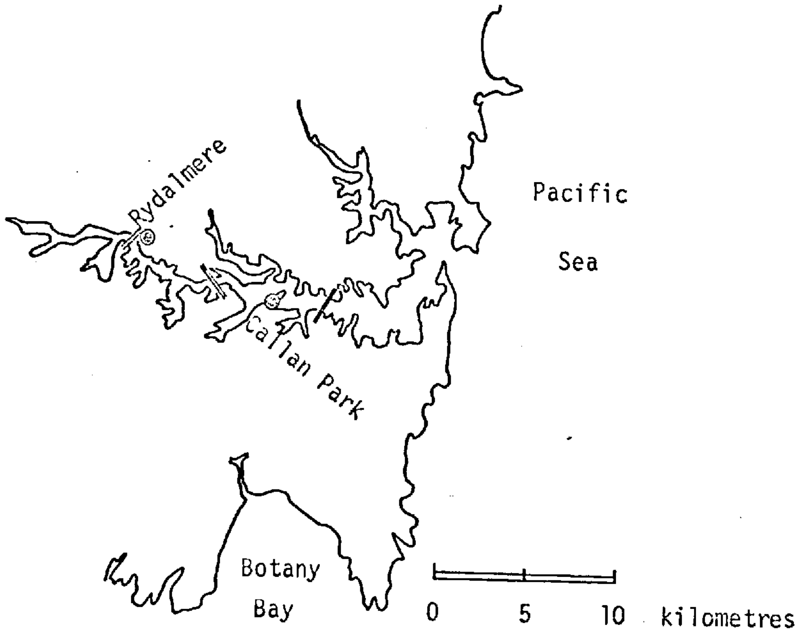


Figure 7.1 Positions of two air pollution monitoring stations in Sydney at which parallel measurements of smoke were made by the Air Pollution Control Branch of the NSW State Department of Health during June 1971. The daily measurements from the various instruments are plotted on Figure 7.2 .

Chapter 7. Order in air chemistry data

The things which we really "know for a fact" about the chemistry of the atmosphere are few and their form is important for they are not always strictly quantitative. Rossby and Egnér did not claim the Cauer process as an established fact, only as the best available explanation of a set of observations. Beside this the other possible explanations, which included laboratory malfunction, did not appear attractive. Later workers have used the supposedly "established fact" of the Cauer process as the foundation for speculation about its mechanism and as the justification of similar characteristics in other sets of observations. The analysis of this thesis does not disprove the existence of the Cauer process. It demonstrates only that the evidence originally adduced in its support was probably faulty and that more recent data has not been capable of use in disproving the null hypothesis that there is no process such as proposed by Cauer and refined by Rossby and Egnér, Eriksson and others.

As a matter of fact the Cauer process is of little value to anyone but the people who monitor the chemistry of air and precipitation. Ecologists did not require it to explain some preference of coastal plants for more sodium and less chloride. The liberation of free chlorine would be an embarrassment in explaining the longevity of ozone in the unpolluted stratosphere. Chemists showed no interest in the possibility of this unsuspected process and cloud physicists have made no appeal to the process. Its only value has been as a convenient explanation for a lack of order in one area of atmospheric chemistry. When the lack of order is due to the measurements rather than to the physical world we should ask whether order should not be restored by ceasing to take measurements.

Insofar as the measurements of sodium and chlorine in rain have found almost no application in twenty years this man-made disorder matters little. There are other areas of atmospheric chemistry which do matter, especially those related to human health and to the welfare of the living world. In this chapter I will discuss a case in which the disorder introduced in the course of measurement has a wide significance. It was revealed in an examination of data on smoke pollution in Sydney. As this and the associated measurement of sulphur dioxide is the most widespread form of air pollution measurement in the world, and is the basis for much research in epidemiology, it is a matter of concern that few authorities making such measurements could determine the cause of such disorder in their data. Its existence can support an erroneous belief that there is a need for complex computer modelling of an urban atmosphere and forecasting of high pollution concentrations, and can then thwart such modelling when it is performed.

In June 1971 there were operating at each of two sites in Sydney two different types of smoke sampler. The two sites, at Rydalmere and Callan Park, are shown in Figure 7.1 . The eight-port sequential sampler of smoke and sulphur dioxide is the standard instrument in urban air pollution monitoring in many parts of the world. In the course of 24 hours it draws two cubic metres of air through a filter and then through a solution of hydrogen peroxide which absorbs any acidic gases, the most plentiful of which is usually sulphur dioxide. After 24 hours collection on one filter and one bubbler the incoming air is diverted to the next filter and bubbler unit in a set of eight. The equipment is serviced

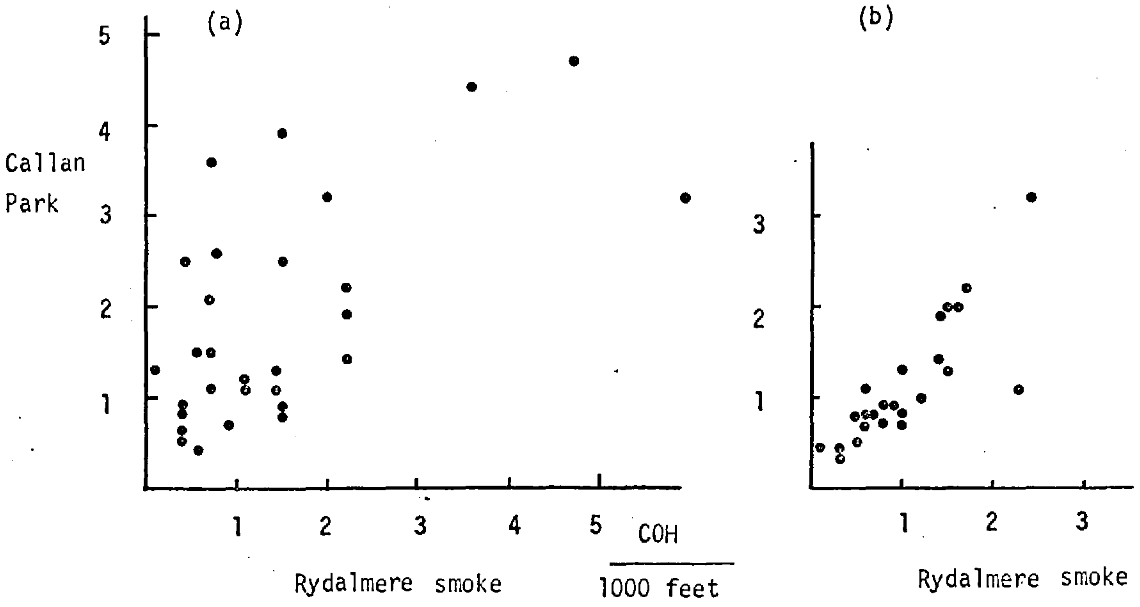


Figure 7.2 Simultaneous 24-hour measurements of smoke at two sites in Sydney using identical instruments.

(a) 8-port sequential sampler of smoke and sulphur dioxide

(b) Hemeon smoke sampler.

once a week and one week's samples analysed in the laboratory. The other smoke sampler used in Sydney is the Hemeon instrument which collects smoke only, on a continuous filter tape, moving the tape on at intervals of two hours. Thus the twenty four hour average smoke concentration is determined from twelve successive samples.

The smoke on the filter paper from each of these instruments is measured by the reduction in reflectance which it causes. Together with the black smoke which causes this reduction there may also be present reflective particles such as clay, fly ash, sea salt or asbestos fibres which are not recorded in the analysis. For this reason the density of smoke is expressed only in terms of units of Coefficient of Haze per one thousand linear feet, the amount of darkening which reduces reflectance by one percent. Some people believe that by a comparison with weighed samples from high-volume air samplers it is possible to express the blackening as an equivalent weight of aerosol. The different particle sizes collected on the different filters and the varying composition of the aerosol with distance from coasts, quarries and coal-fired stations invalidate such an exercise. We can say only that the reflectance measurement records the amount of an aerosol which is variously described as black smoke or as soiling. In urban air such smoke is mainly from coal or oil burning. Once emitted it will stay in the air for a long time, much as the calcium aerosol which was discussed in Chapter 4.

While most of the acidic gas collected in solution is believed to be sulphur dioxide the sulphur dioxide collected is not necessarily the bulk of that which has been emitted into the volume of air which is sampled. Appreciable amounts of SO_2 can be oxidised to sulphate within the time that the air remains in the city. The rate of oxidation depends strongly on the weather conditions at the time. This matter is of great interest in environmental health for it seems that it may be the part which is already oxidised, rather than that which remains as sulphur dioxide, which causes respiratory distress. In the 8-port sequential sampler the oxidised part, in the form of liquid droplets or solid particles, is collected by the filter paper.

Figure 7.2 shows the simultaneous smoke measurements at the two sites, measured by the two methods, during June 1971. In most air pollution surveys it is considered sufficient to collect data such as is shown on the left, the daily measurements of the sequential sampler. This diagram tells two things about smoke at the two sites. It is evident that Callan Park is significantly more smokey than is Rydalmere, which is to be expected from its closeness to the city centre. It also appears that there is little relationship between the individual daily amounts at the two sites. When one unit of smoke is recorded at Rydalmere the amount at Callan Park can be anything from 0.7 to 3.5 units. The smoke concentration at one site is a poor indicator of the concentration at the other. If the pollution situation in Sydney were considered serious enough to merit a detailed real-time monitoring network, with action to be taken to relieve the worst air pollution occasions, then it seems from Figure 7.2(a) that the monitoring and the corrective action must be on a scale which is finer than the eight kilometres distance between these two sites. This is because it is possible to have acceptably clean conditions at one place while another, less than eight kilometres away, suffers up to three times the maximum permissible level of one or the other pollutant. A network to deal with this detail over Sydney would require station separations of no more than five kilometres, implying the use of twenty to thirty sites.

Figure 7.2(b) shows the same type of analysis as 7.2(a) with data from the continuous tape Hemeon smoke sampler. It is again evident that Callan Park is more smokey than Rydalmere. However, the amount of scatter in the results is much smaller in this case. When one unit of smoke is observed at Rydalmere the amount at Callan Park falls within the small range from 0.7 to 1.4 units. The smoke concentration at one site is a very good indicator of the smoke concentration at the other. We would do well to have one sampler at Callan Park and its nearest neighbour perhaps ten to fifteen kilometres away. When we apply this notion to the hypothetical real-time monitoring network it is seen that six, or perhaps only four, stations would be sufficient to cover the Greater Sydney area. Put in more general terms, the results from the 8-port samplers imply that the atmosphere of Sydney, for air pollution considerations, is a complex situation with much local detail and any attempt to analyse its motions and chemistry must also be complex and detailed. The Hemeon results suggest quite the contrary, that the situation is simple, relatively uniform, and that any venture to study it as though it is complex will yield essentially uninteresting results.

There is little doubt that during June, 1971, the Hemeon samplers were reflecting the true state of affairs and that there was some malfunction in the 8-port samplers. And yet the results of the 8-port samplers do not look too unlike those which come from a dozen similar instruments in New South Wales and some hundreds in the United Kingdom. Their monthly average values are quite plausible for the middle of the southern winter, as are the highest daily values also. The only reason to suspect their correctness is the availability in this case of some parallel measurements.

We now know something about the atmosphere of Sydney that a hundred years of sampling with the eight-port sampler might not have revealed. There is a considerable degree of order in the ground level concentration of pollutants emitted at ground level throughout the Greater Sydney Area, as smoke is. What is true of smoke should be true also of sulphur compounds for the emission of sulphur dioxide is less dependent on the fine tuning of furnaces and engines than is the emission of smoke. The main factor which decreases the order in the ground level concentration of sulphur compounds is the widely varying propensity of different surfaces to absorb SO_2 from the air. Otherwise we can say with a high degree of confidence that a day of high smoke concentrations at Rydalmere (or for that matter at Callan Park) is a day of high concentrations of sulphur compounds at Rydalmere and at Callan Park. As I said earlier, this high concentration may not be evident in the 8-port sampler measurement of SO_2 for the oxidation of SO_2 may have progressed almost to completion and the oxidation products, which are in liquid droplets or solid particles, would then be captured on the filter where they remain undetected. If it is the sulphate, or perhaps sulphuric acid, which affects respiration then the worst days must be those with high concentrations of smoke, indicating a high total concentration of sulphur compounds, and low concentrations of SO_2, indicating high concentrations of products of oxidation of SO_2. From the Hemeon sampler results we know that good measurements of smoke and sulphur dioxide at either site would provide good data for use in epidemiological studies. From the 8-port sampler results we know that,in the state they were in during June, 1971, neither of those instruments would provide good data for if they generated disordered data on the concentrations of smoke they would do the same to measurements of SO_2.

