On the Chemical Climate and its Variation with the Atmospheric Circulation Pattern

By

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A study of the chemical composition of monthly precipitation samples from a number of stations in Sweden brings out the existence of significant variations in the relative proportions of chlorides and sodium depending upon the general character of the prevailing circulation. In maritime westerly flows the weight ratio of chloride to sodium decreases eastward to values which lie far below the value characteristic of sea water. In precipitation falling from arctic or polar continental air masses the chloride component is almost completely absent. The highest amounts of chlorides relative to sodium are observed in precipitation from warm and most air masses reaching Sweden from the south or southeast.

Significant variations are observed also in the yearly means of the sodium and sulphur deposits depending upon the dominance of maritime or continental air currents.

A sketch map of the "average" chloride concentration in European precipitation prepared from miscellaneous older data lends support to the results of the analysis of the monthly data. The separation of the chemical components indicated by this study would seem to be of considerable geochemical interest since it would permit different maritime salts to be deposited in widely separated parts of the continents. It is not inconceivable that a detailed study of the association between different circulation patterns and the corresponding chemical climates might permit us to draw inferences concerning variations in the atmospheric circulation during post-glacial times, e.g. from the data on the chemical stratification in raised bogs now becoming available through the investigations by *Mattson* and *Koutler-Andersson*.

It is the specific purpose of this paper to show that the weight ratio of chloride to sodium ions determined through the analysis of monthly accumulated precipitation samples varies in a systematic manner from month to month, and that the value of this ratio closely reflects the trajectory and life history of the principal air mass from which or through which the month's precipitation is falling. The range over which this ratio varies extends from 0.0 to about 3.5, the average value for sea water being about 1.8 and for pure sodium chloride 1.5. The fluctuations here established clearly indicate that Cl^- and Na^+ are not inseparable but rather that they, through various processes about which our knowledge is as yet mainly conjectural, may be detached from each other in leaving the surface of the sea or shortly thereafter. Nuclei containing sodium chloride and then certain other sodium salts appear to be precipitated at the most rapid rate while other chlorides seem to be capable of travelling long distances from their oceanic source regions without precipitation.

The more general purpose of our paper, however, is to call attention to the wealth of fascinating problems created by the availability, since November 1, 1954, of synoptic data (monthly means) on the chemical composition of precipitation and of the surface air at a large number of stations in Denmark, Finland, Norway and Sweden. The data for November and December 1954 are published as an appendix to this issue of Tellus. It is our intention to publish the data for subsequent months in quarterly installments.

The data available for the present study consist of the following:

a) The amounts of the principal chemical constituents contained in monthly precipitation

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samples collected at a network of about 28 Swedish stations, operating from October 1, 1948, until September 30, 1950. A map showing the names and locations of these stations is given in a recent paper in Tellus (EMANUELSSON, ERIKSSON and EGNÉR 1954). Unfortunately, data on sulphur and magnesium are not available for this period.

b) Data on the amounts of various chemical components, including sulphur and magnesium, contained in monthly precipitation samples collected at seven stations in southern Sweden during the period July 1, 1951, until June 30, 1953. These stations were Alnarp, Bräkne-Hoby, Plönninge (Halmstad), Flahult, Bjärka-Säby, Skara (Lanna) and Ultuna. At these stations also air samples were collected monthly by means of continuously operating low capacity pumps (about 30 m^3 per month) and analyzed for the mean monthly concentration of the same elements (exclusive of NO_3—N) as those determined in the precipitation samples.

c) Data from an expanded net of Swedish stations at which both air and precipitation samples have been collected monthly since July 1, 1953. On November 1, 1954, this network was enlarged to include additional stations in Sweden, Norway, Finland and Denmark. The locations of these stations are given in the station map accompanying the chemical data appendix included in the present issue of Tellus. Since July 1, 1953, the hydrogen ion concentration (pH) and the electric conductivity of the monthly precipitation samples have been determined at all stations.

The chemical analyses were carried out at the Royal Agricultural College of Uppsala (Ultuna) under the supervision of one of us (Egnér). The meteorological analyses and the interpretation of the results were carried out at the University of Stockholm. The chemical technique now in use is described in the chemical data appendix.

In the report by Emanuelsson, Eriksson and Egnér, it was shown that during the two-year period October 1, 1948, to September 30, 1950, the weight ratio of the total amount of chloride to the total amount of sodium deposited per hectar and year decreased from a value of about 1.2 on the Skagerrack coast to about 0.6 in the vicinity of Stockholm—Ultuna. The separation of these two constituents was first brought out by CAUER (1949) in his studies of atmospheric condensation nuclei. Cauer states that the sodium and chloride ions added to the atmosphere from the sea through spray or bubble formation go through entirely different cycles. He believes that the chloride ions contained in the sea spray droplets, under the influence of the small amounts of ozone present in the lowest strata of the atmosphere (0—100 μg per m^3), may be oxidized to free chlorine gas which again, in the presence of sunlight and water vapour, is changed into hydrochloric acid. The escaping chlorine would be replaced in the initial droplets by bi-carbonate ions. Since the hydrochloric acid may be transported by the winds as a gas or may form droplets too small to serve as effective condensation nuclei, it is clear that the Cauer process would explain why rains falling within relatively short distances of the coast are characterized by relatively low and landward decreasing values of the weight ratio of chloride to sodium ions. Cauer's hypothesis is now being studied experimentally and theoretically by our collaborators and these studies will be reported in due time. It appears, however, that the effect observed by Cauer and verified by our precipitation data, might be accounted for by one or several alternative processes. KÖHLER and BÅTH (1952) have carried out an interesting experimental study of the separation of sea salt components, by blowing an air stream over a sample of sea water. Droplets of different size were analyzed separately for the main components. However, the maximum separation indicated by these experiments is insufficient to account for the observed geographical variation in Cl/Na.

The Cauer hypothesis, or any equivalent mechanism, carries with it one extremely important implication, apparently overlooked by Cauer but of considerable geochemical interest:

Presumably the proportions of chloride and sodium ions which leave the sea surface are the same as in the water but apparently some sodium is precipitated in combination with other negative ions than chloride in the coastal areas of western Europe. There must then develop an excess of chloride ions or of molecular chlorine in the free atmosphere. Unless one assumes that molecular chlorine is taken up directly by the ground or that

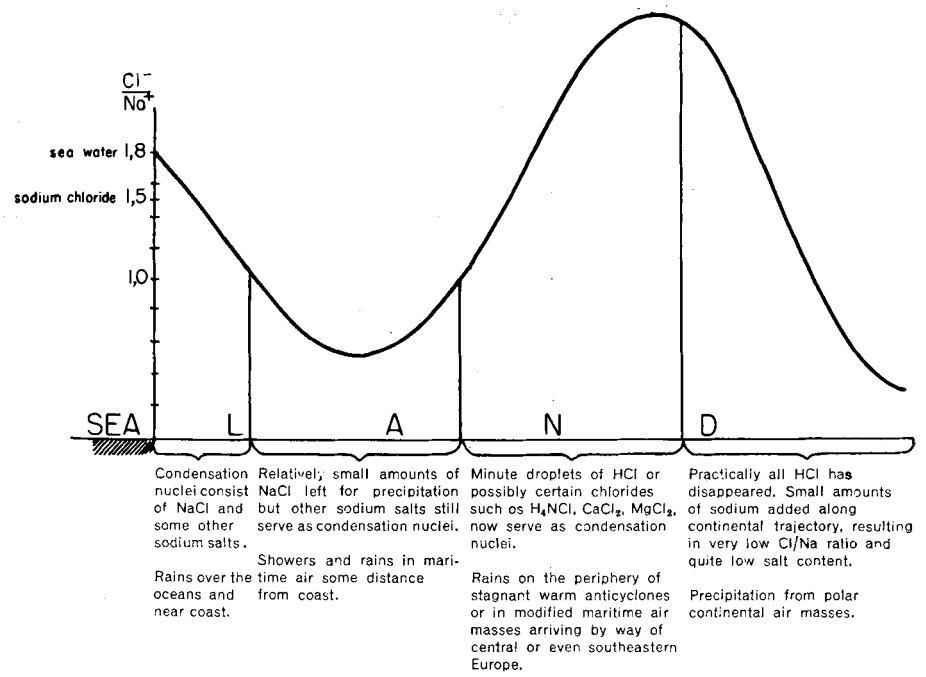

Fig. 1. Schematic representation of the variations in the weight ratio of chloride to sodium in precipitation from an air mass moving in over the continent.

chlorates or hypochlorites not now identified in our precipitation samples maintain the chlorine mass balance in the atmosphere, one is forced to conclude that there must exist continental regions far removed from the oceanic source regions, in which the weight ratio of chloride to sodium in precipitation must be very much in excess of the value characteristic of sea water or of coastal precipitation. If the chlorides (exclusive of sodium chloride) only slowly come into play as condensation nuclei it would in fact be possible for rains in such interior regions to reach a higher absolute chloride concentration than rains falling closer to the coast. It was this paradox that provided the starting point for the present study.

