The Acidity of Scandinavian Precipitation

By

EARL BARRETT, Institute of Meteorology, University of Stockholm and Woods Hole Oceanographic Institution[1]
GUNNAR BRODIN, Royal Agricultural College, Uppsala

(Manuscript received March 3, 1955.)

Abstract

Data on the pH of the total monthly precipitation at stations of a Swedish network for sampling and chemical analysis of precipitation and atmospheric aerosols during the year July 1953—June 1954 are presented and discussed, together with the pH data from the first two months of operation of a larger pan-Scandinavian net. It is found that well-defined regions of acidity and alkalinity relative to the pH of water in equilibrium with atmospheric carbon dioxide exist, and that these regions persist to such an extent that the monthly deviations from the pattern of the annual mean pH at each station are relatively small. The mean pH of the entire network shows a distinct annual cycle, with greatest acidity in winter and greatest alkalinity in late spring. Coastal stations unaffected by local pollution show persistently high acidity, while inland northern stations show equally persistent alkalinity. Some possible reasons for the observed distributions are considered.

Introduction

Although there is doubtless a considerable number of spot observations of the acid-alkaline balance of precipitation which have been made and reported in various journals during the past, there has been no effort (so far as is known to the writers) to systematize such observations and present them in a significant and readily-assimilable form. One can readily recognize two reasons for this; the first reason is that the observations had been made for the most part by workers who are not trained in the concepts and techniques of synoptic observations and analysis, while the second is that, even if the observers felt the desirability of a synoptic presentation, the necessary organized network of stations for the purpose did not exist. Within the last few years both of the obstacles have been overcome to some degree. A network of stations has been established in Sweden for the purpose of analyzing one-month samples of precipitation for the principal ionic constituents. This net, originally established for agricultural purposes by the Royal Agricultural College of Sweden, has been extended by degrees, until, at the time of writing, it provides excellent coverage of Sweden and moderate coverage of Norway, Denmark and Finland. This network and the sampling equipment have been described in previous papers (EGNÉR and ERIKSSON, 1955; ROSSBY and EGNÉR, 1955).

The second obstacle has been removed by the establishment of a co-operative program between the Agricultural College and the Meteorological Institute of the University of Stockholm. The junior author of this paper has had the responsibility for the collection and chemical analysis of the samples, while the senior author has undertaken the work of synoptic analysis and meteorological interpretation of the data.

---

[1] Contribution No. 785 from Woods Cole Oceanographic Institution.

The objective of the paper is to present the results of a preliminary survey of the spatial and temporal variation of the acid-alkaline balance of precipitation. It should be made clear at the outset that this paper will pose many problems and solve few, if any, of them. The atmosphere, considered as a chemical system, is so highly multivariate that it resembles a biological or sociological system in complexity; thus one cannot expect to find the simple logical connections between single causes and effects which one looks for in connection with well-isolated physical systems. The most that one may expect in the preliminary stages of study of such a complex system is to narrow down the field of investigation by looking for the highest correlations, and to subject these to more searching study with the aid, wherever possible, of theoretical models and idealized laboratory experiments. The objective of this paper is the modest one of displaying the data in synoptic form and laying a number of study topics before the attention of others, in the expectation that interest will be stimulated and answers to the questions will be sought by investigators at other institutions at the same time that they are being pursued in Stockholm.