The above comments should not be taken to mean that the 8-port sampler cannot produce good data. It could equally well have happened that the Hemeon samplers were in error and the 8-port samplers were correct. In that case the 8-port sampler results would have revealed the orderly behaviour of the atmosphere of Sydney. If both had been in error there would be no evidence of the true degree of order in the atmosphere of Sydney. We should learn from this that when a high degree of order has once been demonstrated its failure to appear in other studies, before or after, should be taken as evidence of a disordered monitoring system, not a disordered atmosphere. Clearly there is no data from the European Air Chemistry Network which allows such a study of strictly comparable measurements. The best we could achieve there was a comparison at a distance of a hundred kilometres across national boundaries and a comparison within Britain at a distance of one hundred kilometres to an independent station which was operated by the AERE.

In sampling rain which contains much sea salt the orderly behaviour is to be expected in the chlorine/sodium ratio falling close to 1.80 . The earliest suggestion that it might be otherwise arose from studies made in southern Scandanavia. It is here that we should expect the best chance of valid deviations from the orderly case for close to this region are found a large ocean which produces sea salt aerosol both nearby and at a distance, industrial and urban concentrations burning both oil and coal, and a number of atmospheric chemists. The disorder which was at first interpreted as a real phenomenon is now seen to be an artefact. It is important that sufficient data should have been available subsequently from the same area of northwest Europe for a demonstration that the Cauer process is not to be observed in North America (say) would not constitute proof that it does not occur in southern Sweden.

Later sampling in Sweden showed that although the excess of sodium still occurred the amount had fallen by a factor of ten and it tended to occur at a number of stations in the same month. The order involved in this second point seems to support the reality of the atmospheric phenomenon until it is seen that such order does not extend across the boundary between laboratories. Thus, most of the major deviations from R_s in recent Swedish data are seen to be due to laboratory error and effects of the Cauer process, if any occur, must be reflected only in the minor deviations. It must be two orders of magnitude smaller than was originally believed. Such a process, if it exists, has little functional significance. But more important than this is our knowledge that when the Stockholm laboratory, which is as good as any in the EACN, obtains a value of R which is different from R_s at a coastal station it is probably in error. The return to order is complete. In the region where the Cauer process stands its best chance the best-arranged system for sampling and analysis of precipitation cannot detect it. It would be unwise to invoke the Cauer process to explain values of R deviating from R_s in other areas. Brownscombe and Porter (private communication) consider that the deviations at British stations result from the collection of locally-derived material blown up by the wind. That view should be considered as supplementary to, or alternative to, the theory of laboratory malfunction which has been proposed in this thesis. If it proves to be correct then it is an artefact of sampler design or siting. Neither of these phenomena tell us anything of interest about the atmosphere.

The Belgian and German analyses of calcium and magnesium which were considered in Chapter 2 are of suspect quality because of a high degree of order when disorder is more to be expected. Only in the sea is their a constant ratio between the two elements. The variation of their relative amounts in aerosol brought down in precipitation is thought to be due to differences in the contributions of different sources. Therefore, when the trend over a number of years is the same on a North Sea island, where most of each of calcium and magnesium comes from the sea, as it is in Austria, where most of each comes from the land, the order is thought to have arisen in the factor common to both - the laboratory analysis. The same is true of the Belgian results. Their failure to match each other confirms that at least one laboratory is wrong. The failure to find a comparable degree of order in Sweden suggests that both are wrong for the modest degree of order, expressed in correlations between stations, which is found there is generated by topographic factors which are more pronounced in Sweden than in Germany and Austria or in France, Belgium and Holland.

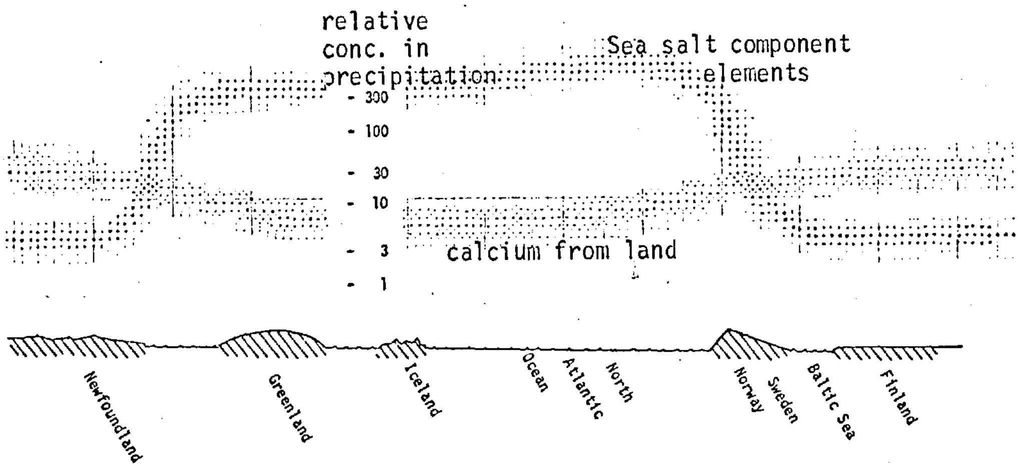


Figure 8.1 Schematic representation of the concentration in precipitation of sea salt and of minerals of land origin, here represented by calcium. The concentration scale is given only in relative units.

Chapter 8. Conclusions

By considering substances which are present in small amounts in rain and snow it has been possible to make some deductions about their transport by the atmosphere. The predominant mineral aerosol from continental sources on average travel further than maritime aerosol. Their washout by rain and snow is markedly affected by topography and the patterns of washout indicate that calcium and magnesium aerosol, the principal substances of land origin which have been considered, are generated either in different geographical areas or from the same area of land in different circumstances. In some circumstances the atmospheric cycle of sodium chloride from the land may be of greater intensity, and greater significance to inland water quality, than the cycle of sodium chloride in sea salt. The precipitation chemistry data which has now been collected by the European Air Chemistry Network is not of sufficient quality to demonstrate the effects of any chemical transformations of sea salt aerosol which might occur. This study has revealed enough inadequacies in the operation of the EACN to merit a fundamental reconsideration of the programme.

A number of other workers have presented evidence of the long-range transport of particles from the land. Prospero et al (1970) and Prospero and Carlson (1972) have identified frequent episodes during which mineral dust from the Sahara reached Barbados in concentrations which were often as high as fifty microgrammes per cubic metre of air at an altitude of two to three kilometres and one third of that concentration below one kilometre. From these measurements they have estimated that each year some tens of millions of tons of mineral dust from the land are transported westward through the longitude of Barbados in the latitude belt between 10°N and 25°N. While much of this dust originates in North Africa some of it undoubtedly comes from Eurasia for North Africa does not constitute a barrier to mineral aerosol which enters it from the direction of the Mediterranean Sea or the Red Sea. Lazrus et al (1970) collected cloud water on a mountain top in Puerto Rico and identified calcium of presumed land origin in concentrations of about 0.4 mg/litre. Eriksson (1957) reported finding calcium in Hawaiian rain in amounts which exceeded the amount from sea salt by about 0.2 to 0.5 mg/litre. For the same reasons which lead us to believe that much of the excess calcium in Icelandic precipitation originated at other land surfaces it seems likely that the calcium in Hawaiian rain has largely originated in distant continental areas. Thus there is evidence of a considerable transport of continental mineral aerosol across both the Pacific and Atlantic Oceans at low latitudes.

From the observations of excess calcium in precipitation which were presented in Chapter 4 there is reason to believe that there is a similar transport in the latitudes around 60°N where the mean wind is from the west rather than from the east as is the case in the tropical belt. Figure 8.1 shows schematically the geographical distribution of calcium from the land and sodium from the sea in precipitation in the latitude belt around 60°N. It is possible that the mid-Atlantic concentrations of calcium from the land have been overestimated due to the presence of a secondary form of calcium in sea salt aerosol, derived from a surface layer of the ocean enriched in calcium-bearing material. It is not possible to estimate the total transport of calcium from the quantity in precipitation for its range of travel, though long, is not known. It is likely that a considerable amount crosses the ocean from one continent to another.

There is good reason to believe that the general characteristics of the atmospheric transport of calcium aerosol apply also to other particles of land origin, whether they are natural or man-made. Cawse and Peirson (1972) found that a number of metals in air at Wraymires, in northwestern England, had deposition velocities significantly lower than that of the calcium particles. Thus their loss from the air by sedimentation is slower than is the loss of calcium particles. From the observation that calcium was found in their rain samples in concentrations comparable with those found in EACN samples we may conclude that their sampling site was clear of local sources of calcium aerosol which might have yielded particles with anomalously high deposition velocities. Thus, if the calcium, which had a deposition velocity estimated to be 0.6 cm/sec., is of the general population of aerosol with a range of transport of hundreds or thousands of kilometres it is likely that the particles containing aluminium, cobalt, lead, copper, zinc and a number of other metals have a similar range of atmospheric transport for their deposition velocities were all estimated to be less than 0.6 cm/sec.

This result implies that the aerosol which is brought down in precipitation has been derived from an area of a million square kilometres or more. Only where there is a strong local source of mineral aerosol would we expect to find the relative abundances of the elements in the aerosol to be related to those in local soils. Such sites could not in general be recommended for monitoring of precipitation chemistry for they can provide no information on the broader scale phenomena of the atmosphere. They are appropriate to areas where industry produces a high concentration of dust and in this application they are called dust deposit gauges.

The large amounts of calcium in aerosol and precipitation at Wraymires led Cawse and Peirson to assume that it is produced by some massive source of air pollution. As we have seen in Chapter 2, the ratio of calcium to magnesium in precipitation over most of Europe is substantially higher than the ratio in crustal rocks. It appears that at places far from the sea the calcium and magnesium components of the aerosol are controlled by the carbonate rocks which are in some cases the skeletal remains of animals. The physical and chemical properties of the natural calcium compounds lead to them being more easily mobilized as an aerosol than are the average crustal rocks and soils, an important factor for life on earth for this element is a fundamental part of the structure of most living things. While the beds of limestone which have been laid down in the sea in the past play an important part in supplying calcium to life on dry land it is only when the calcium is returned to the sea that it becomes available for the eventual replacement of those beds. Life on dry land does little to ensure the replacement of stocks of calcium compounds in forms which will eventually be spread far and wide by the atmosphere with an efficiency greater than that with which many other minerals are spread. Life on dry land is the beneficiary of a slow cycle of calcium which procedes through the ocean and the rocks.

If the processes of aerosol production and transport favour the movement of calcium compounds in this way they might also favour the movement of some other mineral elements. Cawse and Peirson (1972) have assumed that man-made pollution is the source of any element in aerosol or precipitation which is present in greater quantity than in the average soils or local soils, relative to a reference element. In relation to their reference element, scandium, they found aluminium, manganese, iron, rubidium, lanthanum, cerium, thorium and gold to be present in

aerosol and precipitation in their soil abundances. Elements which were enriched relative to scandium, apart from the components of sea salt, were vanadium, chromium, cobalt, nickel, copper, zinc, arsenic, selenium, cadmium, indium, antimony, cesium, mercury, lead and calcium If the enrichment of calcium in aerosol is a natural process the same might be true of some other elements. Zoller et al (1974) analysed snow collected at the South Pole and found no magnesium or calcium in excess of their continental crustal abundances. If there is a cycle in excess calcium from carbonate rocks it does not appear to make its existence felt at the South Pole.

In Chapter 3 the average concentration of sodium in precipitation at Swedish inland stations was shown to be about 0.3 mg/litre. Lazrus et al (1970) found that in sea salt aerosol in cloud droplets the magnesium is enriched relative to chlorine, and therefore also to sodium, by no more than 4%. Therefore in Swedish precipitation the sea supplies no more than 0.05 mg of magnesium per litre of rain. This accounts for only one fifth of the magnesium in Swedish precipitation. We must assume that the other 0.2 mg/litre is derived from the land. In a short period of sampling in the British Isles and elsewhere Cawse et al (1974) found magnesium in precipitation in concentrations between 0.2 and 1.0 mg/litre but on the basis of the concentration of sodium he estimated that in each case no more than one seventh of the magnesium could be attributed to land sources. It appears that in Scandanavia there is considerably more magnesium of land origin in aerosol than there is in the British Isles. It is possible that the short period of sampling by Cawse produced results which are not representative of the long term average.

Valach (1967) reanalysed data of Junge (1956) and Eriksson (1959, 1960) to test the Cauer hypothesis. He assumed that successive measurements of the ratio of chlorine to sodium in giant sea salt particles were independent measurements of the same quantity and decided that, as the sea water ratio (1.80) falls within the range from 1.14 to 1.92 which was observed in the course of Junge's experiment, there was no evidence to support the Cauer hypothesis. He also demonstrated that the mechanism postulated by Eriksson is too slow to release a significant amount of chlorine from the aerosol in the time which is available, no more than a few days.