We have attempted to sketch the variation of the chloride to sodium ratio in precipitation as a function of distance from the oceanic source region in Fig. 1. Leaving out the many important nuclei not containing either sodium or chlorides one would have to assume that the precipitation falling from air masses near the coast contain a mixture of sodium chloride and some other sodium salt. As the air travels further away from the coast most of the sodium chloride would be used up and ultimately the rain drops would contain mainly sodium salts other than sodium chloride. Finally, when also these sodium salts have been consumed, the minute hydrochloric acid droplets or corresponding chlorides would come into play as condensation nuclei. When this happens the chloride to sodium ratio would, of course, rise far in excess of the 1.8 value characteristic of sea water. If the air continues along a continental trajectory without access to chloride sources but is able to pick up small amounts of sodium, it is probable that the chloride to sodium ratio of the precipitation would again decrease.

Figures 2, 3, 4 and 5 represent an attempt to verify the corollary formulated above through a study of the geographic distribution of the chloride to sodium ratio during four selected months of dissimilar circulation patterns. Each figure contains the mean sea level pressure pattern over northern and central Europe for the month in question. The monthly precipitation values in mm at the chemical stations have been entered on each map. In each figure the

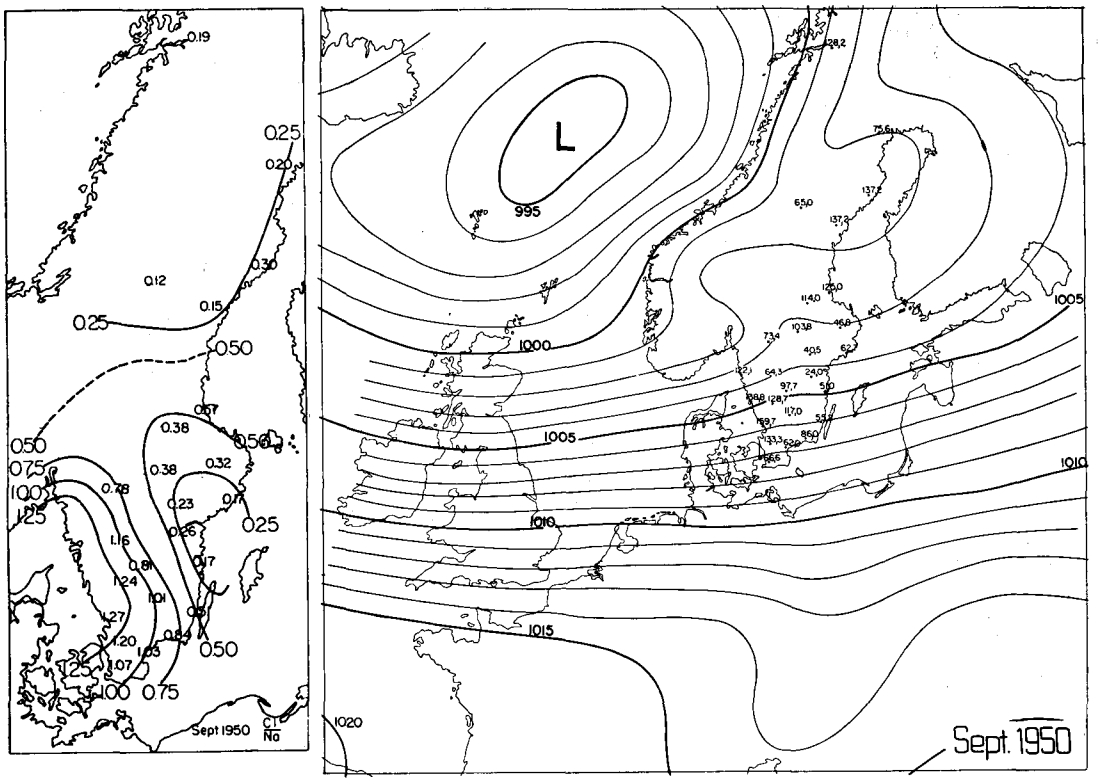

Fig. 2. Mean circulation pattern at sea level over Northwestern Europe during September 1950. The precipitation in mm at the chemical sampling points is entered on the pressure chart. The inset map gives the geographic distribution over Sweden of the weight ratio of chloride to sodium in the accumulated precipitation samples.

inset map gives the geographic distribution over Sweden of the weight ratio of chloride to sodium, expressed through isolines. It should not be necessary to stress that a monthly mean pressure pattern must be used with a great deal of caution in drawing conclusions concerning the paths of the rain-bearing winds; it has been suggested that mean charts should be constructed only for those days on which precipitation fell. However, the number of days with precipitation at any one station in Sweden is quite large and when twenty or thirty stations are considered such a map would become practically identical with the monthly mean chart. Figure 2 shows that in September 1950 straight westerly winds dominated the flow pattern in southern Sweden up to about the latitude of Stockholm. During this month the chloride to sodium ratio fell from about 1.3 on the Kattegatt coast to a minimum of 0.17, less than one tenth of the sea water value, on the Baltic coast. The precipitation decreased markedly from west to east.

December 1949 (fig. 3) was less uniform in its circulation characteristics but by and large it was dominated by strong west winds over southern Sweden. Also in this case the precipitation values decreased from Kattegatt to the Baltic coast and the chloride to sodium ratio decreased eastward, though less rapidly than in September 1950. In both cases this ratio reached very low values in northern Sweden, probably because the air reached that part of the country after a fairly long over-land journey and after considerable lifting over the mountains in Norway. Most of the sodium chloride must have been precipitated by the time the rain-bearing winds reached northern Sweden, other sodium salts than NaCl having taken over the role as condensation nuclei.