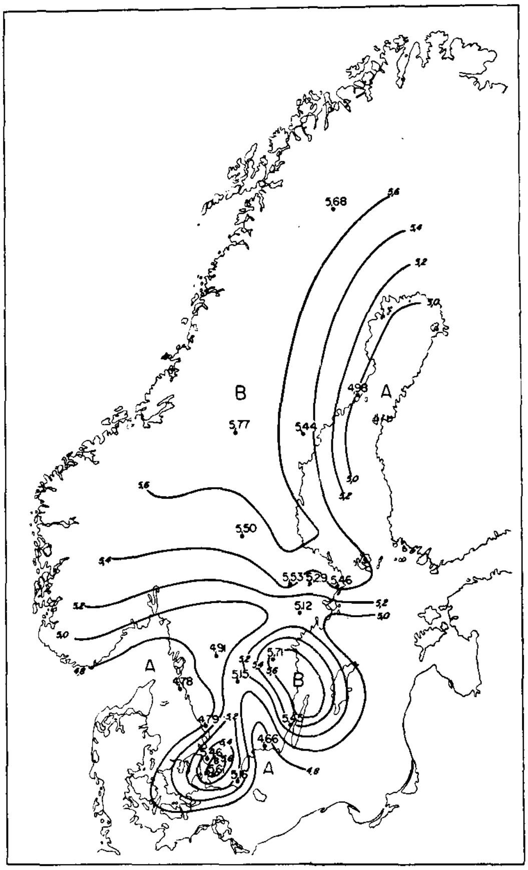

Fig. 1. Annual Mean pH of Precipitation, July 1953—June 1954.

Presentation of the Observations

Samples of rain and/or snow collected by a small heated rain-gauge draining into a plastic sampling bottle are taken during each entire month at all the stations of the network. The data considered in this paper were collected during the period July 1953 through June 1954. During this period the net consisted of 19 stations, all within Sweden and with a maximum density in the southern half of the country. Starting in November 1954 the net became pan-Scandinavian in scope and was increased to a total of 44 stations. The data for the first two months of expanded operations will also be included in the presentation, as they emphasize certain points which are not so clearly illustrated by the smaller net.

The acidity or alkalinity of the samples has been determined by measurement of the electrical potential generated by the galvanic cell using a glass electrode and calomel electrode, with the sample as the electrolyte (Beckman pH meter, model G). The data are reported as pH units, *i.e.*, the negative of the common logarithm of the molar concentration of hydrogen ions in the sample.

It is customary in chemistry to take as neutral the pH value of 7.0 which is characteristic of ideally purified water at room temperature (25° C). However, the water in the atmosphere is in general not in this standard state of purity—in fact, it cannot possibly be. Even if all soluble solid electrolytes and pollution could be kept out of the cloud water, this water would always attempt to achieve equilibrium with the carbon dioxide pressure of the atmosphere. If one assumes that equilibrium is actually reached at the observed mean pressure of CO_2, the pH may be calculated from the known equilibrium constants to be 5.7 at 25° C. The variation with temperature is in the direct sense, although not linear.

Since the samples are measured at room temperature, this value of 5.7 may be regarded as the neutral point for atmospheric water. This convention will be adopted in this paper. Thus pH values lower than 5.7 represent a net acidity for the sample, while values greater than 5.7 indicate a net alkalinity.

The monthly values for all stations have been entered on synoptic charts and isopleths of pH have been drawn for each month. In addition, two kinds of "mean" values have been computed. In calculating these, the pH numbers are converted to their negative antilogarithms (molar concentrations of hydrogen ion); these are then multiplied by the measured amount of the sample. The sum is formed and divided by the sum of the sample volumes; this concentration is then reconverted to a pH value. It is apparent that this procedure, analogous to the method of calculating the mean molecular weight of a mixture, gives the only physically significant mean; a simple arithmetic mean of the pH values is quite without significance because of the variation in precipitation in space and time and the inherently nonlinear nature of the pH unit.

The "mean" obtained by the weighting system described above represents the pH which would be measured by an instrument if all the samples being averaged were poured together into a common vessel and no CO_2 were allowed to escape from the solution; put in another way, it represents the strength of a solution of a completely ionized acid which would have brought the same amount of hydrogen ion per unit area to the ground as was brought by the rainfall. The fact that more alkaline samples would partly neutralize more acid ones if physically mixed is disregarded, since a measure of total acid rather than net acid is the quantity desired. It is clear that the monthly samples actually underestimate the total acid in cases where individual rains fluctuate in pH because of the loss of CO_2 when fractions of different pH combine; thus the pH figures for each month are really slightly too high if interpreted as a measure of total acid brought to the ground.

The mean, or effective, pH for the entire net (areal mean) for each month, and the mean for the year at each station have been calculated by the procedure described above.