In this thesis I have demonstrated that in the records of the EACN the deviations at coastal stations of the Cl/Na ratio from R_s are in most cases due to laboratory errors. Precipitation at inland stations may contain significant amounts of chlorine and/or sodium from sources other than the sea. The apparent excess of chlorine in German and Austrian precipitation may come from coal burning but this is by no means certain. In Australia much of the sodium and chlorine which is deposited on the land falls as a dry aerosol and is derived from soil or from dry salt lakes in the interior of the continent.

I have examined Junge's (1963) assumption that there is a continental floor (incorrectly called a "plateau") in the concentration of sea salt aerosol, caused by the increased vertical mixing as maritime air passes over a continent. If inland areas of Iceland, Ireland and western Norway, between ten and one hundred kilometres from the coast, are considered to be representative of a North Atlantic maritime plateau in sea salt concentration and central Finland is taken as representing the concentration of the continental floor then there is a

factor of at least thirty five between the floor and the plateau. The mixed layer over the continent is of the order of three kilometres deep. By Junge's theory this implies that the mixed layer over the ocean is no more than eighty five metres deep, a result which is unlikely considering that the oceanic sites are so far downwind from the coast. It appears that after travelling one hundred kilometres inland a considerable amount of salt is still to be lost in the next five hundred kilometres by washout and perhaps also by sedimentation. Near the Atlantic coast precipitation is preferentially produced by moist and salt-rich maritime airmasses. For this reason precipitation is a biased sampler of the aerosol which is present in the air over the coastal strip. Junge's theory was based in part on the measured number concentration of sea salt particles in air. As a few large particles can comprise a large fraction of the total weight of aerosol but a negligible fraction of the numbers their loss from the air by washout or sedimentation may produce a big difference in the floor/plateau ratio by weight but a small difference in the ratio by number.

Finally I will comment on the quality of the data which has been accumulated by the European Air Chemistry Network since 1955, and on the factors in the organization which have played a part in determining data quality. The two quality control factors, balance of positive and negative ions and total conductivity which matches ionic conductances, which I described in the introduction have clearly proved inadequate. The Belgian laboratory appears to have suffered very badly. The analyses which I have presented suggest that the Swedish laboratory has performed quite well. However, without the independent contribution of the Danish laboratory between 1957 and 1960 and since 1970 there would have been no way of checking the Swedish results and the question of the dissociation of sea salt aerosol would remain unresolved. If all EACN stations had returned samples to just one laboratory there would have been no independent check on the performance of the system. As we have seen in France/Belgium/Holland and in Germany/Austria, fluctuations in laboratory performance can impose trends upon the data for which we might seek a meteorological or geochemical explanation. Such a malfunction lead Rossby and Egner (1955) and Eriksson (1959, 1960) to propagate the Cauer hypothesis at a great cost to the quality of later data.

The operation of separate regional laboratories makes possible one important aspect of data quality control. A regular practice of exchanging samples, natural and manufactured, which test the entire range of concentrations encountered in real samples will produce a continuous record of each laboratory's performance. In his report of the informal conference which lead to the establishment of the EACN Eriksson (1954) recorded the recommendation that different sections of the network should have one sampling station in common as a check on the analytical results. If no exchange is made then studies such as I have presented here may lead us eventually to identify critical defects in old data which leave us no choice but to discard the data. The cost of such a defect in wasted time, money and opportunity for good measurement is obvious. By the time the defect is discovered it is too late to rectify the situation. There is no point in considering the relative efficiencies of collection by different precipitation samplers, which will change the results at most by twenty percent, until errors of chemical analysis of five times that magnitude have been excluded.

The operation of regional laboratories produces one unfortunate result. Within a region the limited number of people available to analyse and interpret the data usually prevents serious work on data from outside the region. I believe that I have demonstrated that only by considering a wider area can the results from one region be seen in context. There is also the diplomatic difficulty of pointing out errors in the work of a neighbouring region. To dwell on the problems of others at the length required to determine the form and possible cause of an error does seem indelicate. This may be why the first critical evaluation of the performance of the European Air Chemistry Network, in the form of this thesis and related papers, (Paterson & Scorer 1973a,b, 1975 and Paterson 1975) appeared only after twenty years of operation and has been made outside of the participating laboratories.

It appears from the relative success of the Swedish laboratory that the immediate use of data for scientific purposes is an important factor in the control of its quality. The collection and analysis of samples must not be allowed to become just an administrative routine. In such circumstances a monitoring system, however well established at the start, will deteriorate as changes of staff and indifference to the specific results lead to an estrangement from the nature of the environment which is being monitored. Where people with a research interest scrutinise the data as it becomes available it is likely that a serious malfunction will be detected within a few months. The initial analysis of the data enhances its value by verifying its correctness, where this is the case. There is no "ultimate" analysis of a body of environmental data, leaving no information of interest for later study, because a multitude of factors have contributed to producing that state of the environment which has been measured. In general only a few of those factors can be evaluated effectively but the higher the quality of the data the more useful the information which may be extracted. For this reason the easy availability of data for diverse studies lends itself to full value being obtained from the data. One of the admirable aspects of the European Air Chemistry Network has been the willingness with which all participants make their data available to interested researchers.

Acknowledgements

I would like to express my thanks to the participants in the European Air Chemistry Network who have made their data so freely available, and especially to those who have given me additional help with this work. Mr Granat of the Stockholm laboratory kindly agreed to the analysis in that laboratory of the precipitation samples from the North Sea. I also thank the Air Pollution Control Branch of the NSW Department of Health for the use of the data which is discussed in Chapter 7.

Professor Richard Scorer has provided a constantly stimulating environment in the Mathematics Department in which it has been a privilege to work for the past three years.

Shell International Petroleum awarded the research grant which has paid for this work and has given unqualified support in the related matter of precipitation sampling over the North Sea.

References

Bloch, M. R. and W. Luecke (1972) Geochemistry of ocean water bubble spray. J. Geophys. Res. 77 Pp 5100 - 05

Bonython, C. W. (1956) The salt of Lake Eyre - its occurrence in Madigan Gulf and its possible origin. Trans. Roy. Soc. South Aust. 79 Pp 66 - 92

Brownscombe, J. L., Porter, M. R. and Goldsmith, P. (1973) A critical appraisal of the performance of the air sampling equipment used in the European Air Sampling Network. WMO Special Env. Report No. 3, WMO 368. Pp 297 - 306

Bureau of Meteorology, Commonwealth of Australia (1968) The weather and climate of Australia and the TPNG. Bulletin No. 1.

Burridge, D. M. (1974) Some aspects of the climate of the North Sea as observed from offshore installations. London Weather Centre Mem. 22, Addendum No. 3

Cauer, H. (1949) Ergebnisse chemisch-meteorologischer Forschung. Archiv fur Meteorologie, Geophysik und Bioklimatologie, Serie B, Band I, Pp 221 - 56

Cawse, P. A. (1974) A survey of atmospheric trace elements in the U.K. (1972 - 73). AERE R 7669 HMSO

Cawse, P. A. and Peirson, D. H. (1972) An analytical study of trace elements in the atmospheric environment. U.K. Atomic Energy Authority, AERE R7134 HMSO

Degens E. T. (1965) Geochemistry of sediments - a brief survey. Prentice - Hall

Egnér, H. and Eriksson, E. (1955) Current data on the chemical composition of air and precipitation. Tellus 7, Pp 134 - 39

Emanuelsson, A., Eriksson E. and Egnér, H. (1954) Composition of atmospheric precipitation in Sweden. Tellus VI Pp 261 - 7

Eriksson E. (1954) Report on an informal conference in atmospheric chemistry held at the Meteorological Inst, University of Stockholm, May 24 - 6 1954. Tellus VI Pp 302 - 07

Eriksson, E. (1957) The chemical composition of Hawaiian rainfall. Tellus IX Pp 509 - 20

Eriksson, E. (1959) The yearly circulation of chloride and sulphur in nature; meteorological, geochemical and pedalogical implications. Part 1. Tellus XI Pp 375 - 403

Eriksson, E. (1960) The yearly circulation of chloride and sulphur in nature...Part II Tellus XII Pp 63 - 109

Eriksson, E. (1960) Reply to Letter to the Editor by Junge, C. (1960) Tellus XII Pp 465 - 67

Eriksson, E. (1970) The importance of investigating global background pollution. WMO Tech. Note 106: Meteorological Aspects of Air Pollution.

Hutton, J. T. (1958) The chemistry of rainwater with particular reference to conditions in SE Australia. Arid Zone Research XI, UNESCO, Paris. Pp 285 - 90

Hutton J. T. (1965) The redistribution of the more soluble chemical elements associated with soils as indicated by analysis of rainwater, soils and plants. Trans. 9th Int. Congress of Soil Science.

Hutton, J. T. and Leslie, T. I. (1958) Accession of non-nitrogenous ions dissolved in rainwater to soils in Victoria. Aust. J. Agric. Research 9 Pp 492 - 507

Johansson, O. (1959) On sulphur problems in Swedish agriculture. Kungl. Lantbrukshogskolens Annaler 25 Pp 57 - 169

Junge, C. E. (1956) Recent investigations of air chemistry. Tellus VIII Pp 127 - 39

Junge, C. E. (1960) Letter to the Editor on Eriksson, E. (1959, 1960) Tellus XII Pp 463 - 65

Junge, C. E. (1963) Air chemistry and radioactivity. Int. Geophysics Series, Vol 4. AP

Junge, C. E. (1972) The cycle of atmospheric gases - natural and man-made. (Symons Lecture) Quart. J. Royal Meteorological Society 98, Pp 711 - 29

Junge, C. E. and Werby, R. T. (1958) The concentration of chloride, sodium, potassium, calcium and sulphate in rain water over the United States. J. Meteorol. 15 Pp 417 - 25

Kendall, M. G. and Stewart, A. (1967) The advanced theory of statistics. Vol 2, 2nd Ed. Charles Griffin and Co. Ltd, London.

Lazrus, A. L., Baynton, H. W. and Lodge, J. P. (1970) Trace constituents in oceanic cloud water and their origin. Tellus XXII Pp 106 113

Liss, P. S. and Slater P. G. (1974) Flux of gases across the air-sea interface. Nature 247 Pp 181 - 4

Lowry, H. H. (1963) Chemistry of coal utilisation. Supplementary Volume

Monthly Climatic Data for the World. (continuing series)
U.S. Dept. of Commerce, NOAA Environmental Data Service. Ashville, N. Carolina

Munn, R. E. and Rodhe, H. (1971) On the meteorological interpretation of the chemical composition of monthly precipitation samples. Tellus XXIII Pp 1 - 13

Oddie, B. C. V. (1959) The composition of precipitation at Lerwick, Shetland. Quart. J. Royal Meteorological Society 85 Pp 163 - 5

Paterson, M. P. and Scorer, R. S. (1973a) Data quality and the European Air Chemistry Network. Atmos. Environment 7 Pp 1163 - 71

Paterson, M. P. and Scorer, R. S. (1973b) Quality control in global and regional air chemistry monitoring networks: lessons of the EACN
WMO Special Env. Report No. 3, WMO 368. Pp 647 - 55

Paterson, M. P. and Scorer, R. S. (1975) The chemistry of sea salt aerosol and its measurement. Nature (in press)

Peirson, D. H., Cawse, P. A., Salmon, L. and R. S. Cambray (1973)
Trace elements in the atmospheric environment. Nature 241 Pp 252 - 56

Peirson, D. H., Cawse, P. A. and Cambray, R. S. (1974) Chemical uniformity of airborne particulate material, and a maritime effect. Nature 251 Pp 675 - 8

Prospero, J. M. and Carlson, T. N. (1972) Vertical and areal distribution of Sharan dust over the Western Equ. North Atlantic Ocean J Geophys. Research 77 Pp 5255 - 65

Riley, J. P. and G. Skirrow (1965) Chemical Oceanography, Vol 1. Academic Press.