May 1950 (fig. 4) represents a month with a rather unusual circulation pattern, northerly

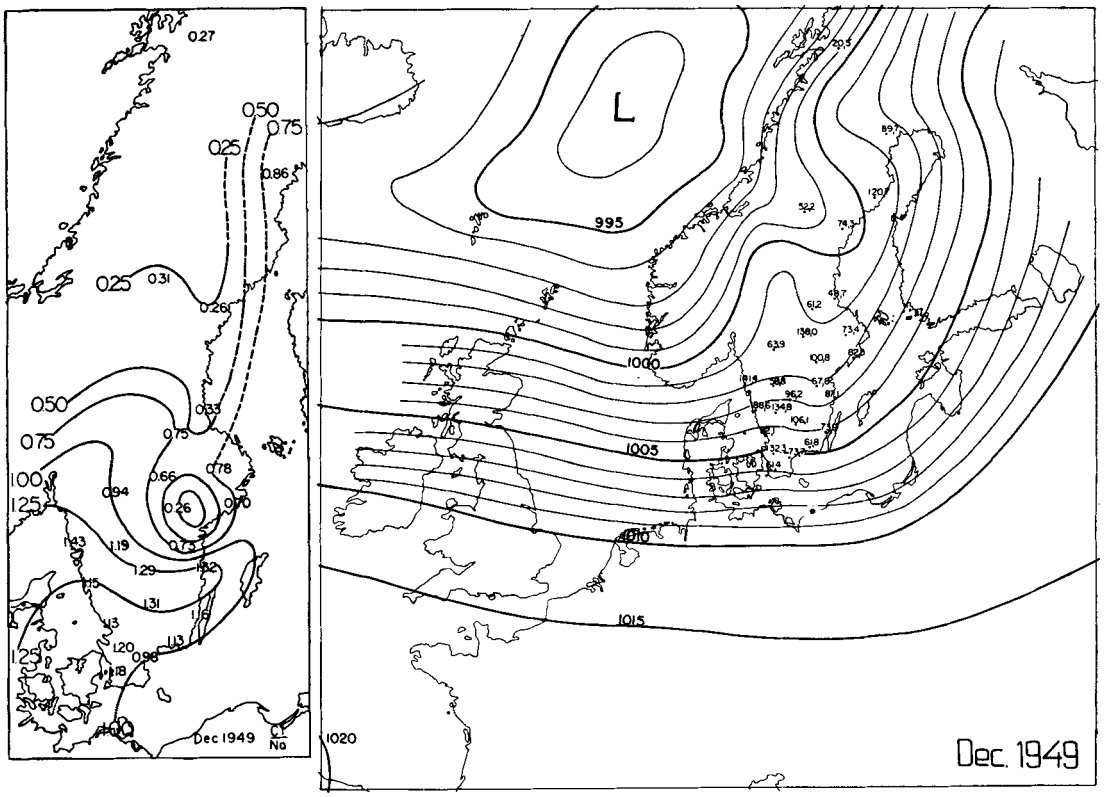

Fig. 3. Circulation pattern and weight ratio of chloride to sodium during December 1949. See legend to Fig. 2 for details.

or even northeasterly winds over the entire country. The precipitation amounts were low but sufficient for analysis. Amazingly low values of the chloride to sodium ratio are observed, less than 0.3 at all stations but one. In view of the hypothesis proposed by Cauer it should be pointed out that northerly winds during the spring presumably are characterized by relatively high ozone concentrations in the lower air strata.

November 1949 (fig. 5) was characterized by persistent advection of warm and moist air from the Mediterranean and Balkan region, air masses of Atlantic origin having made a long sweep eastward over southern Europe. The rainfall in southeastern Sweden during this month was profuse, up to two or three times the normal value. In these rains the chloride to sodium ratio reached values of up to 3.5 along the southern and southeastern coast of Sweden. The absolute amounts of chloride deposited in those districts were relatively large, in excess of 1 kg per hectar (10^4 m^2) at several stations and reaching 2.06 kg per hectar at Tovehult.

The four cases presented above strongly support the proposition that air masses leaving the sea first lose sodium chloride through precipitation, then certain other sodium salts, but that the remaining chlorides, which are not associated with sodium may stay with the moist air masses until long after the major portion of the sodium has been precipitated.

The extremely low chloride ratios observed in May 1950 remain to be explained. It is conceivable that the slight total precipitation observed during that month fell from air masses with a very long continental history, air masses which had moved around the blocked low pressure system located in the White Sea region. In the course of this long continental history, the air would ultimately

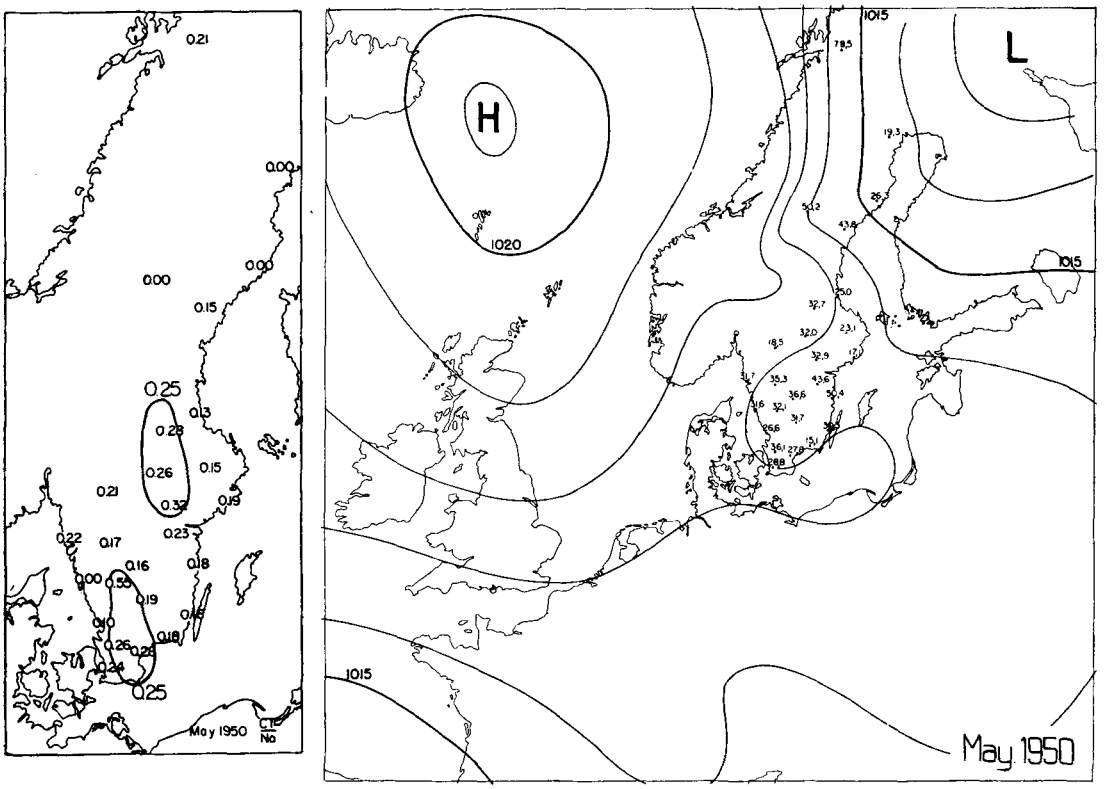

Fig. 4. Circulation pattern and weight ratio of chloride to sodium during May 1950. See legend to Fig. 2 for details.

lose the hydrochloric acid particles or chlorides through precipitation. Since there are no continental sources of chlorides, with the exception of industrial pollution and salt deserts, sources which hardly would have to be considered in these high latitudes, while there always would exist some opportunity for the air to pick up small amounts of sodium together with other typical continental cations, it is conceivable that the low chloride ratio in the precipitation of the northeasterly winds might be explained as associated with a second minimum in the chloride ratio curve, a minimum reached only after most of the chlorides have been precipitated without replacement. This second minimum would evidently be associated with very low salt concentration in the precipitation. To study this problem further we have looked into the precipitation chloride ratio for the month of April 1954. During this month, northerly to northeasterly winds prevailed over northern and central Sweden, northwesterly winds on the west coast of Sweden and in the southernmost parts of the country (fig. 6). It is probable that this last current to a large extent was fed by air from Central Europe brought towards southern Scandinavia in a broad sweep out of a stagnant anticyclone over the British Isles. The inset map shows the distribution of chlorides in mg per liter. On the same chart the lower number at each station gives the chloride to sodium ratio. The contrast between the low chloride concentration in the precipitation from the continental northeasterly current and the extremely high concentration in the precipitation over southern Sweden is striking. The high chloride ratio values in southern Sweden suggest that much of the pure sodium chloride particles already have been removed from the air and that other chlorides to a large extent have taken their place.

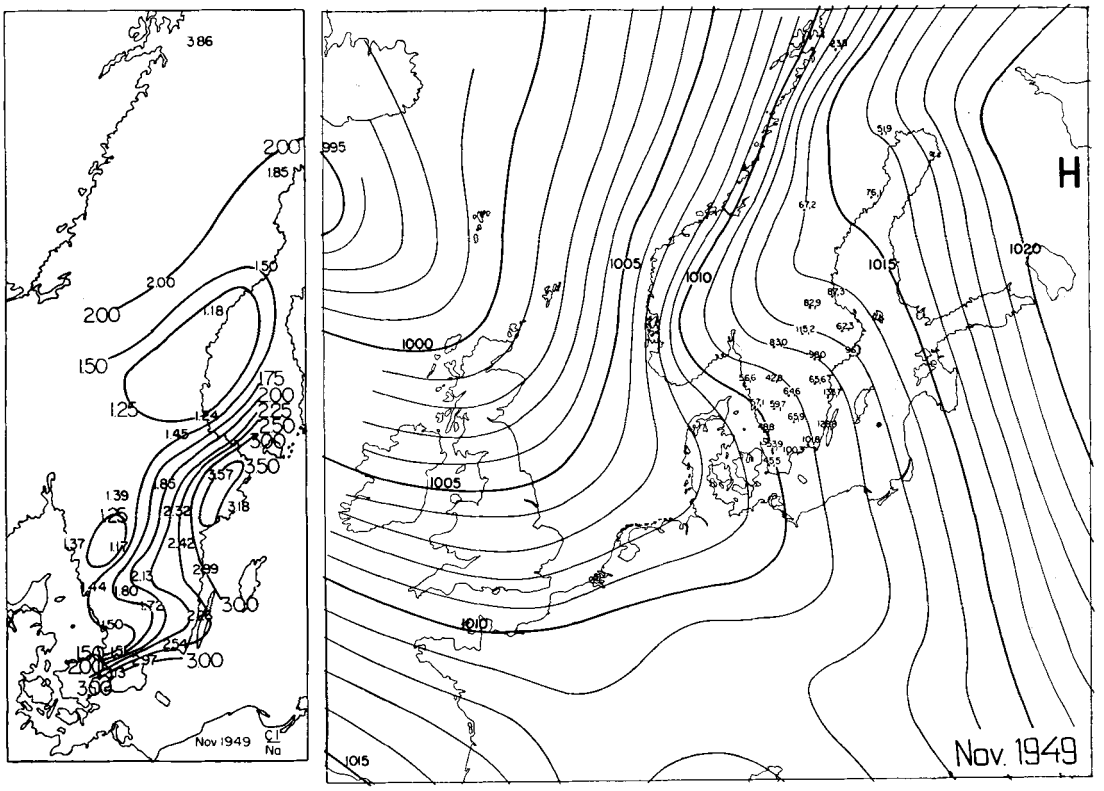

Fig. 5. Circulation pattern and weight ratio of chloride to sodium during November 1949. See legend to Fig. 2 for details.

We have attempted to make use of the combined precipitation and air analyses conducted since July 1, 1953, to study the chloride content in the surface air of currents reaching Sweden from the south. As a first step, we selected eleven stations (fig. 7) in the eastern half of Sweden and plotted for each one of these stations the monthly mean chloride content expressed in micrograms per m^3 of air as a function of time (fig. 8). It is striking that all these curves are characterized by a well-defined maximum in December 1953. We then constructed (fig. 9) curves representing the mean concentration at these eleven stations of chloride, sulphur, sodium and magnesium as functions of time. The sodium and magnesium values for December 1953 exhibit no peculiarities, but the sulphur shows a minimum. (March 1954, on the other hand, is characterized by an extremely high sulphur value.) In December 1953 the ratio of the average chloride concentration to the corresponding sodium concentration as given by the curves in figure 9 reached a value of 4.0. The corresponding ratio computed from the total precipitation deposits at the same eleven stations was 1.74. This suggests the presence in the lowest air layers of HCl in gaseous form or in the form of minute droplets too small to be collected effectively by the falling rain.

The dominant circulation pattern of December 1953 is illustrated by figure 10. It represents the mean sea level pressure pattern for the two-week period December 9—December 23, inclusive, during which southern and central Sweden were dominated by southerly or even southeasterly winds bringing in warm air from southern and central Europe. In the first and the last week of the month moist air was brought into southern Sweden from the southwest and west. The northernmost part of the country was under the intermittent influence of maritime air masses throughout the

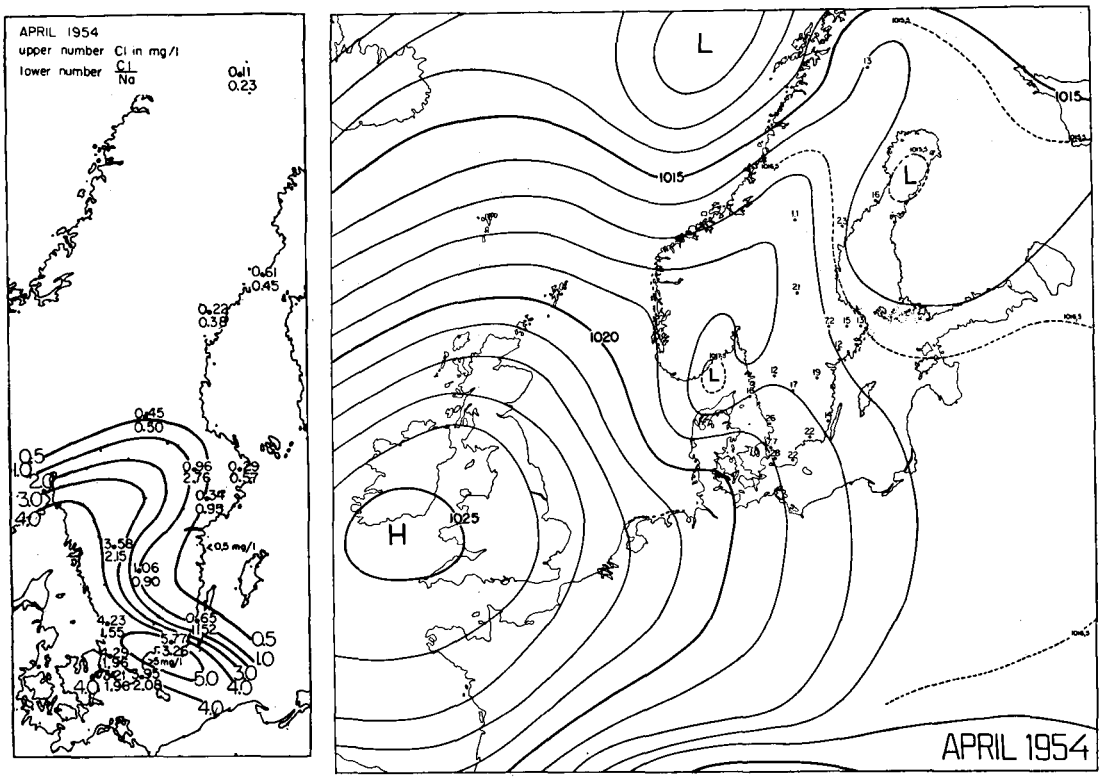

Fig. 6. Mean circulation pattern at sea level during April 1954, with precipitation amounts in mm at the chemical sampling points. The inset map gives the distribution of chlorides in the precipitation (mg pr liter) expressed through "isochlors". The lower figure at each sampling point gives the weight ratio of chloride to sodium.

major part of the month but received very small amounts of precipitation. The mean sea level pressure distribution for the entire month is not reproduced but it shows mean monthly pressures well above normal (10—11 mb in southern Sweden, 1—2 mb in northernmost Lappland). The flow was in the main anticyclonic and hence the precipitation was below normal practically everywhere except in the mountainous western part of northern Sweden.