Ross, F. F. (1972)

Rossby, C.-G. and Egnér, H. (1955) The chemical climate and its variation.
Tellus VII Pp 118 - 33

Schmidt, F. H. and Velds, C. A. (1969) Changing meteorological circumstances and the decrease in SO_2 concentrations around Rotterdam. Atmos. Environment 3 Pp 455 - 60

Skipsey, E. (1974) Distribution of alkali chlorides in British coal seams.
Fuel 53 Pp 258 - 67

Stevenson, C. M. (1967) Chemical composition of rainwater and air over the British Isles and Eire for the years 1959 - 64. Quart. J. Royal Meteorological Society 84 Pp 46 - 55

Swedish Case Study (1972) Air Pollution across National Boundaries. The impact on the environment of sulphur in air and precipitation.
Sweden's case study for the United Nations conference on the human environment, Stockholm 1972. Royal Ministry for Foreign Affairs, Royal Ministry for Agriculture

Taylor, S. R. (1964) Abundance of chemical elements in the continental crust: a new table. Geochimica et Cosmochimica Acta 28 Pp 1273 - 85

Twomey, S. (1960) On the nature and origin of natural cloud nuclei. Bulletin Obs. Puy de Dome 1960 Pp 1 - 19

Valach, R. (1967) The origin of the gaseous form of natural atmospheric chlorine. Tellus XIX Pp 509 - 16

Wallén, C. C. (1970) Climates of Northern and Western Europe. World Survey of Climatology, Vol 5 Elsevier

Zoller, W. H., Gladney, E. S. and Duce, R. A. (1974) Atmospheric concentrations and sources of trace metals at the South Pole. Science 183 Pp 198 - 200

Appendix A. Precipitation samples in the EACN records.

Table A.1 is a record of the EACN precipitation data which has been published by April 1975. The co-ordinates of the stations are given in Table A.2. The stations are grouped by country. The laboratory reposible for the analysis has been identified but in some cases where there has been a change of laboratory there is some uncertainty over the date of the change. In Table A.1 the stations and laboratories are identified only by number. Laboratories are listed below.

① International Meteorological Institute
University of Stockholm
SWEDEN
formerly
National Agricultural College
Uppsala
SWEDEN

② Statens Planteavls-Laboratorium
Copenhagen
DENMARK

③ Oceanographic Institute
Helsinki
FINLAND

④ Landwirtschaftliche Hochschule
Karlesruhe-Durlach
WEST GERMANY

⑤ Institut d'Hygiene et d'Epidemiologie
Laboratorie de Chimie et de Physique
Bruxelles
BELGIUM

⑥ Meteorological Office
Bracknell
ENGLAND

⑦ Meteorological Service
Department of Transport and Power
Dublin
EIRE

Table A.1 includes all data recorded in data sets I to V for countries which have participated in the EACN for more than five years. While some recent data is yet to be published in Sweden, and therefore has not been recorded here, it is generally available upon request to the participating country.

This thesis points out some of the dangers of considering data from one country or one laboratory in isolation. It is to be hoped that people analysing EACN data in future will consider wider regions so as to confirm the reality of the subjects which they study. Only by the free flow of such results and consultation on problems as they are revealed will the quality of the Network in all participating countries be raised.

Table A.1 Record of return of monthly precipitation samples by stations of the European Air Chemistry Network. The analyses of samples recorded in this Table have been published in data sets I to V by the International Meteorological Institute of the University of Stockholm. The laboratory responsible for each analysis is recorded by the circled laboratory number on the left.

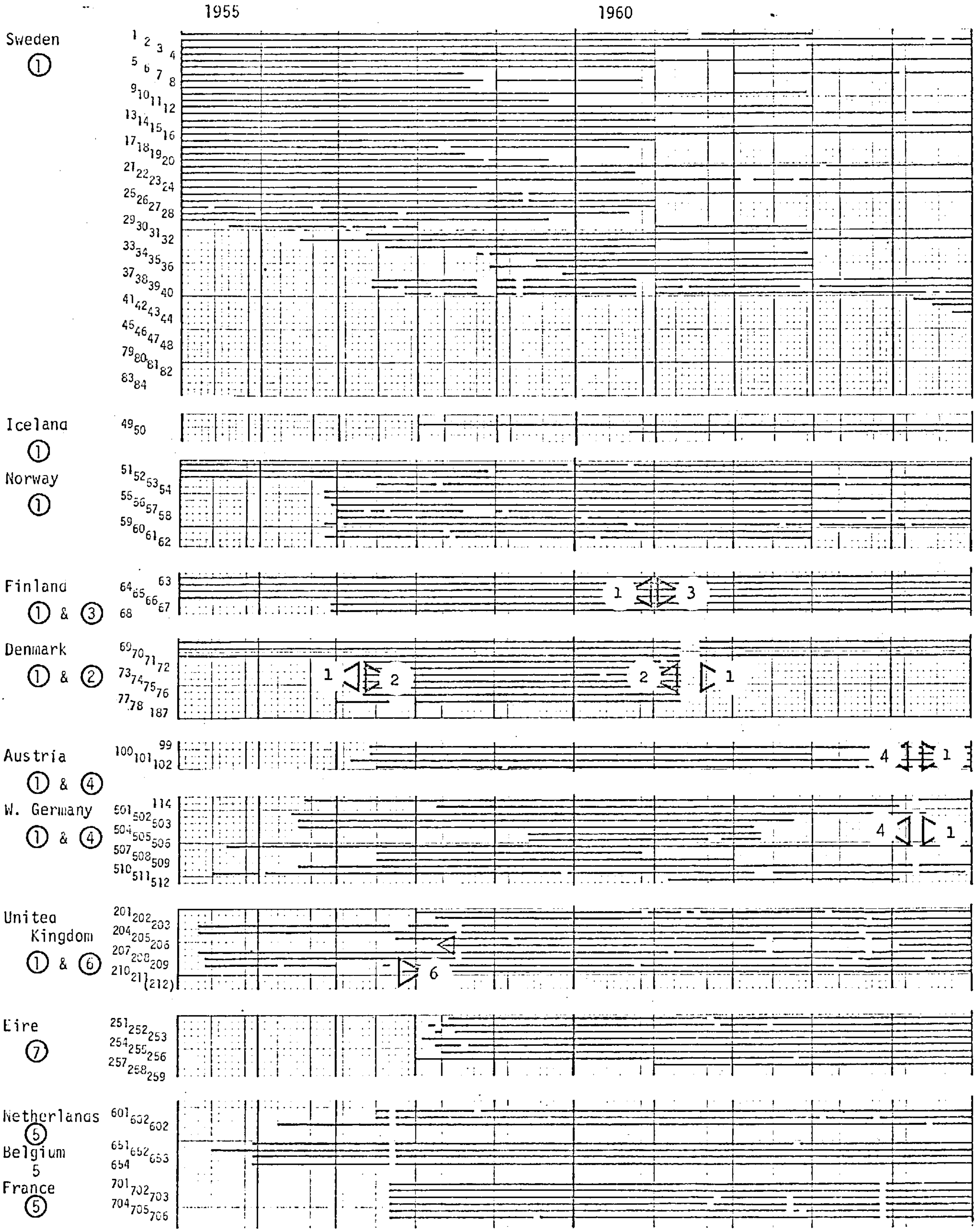


Table A.1 (continued)

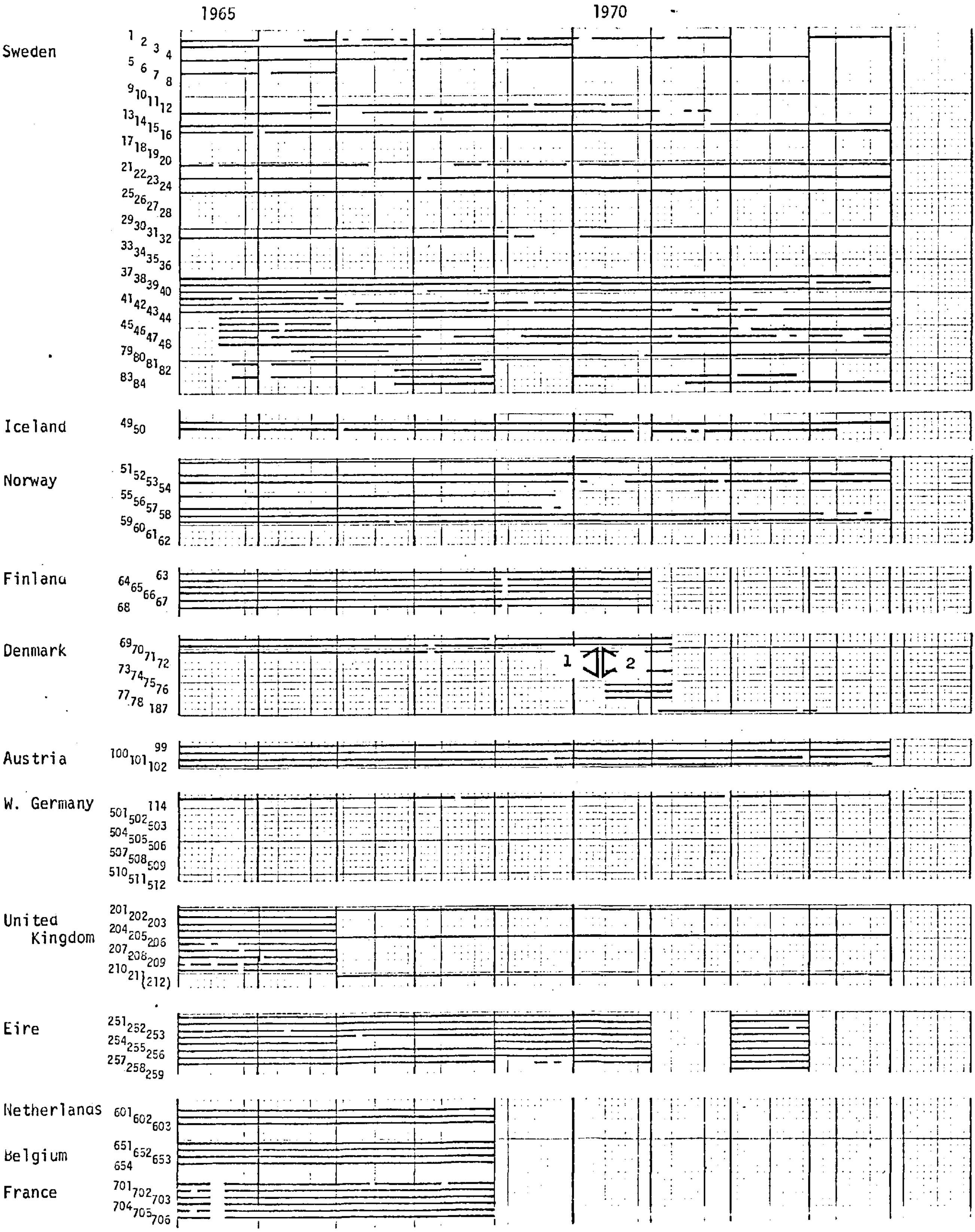


Table A.2 List of stations and their geographical co-ordinates for which the return of monthly precipitation samples are recorded in Table A.1 .

SWEDEN		Alt.	Lat.	Long.
1	Riksgränsen	508m	66°26'	18°08'
2	Kiruna	412	67°52'	20°35'
3	Arjeplog	434	66°03'	17°54'
4	Öjebyn	5	65°24'	21°30'
5	Röbäcksdalen	15	63°48'	20°12'
6	Offer	27	63°12'	17°48'
7	Bredkälen	400	63°54'	15°18'
8	Åre	440	63°24'	13°06'
9	Sveg	356	62°02'	14°22'
10	Åmot	175	60°53'	16°25'
11	Sala	80	68°00'	16°36'
12	Ultuna	50	59°48'	17°42'
13	Erken	12	59°54'	18°42'
14	Strängnäs	20	59°18'	17°06'
15	Forshult	192	60°05'	13°47'
16	Kvarntorp	100	59°12'	15°23'
17	Lanna	100	58°26'	13°08'
18	Bornö	5	58°24'	11°36'
19	Vinga	19	57°38'	11°37'
20	Falsterbobruk	50	57°42'	16°12'
21	Flahult	225	57°42'	13°12'
22	Ambjörnarp	220	57°25'	13°17'
23	Plönninge	50	56°42'	12°45'
24	Söraby	180	57°00'	14°54'
25	Smedby	20	56°42'	16°12'
26	Sylfaste	40	57°36'	18°24'
27	Bräkne-Hoby	40	56°12'	15°06'
28	Alnorp	20	55°42'	13°06'
29	Hilleshög	50	55°54'	12°54'
30	Rättvik	200	60°54'	15°06'
31	Vreta Kloster	40	58°36'	15°38'
32	Skurup	40	55°28'	13°30'
33	Frösön	364	63°12'	14°29'
34	Ömnestad		56°03'	14°01'
35	Högaryd		56°43'	14°10'
36	Östra Torsås	189	56°45'	14°54'
37	Gamleby	34	57°54'	16°25'
38	Göteborg	15	57°42'	11°58'
39	Stockholm	60	59°19'	18°02'
40	Bohus-Malmön	27	58°12'	11°22'
41	Skutskär	5	60°38'	17°25'
42	Ryda Kungsgård	15	59°45'	17°08'
43	Uppsala Näs	12	59°45'	17°37'
44	Klunkhyttan	158	59°16'	14°53'
45	Stångfallet	100	59°55'	14°56'
46	Färna Bruk	65	59°47'	15°51'
47	Björsund	5	59°28'	16°49'
48	Tärna	51	59°51'	16°38'
79	Nyboda	40	59°25'	18°11'
80	Sjöängen	128	52°46'	14°18'
81	Bredkälen	400	63°54'	15°18'
82, 83, 84	(& 7)	"	" "	" "

Stations 115 to 130, which are also in Sweden, are not included.

ICELAND

49	Rjupnahed	120	64°05'	21°51'W
50	Vegatunga	100	64°10'	20°29'W

NORWAY

51	Ås	95	59°40'	10°47'
52	Vågamo	371	61°52'	9°06'
53	Lista	14	58°06'	6°34'
54	Tana	9	70°24'	28°12'
55	Ytteröy	74	63°48'	11°13'
56	Gjermundnes	51	62°37'	7°10'
57	Fortun	27	61°30'	7°42'
58	Fanaråken	2026	61°31'	7°54'
59	Trysil	362	61°20'	12°15'
60	Kise	128	60°46'	10°49'
61	Stend		60°17'	5°20'
62	Dalen	77	59°27'	8°00'

Stations 165 and 166, which are also in Norway, are not included.

FINLAND

63	Kuahava	50	63°06'	23°03'E
64	Kuopio	95	63°00'	27°44'
65	Jyväskylä	145	62°24'	25°40'
66	Tvärminne	5	59°54'	23°12'
67	Sodankylä	180	67°22'	26°39'
68	Punkaharju	90	61°48'	29°20'

Stations 175 - 183, which are also in Finland, are not included.

DENMARK

69	Ödum	61	56°18'	10°07'E
70	Askov	63	55°28'	9°06'
71	Tystofte	13	55°14'	11°19'
72	Vildmosen	8	57°12'	9°48'
73	Grenå	8	56°25'	10°53'
74	Borris	25	55°57'	8°38'
75	Lyngby	35	55°47'	12°29'
76	Blangestedgård	15	55°23'	10°27'
77	Höjer	1	54°57'	8°41'
78	Abed	8	54°50'	11°20'
187	Faeröerne (approx)	24	62°01'	6°46'W

Stations 186 - 199, which are also in Denmark, are not included.

UNITED KINGDOM

201	Lerwick	83	60°08'	1°11'W
202	Stornoway	14	58°13'	6°19'
203	Aberdeen	66	57°10'	2°15'
204	Edinburgh	187	55°53'	3°15'
205	Eskdalemuir	242	55°19'	3°12'
206	Aldergrove	67	54°39'	6°13'
207	Leeds	53	53°50'	1°20'
208	Rothamsted	126	51°48'	0°20'
209	Newton Abbot	82	50°32'	3°23'
210	Camborne	88	50°13'	5°19'
211	Bracknell	73	51°25'	0°15'
212	Leman Bank	26	53°06'	2°09'E

EIRE

251	Malin Head	20	55°22'	7°20'W
252	Belmullet	9	54°14'	10°00'
253	Clones	87	54°11'	7°14'
254	Dublin Airport	68	53°26'	6°15'
255	Birr	70	53°05'	7°35'
256	Rosslare	23	52°15'	6°20'
257	Valentia	9	51°56'	10°15'
258	Shannon Airport	2	52°41'	8°55'
259	Cork	151	51°56'	8°30'

AUSTRIA

99	Retz	243	48°46'	15°58'E
100	Wien	203	48°15'	16°22'
101	Linz	309	48°04'	14°25'
102	Klagenfurt	448	46°39'	14°20'

GERMANY

114	Hohenpeissenberg	975	47°48'	11°01'E
501	Westerland	12	54°55'	8°20'
502	Schleswig	48	54°30'	9°32'
503	Braunschweig	83	52°17'	10°44'
504	Bonn	62	50°45'	7°06'
505	Königstuhl	590	49°24'	8°44'
506	Leimen	140	49°23'	8°39'
507	Augustenberg	145	49°00'	8°30'
508	Ettenheim	202	48°16'	7°49'
509	Ringsheim	170	48°15'	7°46'
510	Baldenwegerhof	340	47°59'	7°57'
511	Feldberg	1493	47°52'	8°01'
512.	Stade (approx)		53°35'	9°30'

THE NETHERLANDS

601	Den Helder	6	52°53'	4°45'E
602	Witteven	18	52°48'	8°40'
603	De Bilt	10	52°06'	5°11'

BELGIUM

651	St André	14	51°10'	8°11'E
652	Uccle	100	50°48'	4°21'
653	Botrange	694	50°30'	6°06'
654	Dourbes	224	50°06'	4°36'

FRANCE

701	Magny-les Hameaux	168	48°44'	2°04'E
702	Rostenen	264	48°14'	3°20'W
703	Le Mans	58	47°56'	0°12'E
704	Luxeuil	275	47°47'	6°21'E
705	Bourges	158	47°04'	2°22'E
706	Amberieu	254	45°59'	5°20'E

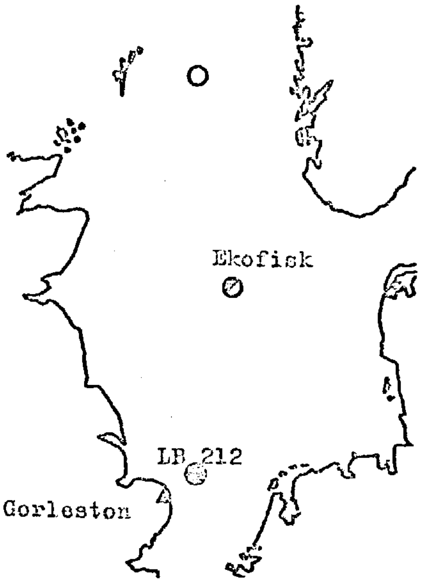


Figure B.1 Positions of the existing and proposed precipitation samplers on gas and oil production platforms in the North Sea. LB 212 is serviced from England and the samples analysed in Stockholm. Gorleston is the nearest meteorological station on land.

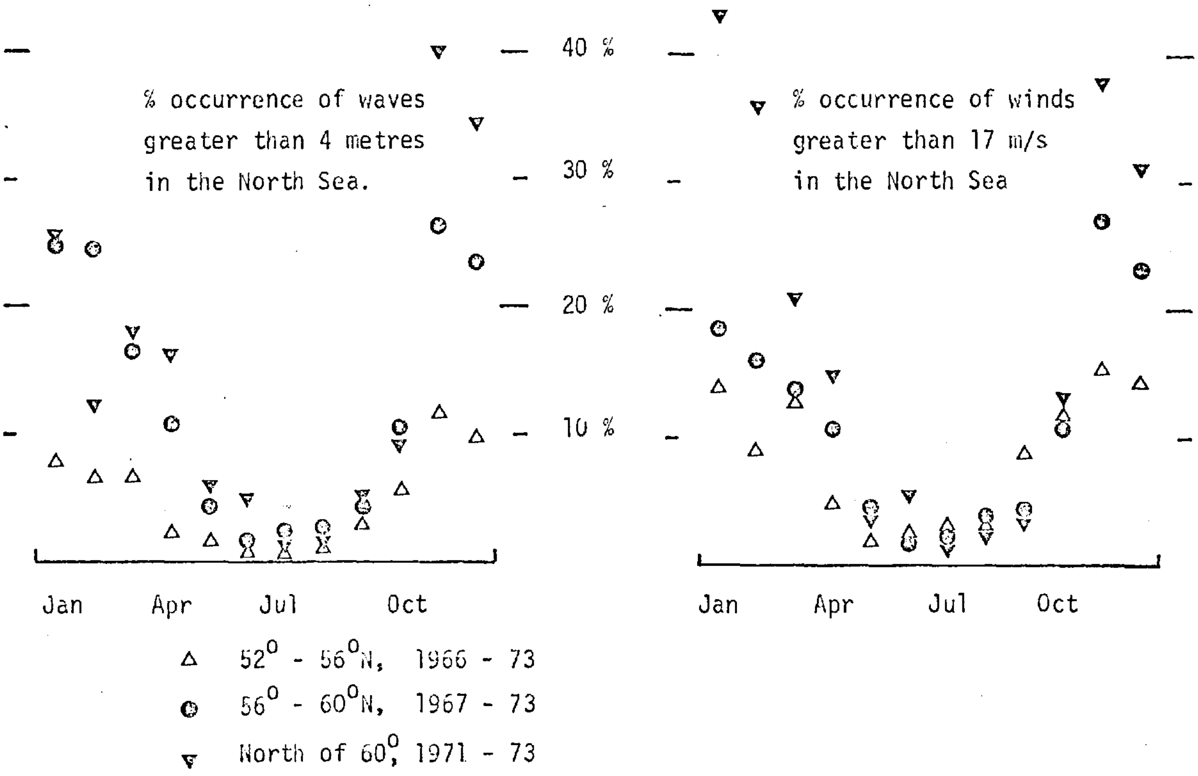


Figure B.2 Frequency of occurrence of high waves and strong winds at different latitudes in the North Sea. Periods of observation are short and may not give a fully representative average.

Appendix B Precipitation over the North Sea

One obvious gap in our knowledge of precipitation chemistry is the almost total lack of information on the composition, or even the amount, of rain at sea. As the North Sea comprises a substantial part of the area of northwest Europe it is impossible to account for the transport of substances by the atmosphere without knowing what arises from or is deposited in the sea. I was pleased to accept the offer by Mr. A. D. P. Pride of Shell International Petroleum to arrange facilities for routine precipitation sampling on North Sea gas or oil production platforms as an extension of the European Air Chemistry Network programme.

In July 1973 a temporary sampler, constructed in the workshop of the Mathematics Department at Imperial College, was set up on the Shell/Esso Leman A gas production platform. Its installation had been slightly delayed to allow completion of cleaning and repainting of the platform. In November 1973 the temporary sampler was replaced by a standard sampler from the International Meteorological Institute in Stockholm. The Atomic Energy Research Establishment Department of Health Physics had sampled air and precipitation at the nearby Leman B(T) platform during 1972-3 and analysed the samples for a number of trace elements, principally metals. Some of that work has been described by Peirson, Cawse and Cambray (1974).

Figure B.1 shows the position of the Leman A station, with its EACN designation LB 212, and the positions of two further proposed sampling sites. Sampling at Ekofisk has been imminent since the summer of 1973. Figure B.2 shows the frequency of occurrence of high waves and strong winds in different latitudes of the North Sea. It is evident that the conditions for sampling become increasingly difficult with distance to the north. Whereas it has been possible to operate at LB 212 without heating to melt snow and prevent freezing of the sample it may not be possible to do so at other sites further to the north where cold winds from northern Europe are to be expected. Outside areas of the platforms have Division 2 safety ratings and so require all electrical equipment to be explosion-proof. This makes the operation of a thermostated heater difficult but not impossible. It may make it impossible to operate a covered sampler which opens automatically during precipitation. Where high waves and strong winds produce a great deal of sea spray at times when it is not raining the covered sampler may be necessary.