The dominant southerly to southeasterly flow in southern Sweden during December 1953 was associated with a tongue of quite low pH-values in the precipitation samples (fig. 11). This observation supports the assumption that the prevailing air current contained droplets of hydrochloric acid. It is of some interest to compare this month with March 1954 (fig. 12), the month during which the concentration of sulphur (sulphate and sulphite ions) in the air samples from the eleven eastern stations reached a pronounced maximum. Also during this month southerly winds prevailed in southern and central Sweden, southerly to southwesterly winds in northern Sweden. In December 1953, temperatures were well above normal in southern Sweden, while March 1954 was characterized by about normal temperatures except in the north where they were in excess of normal. The March precipitation fell in the form of snow, except far south, the December precipitation mainly in the form of rain. One may perhaps infer that the December circulation pattern was dominated by air masses originally of maritime origin but having made a broad sweep over southern Europe. During March 1954 the country must at least at times have been under the influence of truly continental air masses from the interior of the Eurasian continent. The maximum of sulphur observed during this month may then have been the result, at least in part, of

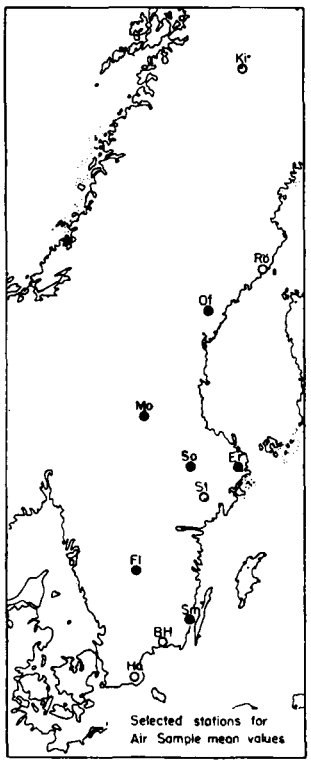

Fig. 7. Location of eleven sampling stations utilized in the analysis of the month-to-month fluctuations in the chemical content of the air.

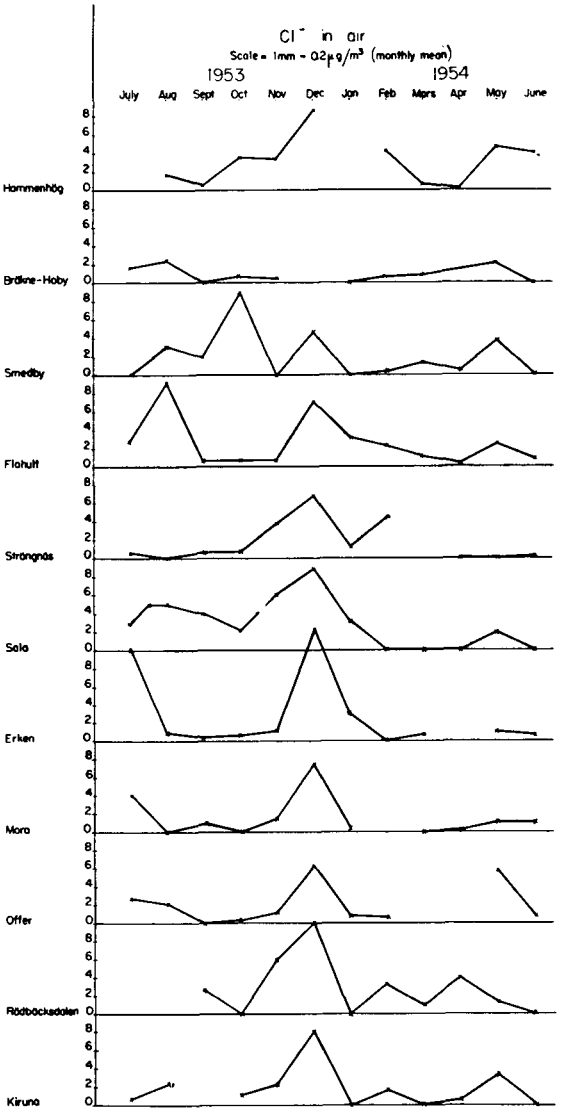

Fig. 8. Variation with time of the chloride content of the air (in μg per m^3) at eleven sampling points.

increased winter time combustion in central and eastern Europe.[1]

[1] Mr. Claes Rooth of the Institute of Meteorology has looked into the air circulation over Europe in March 1954. His comments follow:

"The mean pressure chart for the month shows a well developed continental anticyclone together with a fairly deep cyclone over the north Atlantic. This indicates predominantly southerly flow over Scandinavia during the period. An inspection of the daily charts prepared by the Swedish weather service shows, as might be expected, a sequence of cyclonic and anticyclonic weather patterns over northern Europe. In central Europe, however, a weak anticyclonic circulation with wide areas of fog and low stratus dominated the month, preventing the vertical spreading of the pollution from the large industrial and urban areas. Extreme cases of such concentrations of highly polluted air under an inversion are known from Belgium, England and the United States where they have had even fatal consequences.

From the reservoir thus formed, contaminated air has apparently been brought up towards Scandinavia during the periods of SW—to SE flow. It has been stated by several workers that minute droplets of sulphuric acid are among the most persistent of the air pollutants that have been studied, which might explain partly why only the sulphur concentrations are abnormal in the air samples and partly why these high values are not reflected in the precipitation samples, which in fact show sulphur minima at several stations. In connection with the latter question it must be noted, however, that most of the precipitation fell during the first week of the month before the characteristic pattern described above had developed."

The study of these two months suggests that blocking of the "normal" west-wind circulation over northern Europe may be associated with marked changes in the chemical composition both of the precipitation and of the air. We have attempted to explore this possibility further by a study of changes in

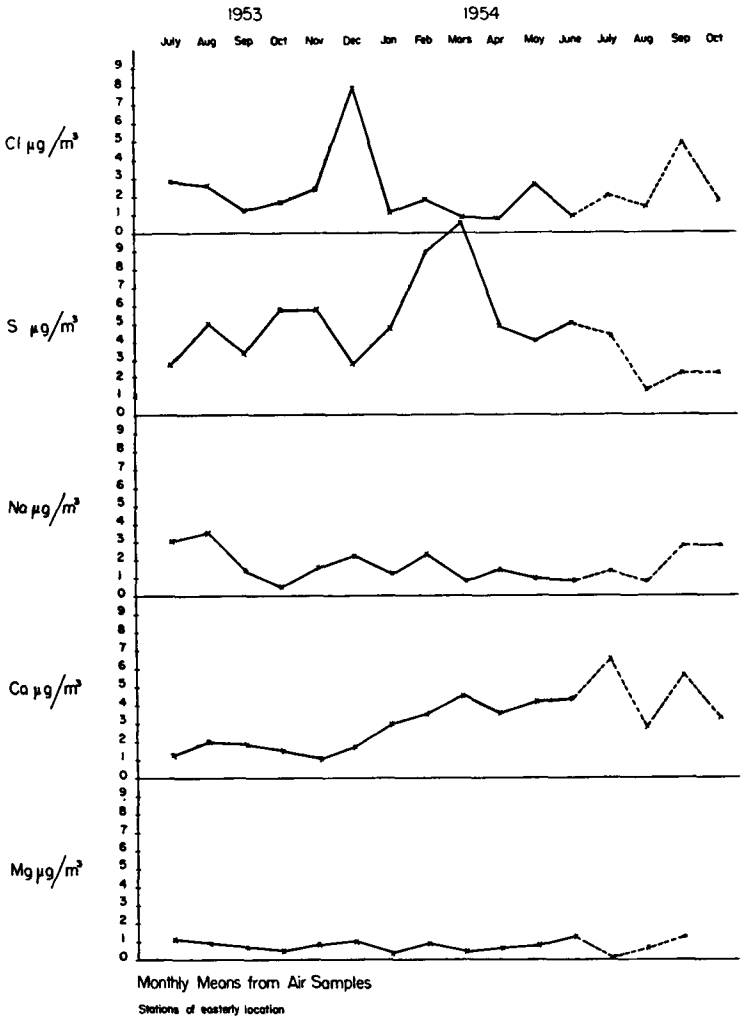

Fig. 9. Variation with time of the average concentration of chlorides, sulphur, sodium, calcium and magnesium (in μg per m^3 of air). Curves represented in this figure obtained by averaging the concentrations measured in he monthly samples from the eleven stations in Fig. 7.