The samples from LB 212 have been analysed in the Stockholm laboratory. Provisional results of the analysis are recorded in Table B.1 . The results must be used with care for there are a number of substantial and trivial sources of possible contamination. The lift which is provided by the airflow over the platform attracts a constant escort of sea birds which soar above the leading edge of the platform. When the wind is from the east this brings them over the remote corner of the platform where the sampler is situated and a single dropping would dominate the trace substances in the precipitation sample. The sampler has a ring of spikes to deter the perching of land birds, notably starlings and pigeons, which visit the platform from time to time. Insects or insect parts have been

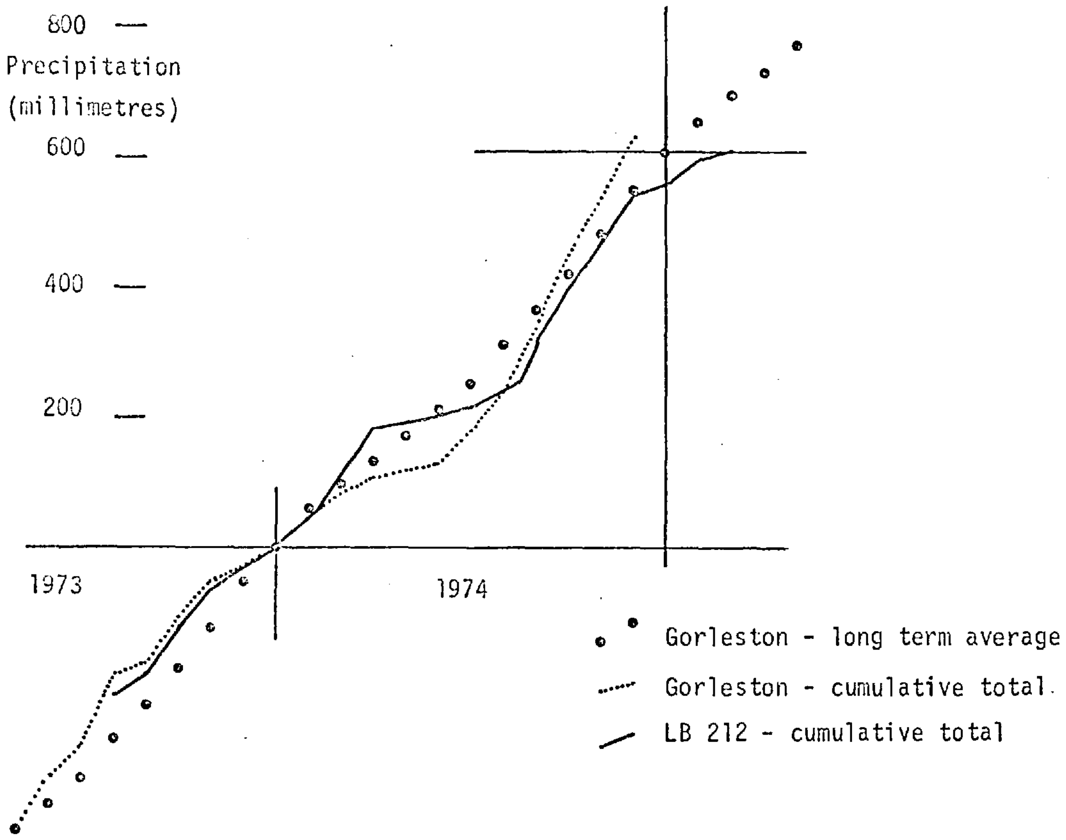


Figure B.3 Precipitation at LB 212, on the Leman A platform 50 km off the Norfolk coast, compared with Gorleston, the nearest meteorological station on land.

found in samples 10, 11 and 13. The insects are presumably attracted at night by the nearby lights on the platform. There is a possibility that large amounts of sea spray are splashed into the sampler but the slim legs of the Leman A platform offer little resistance to the waves and it is likely that most of that which is collected is there independently of the presence of the platform. Where heavier structures are used in deeper and rougher waters further to the north the breaking of waves on the platform supports may produce a significant part of the total collection. There are few sources of contamination on the platform as little power is used and any venting of gas is at a much higher level than the deck.

The high mobility of staff in the off-shore gas and oil industry has at times made it hard to ensure continuity of sampling. However, those who have been asked to help have given enthusiastic support whenever it was requested. Short term samples, taken only while the rain falls, are now being collected by two methods. A sampler with a 310 mm diameter polypropylene funnel is rinsed with distilled water and then exposed during precipitation. In addition, clean polypropylene dishes which are tied down by their feet to prevent them blowing away are set out and their contents poured into a bottle when sufficient sample has been collected. The three results in Table B.2 describe the aerosol which was collected when the samplers were exposed for fifteen hours during dry weather and then rinsed with 200 ml of distilled water. Several short-term rain samples have now been collected and are being analysed. The results of the analysis will be available upon request.

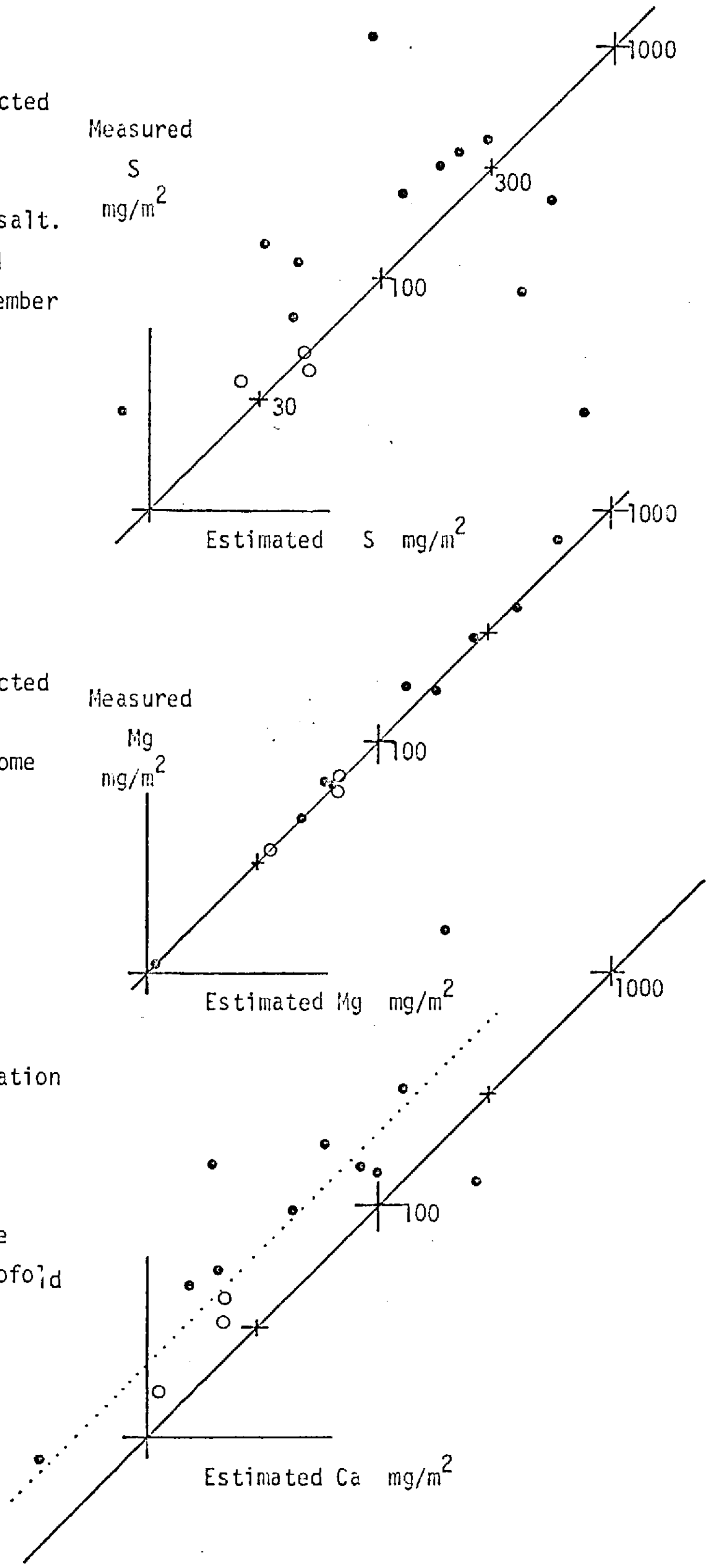
Results of the analysis

Figure B.3 shows the cumulative total of precipitation at LB 212 since sampling began. This form of presentation allows comparison with monthly data from other stations without distortion due to the sometimes irregular exchange of the sample bottles. Data from Gorleston has been substituted for October 1973 when the sample was lost due to inadequate instructions being provided with the sampler. For comparison over the period of sampling the cumulative total of precipitation at Gorleston, both for this period and for average conditions, has been plotted on the same Figure. It is evident that the amount of precipitation at the platform, which is fifty kilometres from the coast, is comparable with that on the adjacent land. There may be a different seasonal distribution but a longer record would be needed to determine that.

Figure B.4 shows some of the results of chemical analysis. The amounts of sulphate sulphur, magnesium and calcium which were recorded are plotted against the amounts estimated to have come from sea salt. As the Cl/Na ratios range from 1.6 to 3.3 a compromise has been reached and the amount of the ion is compared with the sum of Cl^- and Na^+. This ensures that the results are more often incorrect but by a smaller amount than might otherwise be the case. The aerosol results from Table B.2 are shown with open circles.

First consider Figure B.4(b). This indicates that the precipitation samples only occasionally contain an excess of magnesium which was greater than the expected measurement errors. There is no significant source of magnesium contributing to this precipitation other than the sea. The same is true of the aerosol captured on dry polypropylene surfaces.

Figure B.4



(a) sulphate sulphur in monthly precipitation samples collected at LB 212 compared with the amounts estimated to have come as a component of sea salt. The open circles are aerosol samples collected 19/20 December 1974.

(b) magnesium in monthly precipitation samples collected at LB 212 compared with the amounts estimated to have come as a component of sea salt.

(c) calcium in monthly precipitation samples colle ted at LB 212 compared with the amounts estimated to have come as a component of sea salt. The dotted line represents a twofold enrichment of calcium.

This good fit tends to confirm the validity of estimating the amount of sea salt from the sum of the sodium and chloride. Figure B.4(a) shows the amount of sulphate. It is difficult to explain the gross deficits of sulphate in two months for there is no known process which will remove sulphate from a sea salt aerosol or from precipitation. The absence of excess sulphate in the three aerosol samples suggests that the excess sulphate reaches the sampler principally in precipitation. However, the tendency for greater sulphate excesses to be associated with greater amounts of sea salt (bearing in mind that the scales are logarithmic) is not consistent with such a view.

Apart from one month when a deficit of calcium was recorded all precipitation samples and all three aerosol samples contained excess calcium, as seen in Figure B.4(c). The excess appears to be roughly proportional to the amount of sea salt and of a rather greater order of magnitude than the amount of calcium in sea salt. The dotted line indicates a twofold enrichment of calcium relative to sea salt. The fractional excess was greater in the precipitation samples than in the aerosol samples. Thus, while some of the excess calcium possibly comes from the sea it appears that some comes from a distant source of aerosol and is brought down in the rain. A small amount of the excess in the three aerosol samples may also be from a distant land source. It is conceivable that the difference between the aerosol and the precipitation is due to seasonal effects, with the aerosol being collected in December and the other samples being from all months of the year. Thus it is possible, but not certain, that these results support the contention in Chapter 4 that there may be some excess calcium in sea salt aerosol, derived from a process which enriches the surface layer of the sea, but that much of the excess calcium comes from the land. One reason for sampling on a platform such as this is that we can be certain that the calcium does not come from a nearby land surface.

The results which have already been derived from the North Sea sampling give us some information on the quantity and chemistry of rain at sea. They do not simply repeat the work of the AERE group for the EACN analysis is at its best, for magnesium, calcium and sulphate, where the EACN analysis is least sensitive or quite unsatisfactory. The greatest value will be derived from the North Sea sampling results when an independent set of measurements is available from another platform. If conditions in the northern North Sea prove too harsh for successful monitoring of the chemistry of rain there would be good reasons for establishing another sampler in the southern region.

No.	Period	Pptn	S	Cl	NO_3^- N	NH_4^+ N	Na	K	Mg	Ca	pH	Alk	Cond.
		mm	mg/m^2										
01	17/7 - 1/8/73	30	27	159	7	4	91	4	11	8			
02	1/8 - 1/9/73	30	230	2600	21	39	1600	90	168	180			
03	1/9 - 1/10/73	75	395	5850	62	18	3480	-	380	320			
04	lost	(55)	Gorleston										
05	30/10 - 19/12/73	60	352	4560	111	5	2620	109	-	138	4.4	- 44	367
06	19/12 - 12/2/74	63											
07	12/2/- 1/4/74	110	640	5100	150	260	2600	140	350	290	3.8	164	299
08	1/4 - 1/5/74	nil											
09	1/5 - 3/6/74	8	88	10,600	56	320	3200	96	760	1660	4.0	599	4370
10	3/6 - 4/7/74	18	68	960	40	44	420	16	68	150	4.5	- 44	230
11	4/7 - 15/8/74	39				49	50		54		6.2	17	100
12	15/8 - 1/9/74	65	140	700	54	70	366	43	47	54	4.7		
13	1/9 - 1/10/74	79	304	3920	450	340	2100	207	280	144	6.6	94	26
14	1/10 - 31/10/74	73	1090	1890	360	-	1160	179	175	94	4.5	- 38	220
15	31/10 - 1/12/74	68	220	11,800	54	-	6100	98	2700	125	4.3	- 69	620
16	1/12 - 5/1/75	21			35			76	217	111			620
17	5/1 - 1/2/75	33											
18	1/2 - 1/3/75	12											

Table B.1 Provisional data on precipitation amount and composition for the sampler on the Leman A gas production platform. Revisions and more recent data will be available on request.

No.	Period	Pptn	S	Cl	NO_3^- N	NH_4^+ N	Na	K	Mg	Ca	pH	Alk	Cond.
		mm	mg/m^2										
S07	20/12/74 accumulated on clean polypropylene surfaces exposed for 15 hours in Force 4 - 7 wind. Washed with 200 ml of dist. water.	nil	48	998	8	-	524	-	62	32	5.6	106	19
S16		nil	40	1034	12	-	594	-	72	40	5.7	97	20
S14		nil	36	546	14	-	284	-	34	16	5.8	105	13

Table B.2 Composition of sea salt aerosol collected by impaction on a clean polypropylene surface exposed for fifteen hours on the Leman A platform on the night of the 19th-20th December 1974. A number of short-term rain samples have now been collected and their analyses will be available on request.