the annual mean values of the various chemical components brought to the ground by precipitation and by a comparison of these changes with the changes in the corresponding mean annual circulation patterns. The data at our disposal are inadequate but they suggest nevertheless that the "ventilation" of southern Sweden by fresh maritime air masses decreased successively from 1949 until 1953 and that southern and southeastern Sweden during these years gradually became more exposed to air masses which had spent some time over central Europe and thus lost much of their original sodium content. To demonstrate this, it is perhaps sufficient to point out the trends of the annual deposits of various chemical components at a few representative stations situated away from the coast where data are available for several years and where local sources of pollution appear relatively unimportant:

Sodium deposit in kg per har and year

	1949	1952	1953	July 1, 1953—June 30, 1954
Skara	9.46	4.46	4.48	3.92
Flahult	9.20	3.74	3.65	4.32
Bräkne-Hoby	5.80	5.23	3.90	4.88

Chloride deposit in kg per har and year

	1949	1952	1953	July 1, 1953—June 30, 1954
Skara	9.37	7.28	7.00	6.61
Flahult	10.34	5.72	5.14	5.71
Bräkne-Hoby	8.03	7.59	6.30	8.54

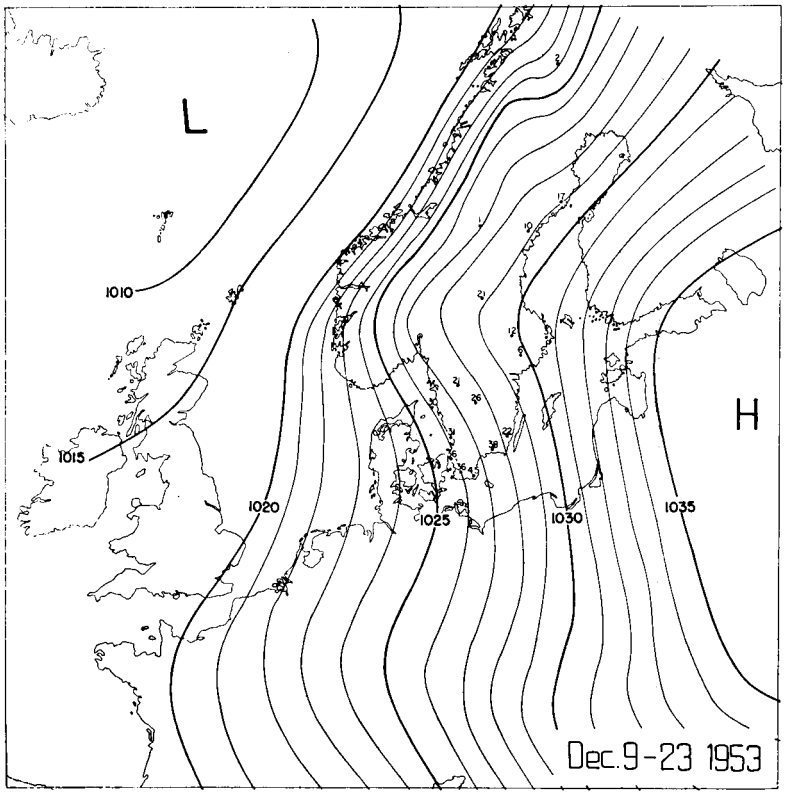

Fig. 10. Mean circulation pattern at sea level during the period December 9—23, inclusive, 1953.

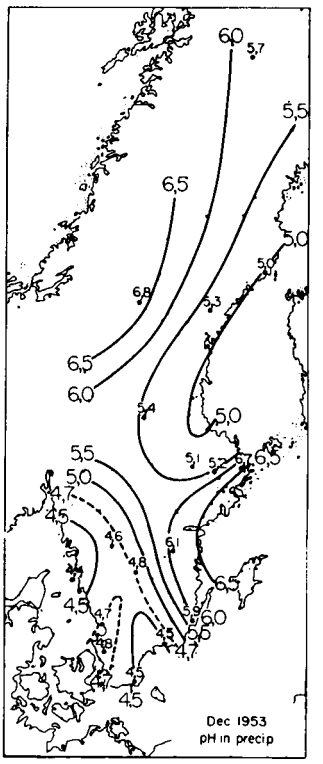

Fig. 11. Geographic distribution of the hydrogen-ion concentration in the accumulated precipitation for December 1953.

	Ratio of chloride to sodium			
	1949	1952	1953	1953—1954
Skara	0.99	1.63	1.56	1.69
Flahult	1.12	1.53	1.41	1.32
Bräkne-Hoby	1.05	1.45	1.62	1.75

	Annual precipitation in mm			
	1949	1952	1953	1953—1954
Skara.....	547	398	624	516
Flahult	773	611	705	739
Bräkne-Hoby	515	645	346	470

Data on the sulphur content are not available for the entire period and thus we have been forced to group the observations differently to bring out such trends as may exist. Hence, one finds:

	Annual deposit of sulphur in kg per hectar and year		
12 month period	July 1951— June 1952	July 1952— June 1953	July 1953— June 1954
Skara.....	6.10	6.12	5.94
Flahult	5.24	5.28	7.05
Bräkne-Hoby	6.37	7.47	8.81

Between 1949 and 1953 the sodium deposits fell off to one half or one third of their original value. The chloride deposits decreased too, but much less markedly. On the other hand, the two southeastern and eastern stations (Bräkne-Hoby and Flahult) showed rising deposits of sulphur. Taken together, the data point to an increasing frequency of air mass invasions from central Europe. To test this conclusion we have computed sea level mean pressure charts for the two years 1949 and 1952. (Figures 13 and 14.) The chart for 1949 shows a marked west wind circulation over the entire Scandinavian peninsula. In 1952, on the other hand, the most striking feature of the mean chart is a narrow high-pressure ridge which extends northward through the major part of Scandinavia. It follows that in 1952 the geostrophic winds across central Sweden must have blown almost as often from the

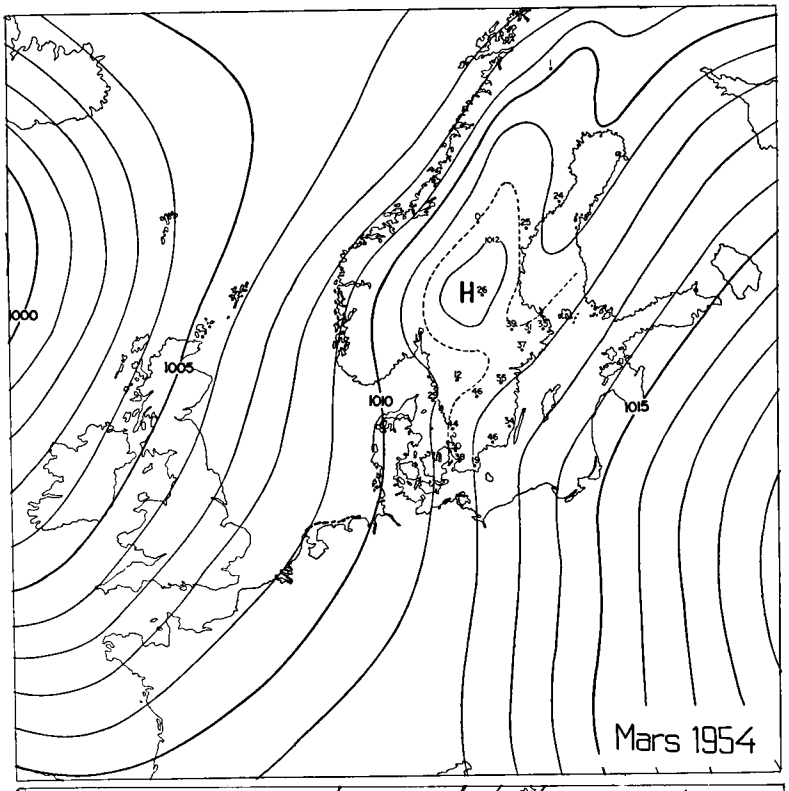

Fig. 12. Mean circulation pattern at sea level during March 1954.

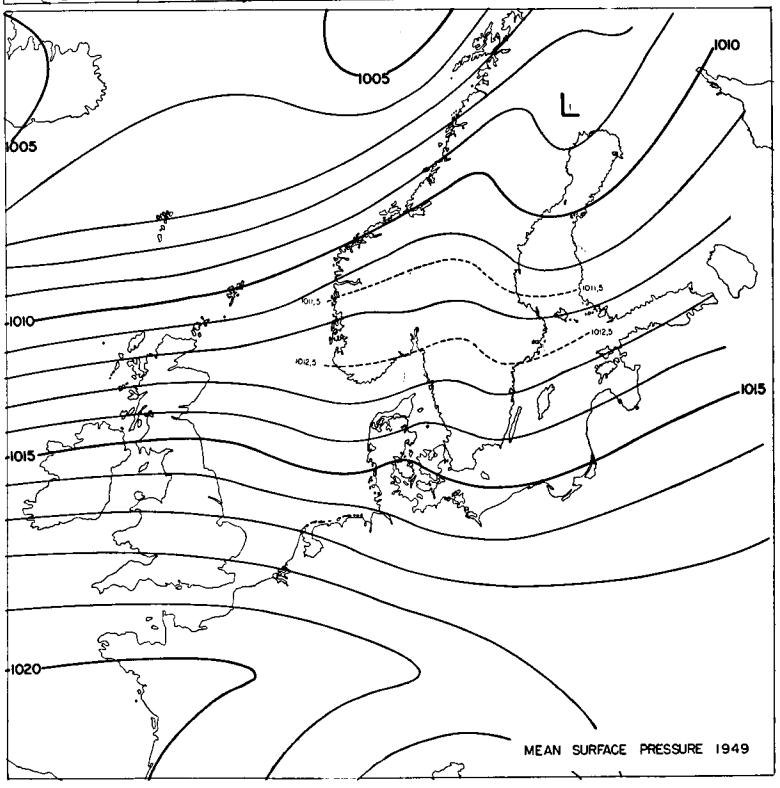

Fig. 13. Mean circulation pattern at sea level during the calendar year 1949.

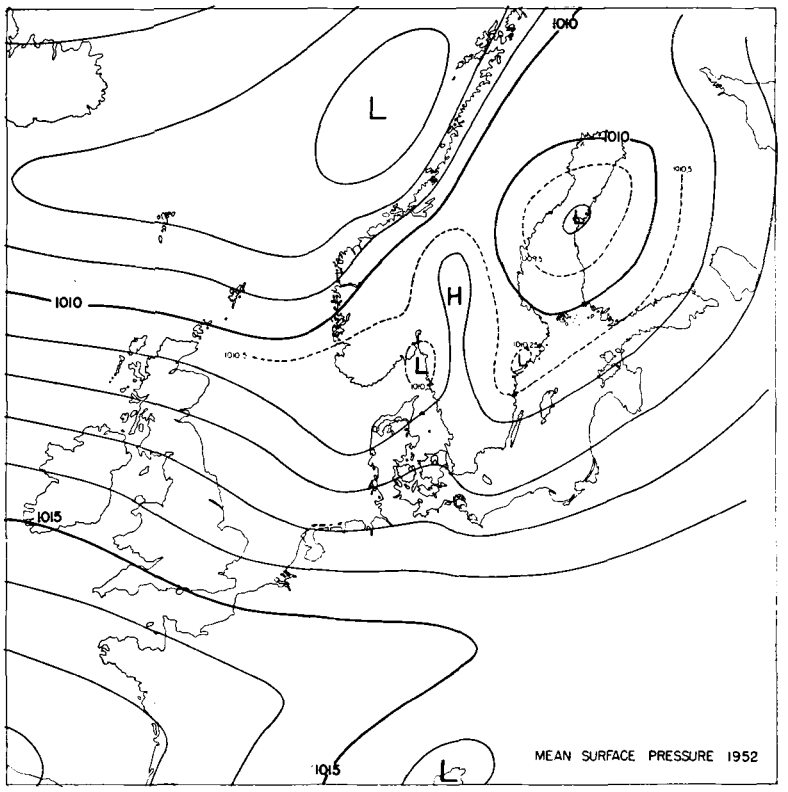

Fig. 14. Mean circulation pattern at sea level during the calendar year 1952.

east as from the west, *i.e.* the normal westwind "ventilation" of the peninsula had to a large extent been replaced by air currents from the interior of the continent. This point is brought out quite clearly by the graphical representation in fig. 15 of the frequency distribution of easterly and westerly geostrophic sea level winds across a north-south section in south-central Sweden.

The great variations from year to year demonstrated above show that the mean charts presented by EMANUELSSON, ERIKSSON and EGNÉR (loc. cit.) in no sense may be regarded as "normals" but merely as cartographic representations of the chemical composition of the precipitation in Sweden during one particular two-year period.

We shall finally attempt to check the various indications obtained from the study of our own data through an inspection of measurements in other parts of Europe. For this purpose we have attempted to sketch, in Fig. 16, the probable "average" distribution of chlorides in precipitation over northern and central Europa generally. The data for this sketch map have been obtained from the rather complete references contained in the survey by E. ERIKSSON (1952). A similar very useful tabulation of chloride data has been made by DRISCHEL (1940).

All chloride values entered on the sketch map in Fig. 16 have been expressed in mg per liter and it has been necessary to piece together data from periods widely separated in time. Observation series extending through less than one full year have not been used since the variations in the chloride content from month to month are extremely large. Likewise we have omitted many observation series from sampling points near the exposed western coasts of Europe, since the exact values of the high concentrations in the immediate vicinity of a coast clearly depend upon accidental details of orography and exposure. Valuable general information concerning the strong coastal gradients of the chloride concentra-

tion may be obtained from the investigations by FARCY (1931) and by LEEFLANG (1938).

The data from the British Isles (for instance RUSSEL and RICHARDS 1919) show a well-defined minimum in the interior of England (Cirencester 3.2 mg per liter, 26 years, Rothamsted 2.4 mg per liter, 27 years). Apart from the excellent coastal gradient data collected by FARCY (l. c.) the observations from France are inadequate but there are old series from Paris (one year, 1851) which gives a concentration of 2.3 mg per liter, in good agreement with the data from Cirencester and Rothamsted. A similar series from Nantes (about 90 km from the coast) for 1863 gives 8.4 mg per liter (this value is placed in the wrong column in table 10, p. 286 of ERIKSSONS survey (l. c.)).

In Germany data are available from several large industrial cities including Berlin, Dortmund and Essen. All these places show much higher values than the interior of England and represent undoubtedly the effects of strong local industrial pollution. There remains a one-year series from an apparently undisturbed sampling point at Müncheberg, approximately 50 km E of Berlin, with a concentration of 3.6 mg per liter (one year 1933—1934, LIESEGANG, 1934).

We have entered on the map the danish data (a one-year series for 1925—1926) obtained by HANSEN (1931). Likewise we have included a selection of the Swedish sampling points analyzed by EMANUELSSON, EGNÉR and ERIKSSON (1954). These data pertain to the calendar year 1949.

The data from the European part of the USSR are based on measurements made in 1909—1910 by WITUYNJ (1911). A statement by G. A. MAKSIMOVITJ (1953) in a lecture before the USSR Academy of Sciences seems to imply that these values still are accepted by USSR scientists as representative. Wituynj's measurements show notably high concentrations of chlorides in the Black Sea region decreasing northwards and towards Asia.