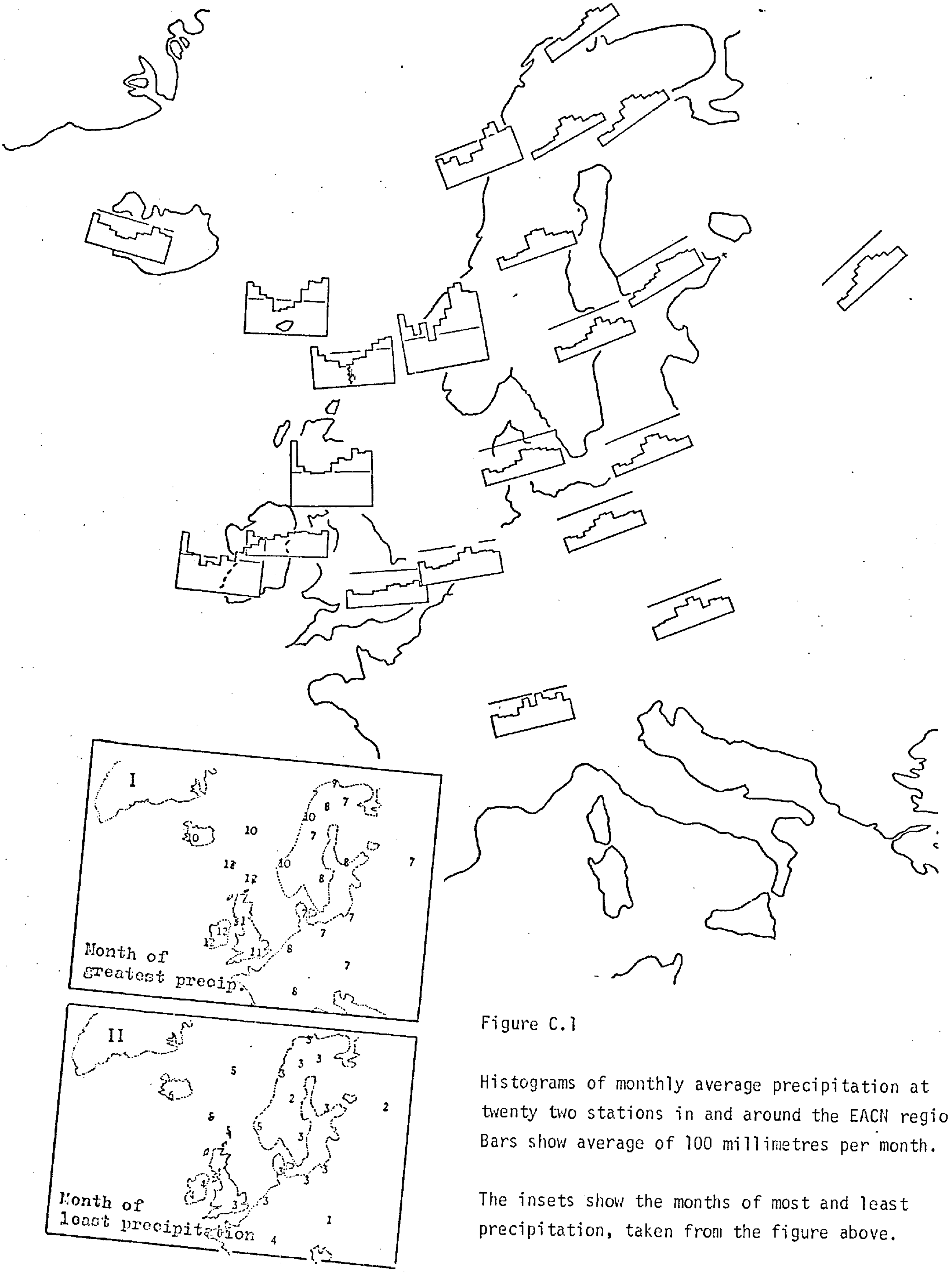


Figure C.1

Histograms of monthly average precipitation at twenty two stations in and around the EACN region. Bars show average of 100 millimetres per month.

The insets show the months of most and least precipitation, taken from the figure above.

Appendix C. Precipitation in the EACN region

Various characteristics of precipitation in northwest Europe and the northeast Atlantic have been referred to in this thesis. As these comments did not merit a detailed discussion of the particular aspect of precipitation in the text of the main chapters it is appropriate to collect together the relevant information in one Appendix. Other supporting information is included for the sake of completeness. This Appendix contains that information in diagrammatic form with the supporting comments below.

1. Average monthly precipitation

Figure C.1 shows histograms of the average monthly precipitation at twenty one island and mainland stations superimposed on a map of the region. These 30-year averages have been taken from Monthly Climatic Data for the World. The scale of precipitation amount is shown by the horizontal bar which has been drawn on most of the histograms to represent an amount of 100 mm per month. On each histogram the January precipitation is represented by the first column and December by the last. Inset I shows the month of greatest precipitation at each station. There is a clear trend from a July maximum in central and eastern Europe to an Autumn and early Winter maximum on the west coast and European Islands. Inset II shows the month of least precipitation. Again there is a steady trend from an early minimum (midwinter) in central and eastern Europe to a Spring minimum on the European Islands.

2. Continuous snow cover

The distribution of continuous snow cover which is shown in Figure C.2 has been taken from Wallén's Vol 5 of World Survey of Climatology. Note that some but not all of the stations of the Inland Network are in the region which has continuous snow cover for three or four months in the winter. This has been referred to in Chapter 3, in which it was suggested that this snow cover precludes the nearby ground surface being the source of magnesium, calcium or potassium which is found in snow which falls during the winter.

3. Swedish monthly average precipitation - amount and the number of days.

Figure C.3 shows the average monthly precipitation at four high altitude stations and at three stations on the Baltic. The data are from the Monthly Climatic Data for the World. The high altitude stations, which correspond to some extent to the stations of the Inland Network, have a clear mid-summer maximum in precipitation amount. Karesuando, in the extreme north, receives a little over half the amount at Jonkoping during the winter and

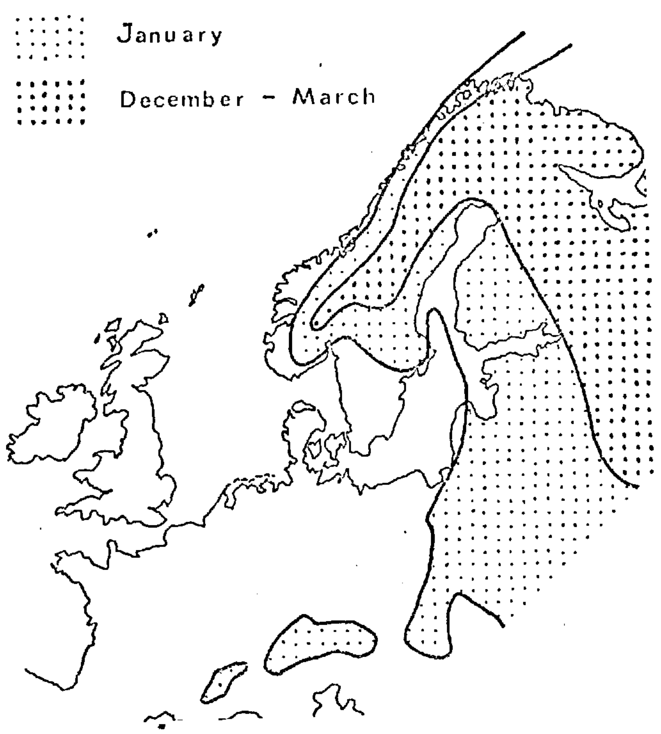
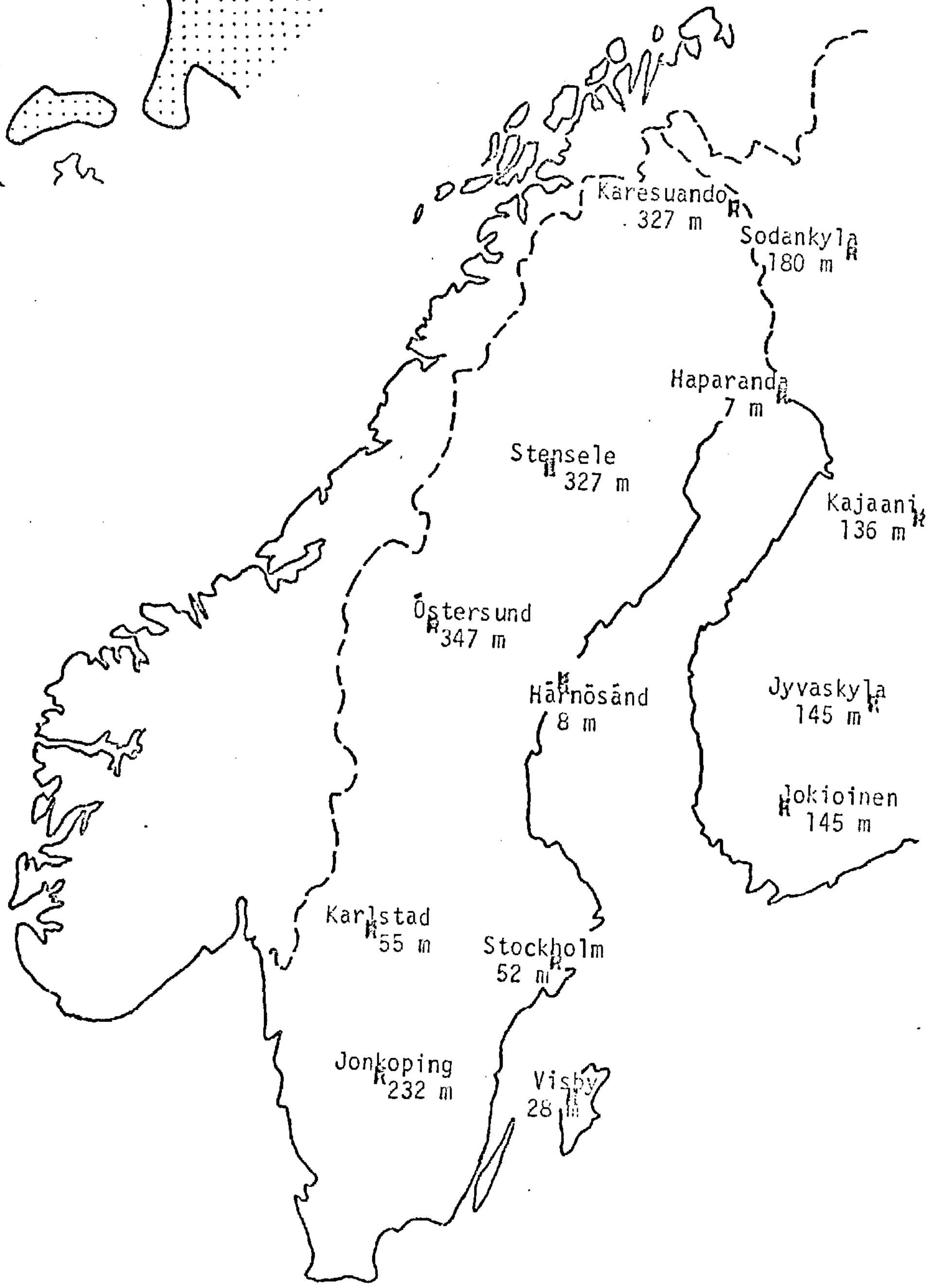


Figure C.2 Snow cover and positions of climatological precipitation stations in Scandanavia.

(a) Average period of continuous snow cover .

(b) Stations in Sweden and Finland for which the monthly precipitation amounts are considered in Figs. C.3 to C.5 Station altitudes in metres are given.



almost the same amount as Jonkoping in the summer. The average number of days with more than 1 millimetre of precipitation has been calculated for 1961 - 1971 from data in Monthly Climatic Data for the World. The annual cycle in precipitation amounts is of greater amplitude at the high altitude stations while the annual cycle in number of days of precipitation is greater at the coastal stations. At high altitude July is conspicuous as a month with more days of precipitation than either June or August while at sea level it is the first of three similar months and a significant increase on June. Comparable data for three Finnish stations is shown as squares on Figure C.3. These show that during those four months the trend on the east coast of Sweden is similar to that in Finland although the Finnish stations experience significantly more wet days.