The most striking features in our sketch map are the existence of a chloride minimum extending from the interior of France towards eastern Sweden and the existence of a marked second chloride maximum in the eastern and southeastern part of Europe. This second maximum fits in well with the high chloride concentrations observed in SE Sweden during

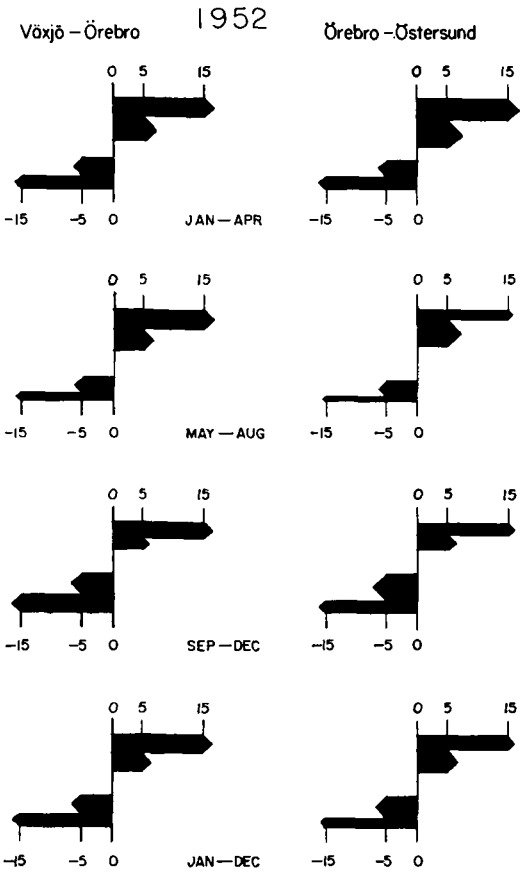

Fig. 15. Sea level frequency distributions for the year 1952 of geostrophic wind components from the west and from the east across two north—south sections in southern Sweden (Växjö—Örebro) and central Sweden (Örebro—Östersund). Thickness of arrows measures relative frequency of occurrence. Wind velocities expressed in mps.

November 1949 and in the air samples for December 1953. The explanation of this secondary maximum may lie in some process of ion separation operating on the sea salt nuclei but one can not a priori exclude as insignificant such other effects as volcanic and other continental sources of chlorides.

The separation of the individual chemical components of the nuclei brought out by some of the monthly patterns analyzed above would seem to fit in well with the results by JUNGE (1952, 1954) and WOODCOCK (1952) concerning the rôle of the giant nuclei in the precipitation mechanism. According to these authors the

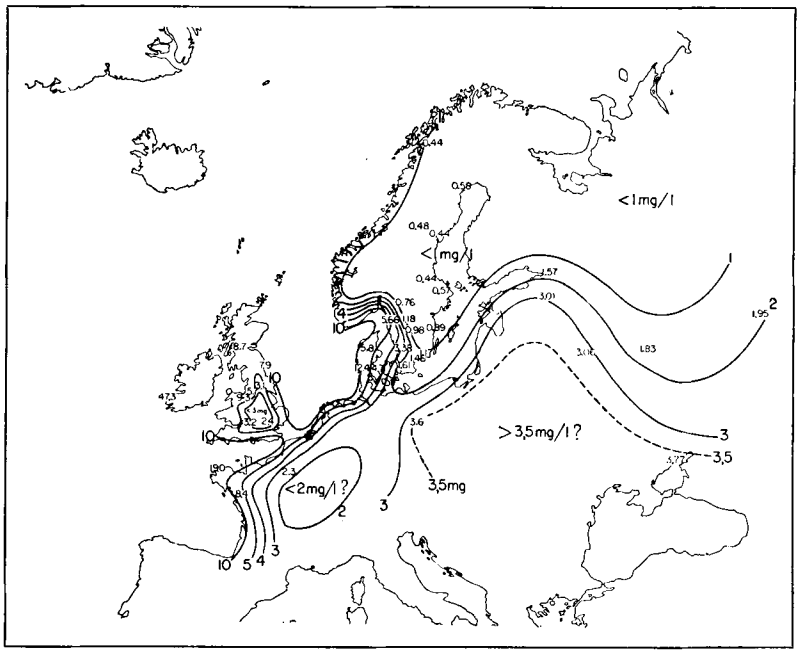

Fig. 16. A preliminary map of average concentration of chlorides (in mg per liter) in precipitation over Europe. Analysis based on records from different epochs and of very different length. Note proposed existence of minimum extending from central France towards eastern Sweden and of a secondary maximum over southern Russia.

largest nuclei consist mainly of sodium chloride and it is these nuclei which most readily lead to the formation of cloud droplets of precipitable size. One should therefore expect precipitation at stations not too far removed from the coast to possess a characteristic chloride over sodium ratio of about 1.5. After the precipitation of the sodium chloride particles there would remain in the air, or in the clouds, an excess of chlorides, perhaps in the form of H_4NCl or $MgCl_2$. The fact that the Cl/Na ratio even in straight westerly flows may drop to values considerably below 1.5 suggests however, that other sodium-containing nuclei become active before the chloride nuclei take over the precipitation-forming mechanim. With Dr JUNGE's permission we include a statement in a recent letter (February 20, 1955) to one of us (C.-G.R.):

"... Es waren mir zwar schon, auch von eigenen Untersuchungen, starke Abweichungen des Cl/Na-Wertes von dem des Seewassers bekannt, dass sie aber so stark sind und so augenscheinlich mit der Grosszirkulation verbunden sind, war doch eine Überraschung. Wenn ich Ihre Ergebnisse mit den meinen vergleiche, kommt mir der Verdacht, dass wir möglicherweise drei Komponenten unterscheiden müssen, die zum Gehalt des Regenwassers beitragen: Die Seesalzkomponente, die im wesentlichen 1.8 liefert, eine Gaskomponente, die eine Erhöhung dieses Wertes liefern würde und die ich jedenfalls in südlichen Breiten einwandfrei nachweisen konnte und drittens eine mineralische Staubkomponente, die zusätzliches Na liefert und das Verhältnis unter 1.8 sinken lässt.

"Das gefundene Verhältnis würde dann eine Mischung dieser drei Komponenten darstellen und natürlich von der Grosszirkulation abhängen. Nun ist die Lage Schwedens offenbar so, dass selbst bei überwiegenden Westwinden keineswegs mit einer reinen Seesalzkomponente zu rechnen ist. Den starken Anstieg der Werte bei südlicher Luftzufuhr würde ich als das Auftauchen der Gaskomponente deuten, möglicherweise unterstützt von industriellen Verunreinigungen. Das starke Absinken bei östlichen und nördlichen Winden wäre das Überwiegen der mineralischen Staubkomponent die ebenfalls noch bei westlichen Winden von Einfluss ist."

Regardless of the nature of the mechanism or mechanisms responsible for the separation of the individual chemical components observed in precipitation or in the air, it is quite evident from the data presented above that the chemical climate varies in a striking

manner with changes in the circulation patterns. In certain respects the association of a specific chemical climate with a specific circulation type may to some extent depend on man-made sources of pollution. By and large, however, one should expect the association to be stable and applicable also to past climates. The relative fluctuations in the temperature and precipitation climates with changes in circulation pattern are, at least in Northwestern Europe, small compared with the fluctuations in the chemical climate. There might therefore exist a possibility to trace post-glacial climatic fluctuations through their chemical consequences. In a recent major investigation MATTSON and COUTLER-ANDERSSON (1954) have made a detailed study of the chemical composition of different strata in a raised bog in SW Sweden. They find striking variations in the relative proportions of various elements and in the pH. It is tempting to try to associate these variations with variations in the circulation pattern, to check conclusions concerning post-glacial climatic fluctuations which have been drawn previously mainly from pollen-analytical studies. Such an attempt would, however, require a detailed investigation of the association between the circulation pattern and the deposition through precipitation of the bivalent ions, for instance Ca^{++} and Mg^{++}, which are most closely bound by the humic acids, and which therefore are capable of exhibiting a measurable stratification.

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