There is some interest in identifying the mechanism responsible for the high correlations between amounts of precipitation at Inland Network stations in June which was first noted in Chapter 3. It will be recalled that high correlations were also found in the amounts of magnesium and calcium from the northernmost to southernmost station. In Sweden during the period from 1955 to 1967 there was a clear tendency for a dry May to be followed by a wet June and vice versa, as is shown in Figure C.4. On the other hand there was a tendency for a wet June to be followed by a wet July and a wet July to be followed by a wet August. That period covers most of the period for which the correlations in Chapter 3 were calculated. The pattern was not obvious after 1967. While it persisted the June precipitation tended to set the pattern for the summer, which was the opposite of the May precipitation. In Figure C.4 the amounts of precipitation are given in terms of quintiles which are five equally populated ranges of precipitation amount estimated from the standard thirty year period. The first quintile is the range covered by the lowest twenty percent of monthly rainfalls. Where there was no drought in the standard period we sometimes find a zeroeth quintile which indicates less precipitation than at any time during the standard period. The sixth quintile describes rainfall greater than any recorded during the standard period. There are seven quintile ranges.

The correlations between amounts of precipitation at different distances over Finland and Sweden between May and August are shown in Figure C.5 . There is a reasonable degree of correlation within the group of three stations in southern and central Finland, shown in the centre row, in all months. Between those stations and Sodankyla in the north there is a clear positive correlation only in July. Between Jokioinen in southern Finland and Stensele, Östersund and Jonkoping in the high country of Sweden there is a strong positive correlation in July and a weaker relationship in June.

There appears to be a feature of the circulation over Scandanavia east of the mountains in summer which affects the pattern of precipitation amounts in the following way. The summer pattern is established in June and tends to persist through July and August. In July the pattern is similar over a very wide area, from northern Finland to southern Sweden, as indicated by Figure C.5 . The Inland Network lies on the western edge of this region and, as seen in Table 3.1 , it experiences the highest correlations between amounts of precipitation (as well as magnesium and calcium) in June and the lowest in August. In the Inland Network region June is a time of fast-increasing precipitation, as shown in

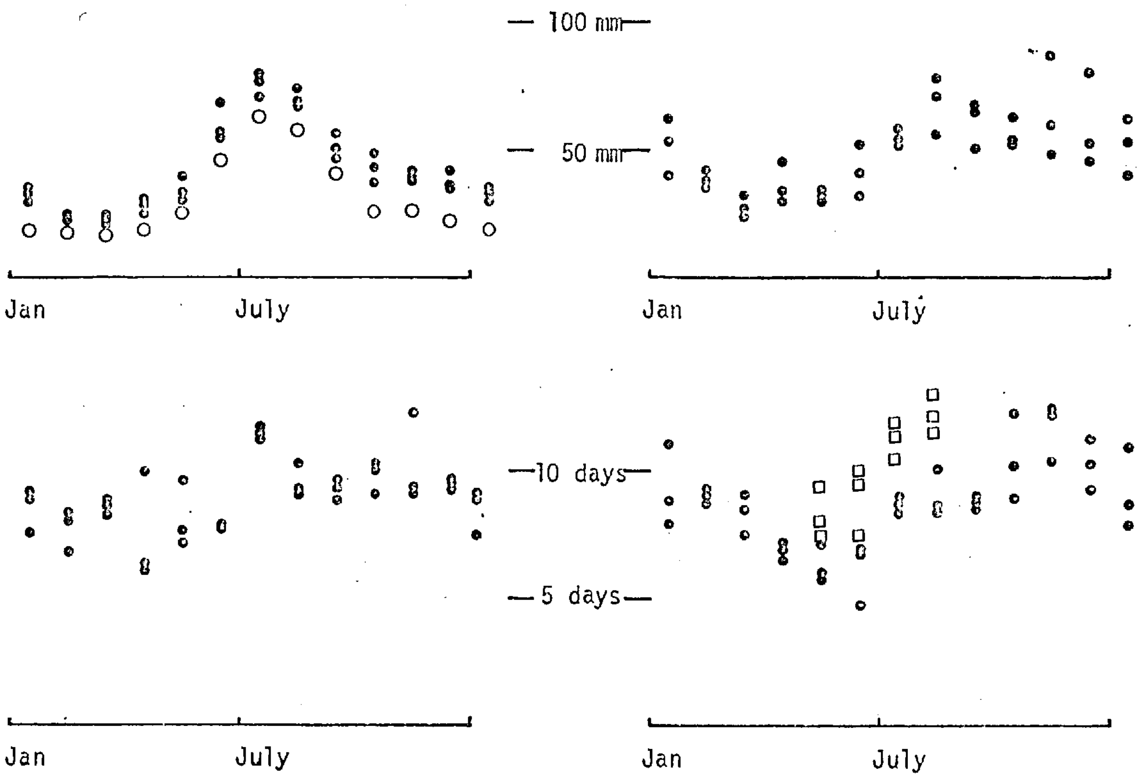


Figure C.3 (above)

Average precipitation amounts and number of days with more than 1 mm, 1960 - 70.
At left are Stensele, Östersund, Jonkoping and (open cirles) Karesuando, all at high altitude.
At right are Haparanda, Härnösand and Visby, at sea level. Open squares are for Sodankyla, Kajaani and Jokioinen in Finland.

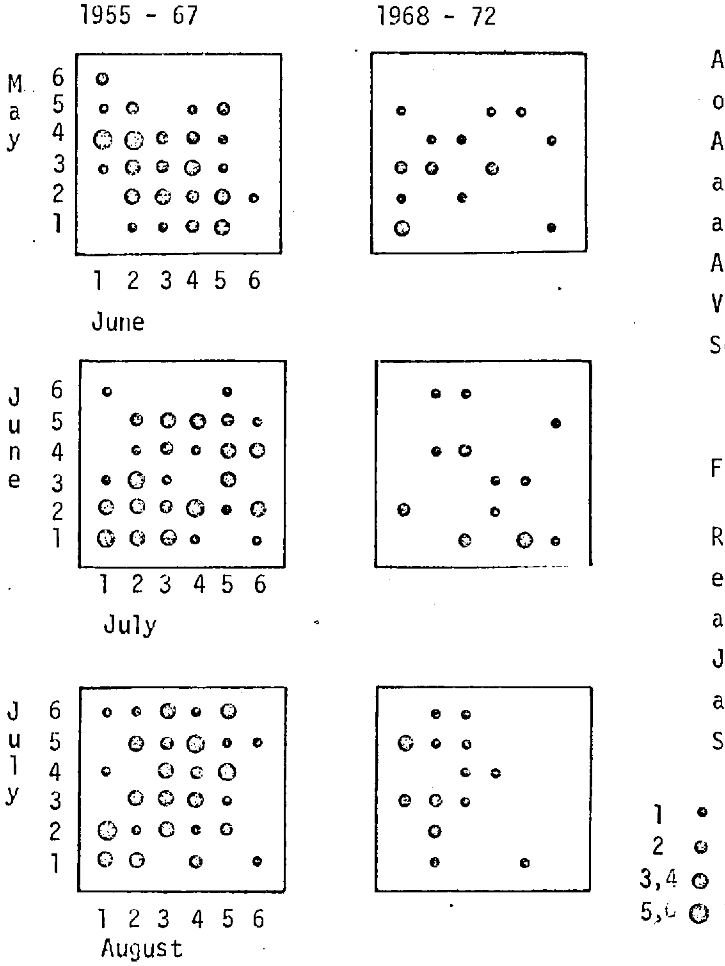


Figure C.4 (at left)

Relationship between precipitation amounts, expressed in quintiles, in successive months at Stensele, Östersund, Härnösand, Karlstad, Jonkoping and Stockholm. Number of occurrences approximately proportional to area of circle. See key below.

Figure C.3 . This is presumably due to the increasing depth of convection in unstable continental air. Less stable conditions in June favour greater than average precipitation on the east slope of the mountains and these, for unknown reasons, tend to occur after a dry May. During the summer it rains more often in Finland than along the east coast of Sweden but the total amount of rain is no greater. The change in the amount of rain, and the number of occasions of rain, from month to month is similar in both eastern Sweden and central Finland between May and August.

I have not been able to determine the nature of the phenomenon which causes singularly high correlations between amounts of precipitation at stations of the Inland Network in June. The same phenomenon appears to affect the atmospheric circulation and washout of magnesium and calcium. There is some indication that it is related to the position of the Inland Network at the boundary of a summer circulation pattern and to the onset of that circulation in June. In this appendix I have presented such information as I have so that it should be available to anyone who might be interested in the problem.

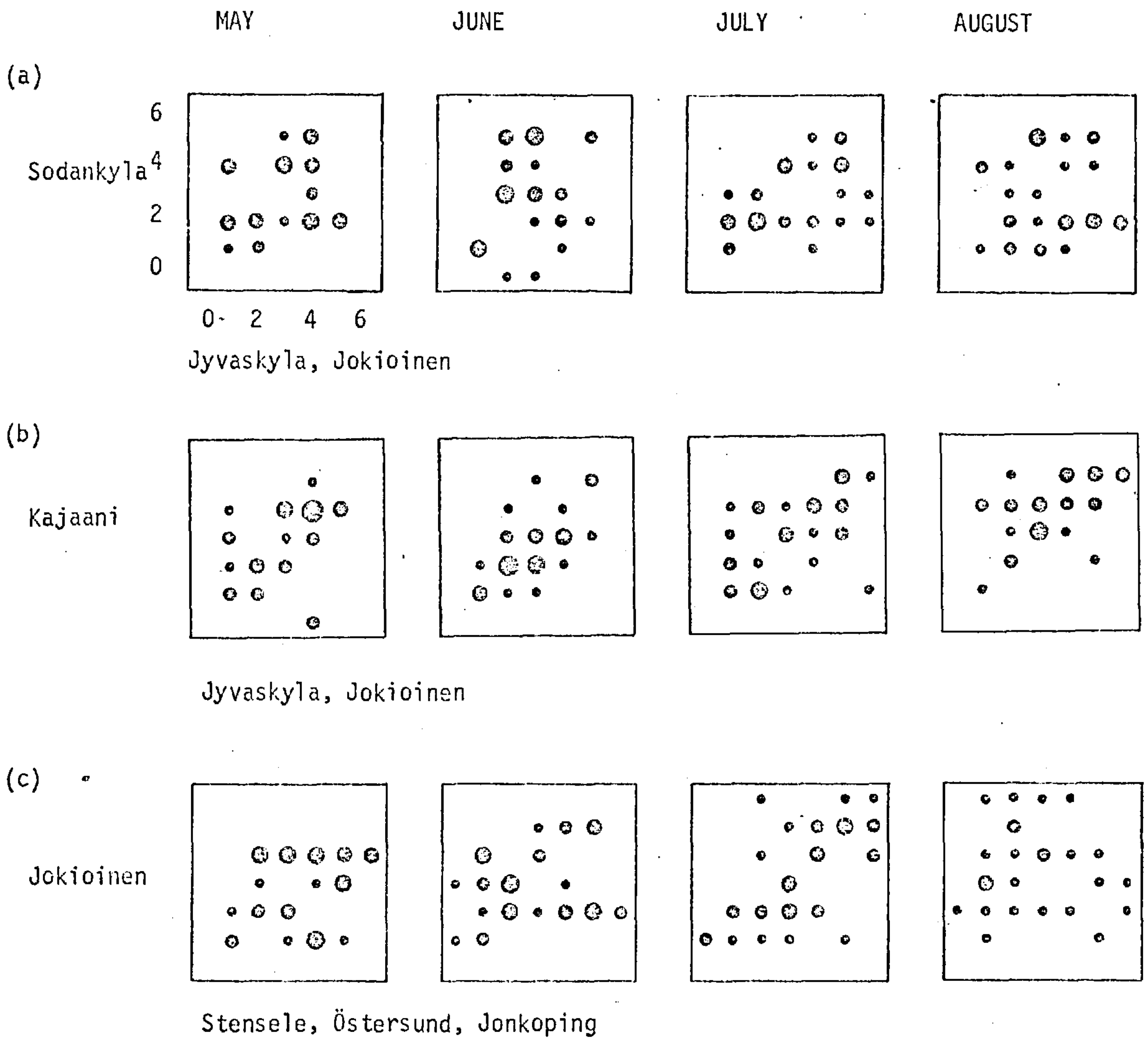


Figure C.5 Amounts of precipitation, expressed in quintiles, at different stations in the same month, for May, June, July and August in the period 1955 - 1973. Number of occurrences is approximately proportional to the area of the circle.

(a) Sodankyla, in N. Finland, with Jyvaskyla and Jokioinen in S. Finland

(b) Kajaani, in central Finland with Jyvaskyla and Jokioinen in S. Finland

(c) Jokioinen, in S. Finland, with Stensele, Östersund and Jonkoping in Sweden.

Note that only in July is there a good correlation between all stations.