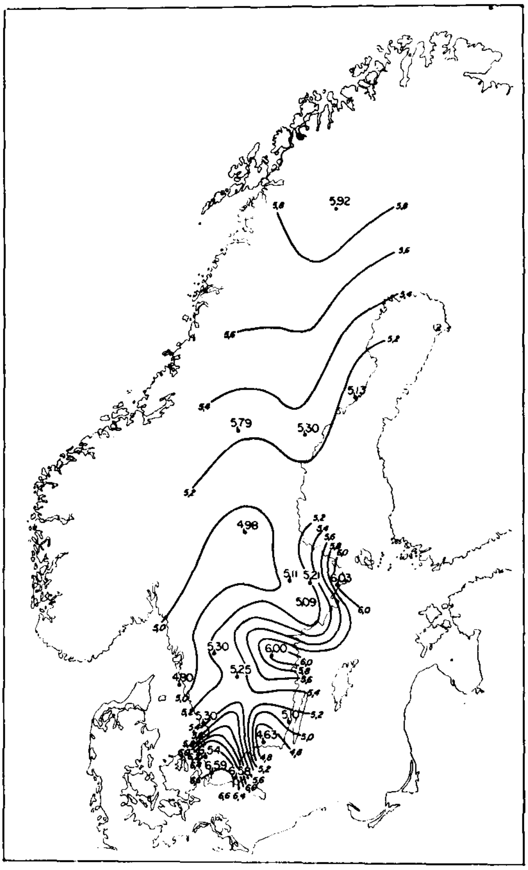

Fig. 2. pH of Precipitation, Sept. 1953.

Economy of page space does not permit the inclusion of the 15 charts which have been prepared. Figure 1 shows the distribution of the annual mean for each station for the year July 1953 to June 1954; this single chart displays most of the significant details which appear on the monthly charts. The two most atypical monthly charts are shown in Figs 2 and 3.

The principal features of the chart of Fig. 1 are: (a) the region of acid precipitation along the west coast; (b) the nearly neutral areas at the southwest tip of Sweden (Skåne) and along the southeast coast; (c) the acid tongue which separates these two neutral regions; (d) the acid region along the northeast (Bothnian) shore; (e) the large neutral or alkaline region covering the more elevated interior of Northern Sweden; (f) the acid "corridor" which joins the west-coast and Bothnian

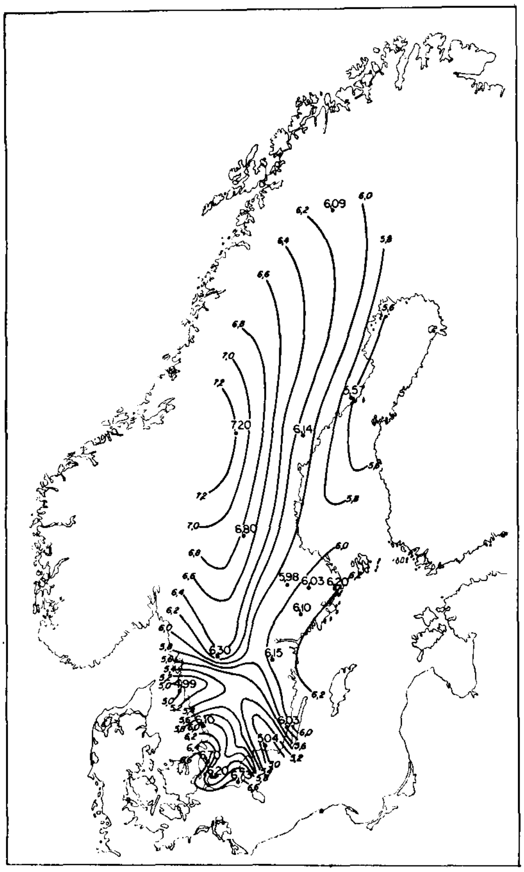

Fig. 3. pH of Precipitation, May 1954.

acid regions. This corridor shows a marked tendency to meander from month to month; in Fig. 2 it is shown displaced toward the northwest. When such a displacement occurs, a new region of alkalinity appears over the easternmost coastal region (Uppland). On other occasions the inland alkaline region extends southward to Uppland; the acid corridor then enters the Baltic farther south and the alkaline or neutral region of the southeast weakens strongly.

An examination of the monthly charts shows that the features discussed above are, in fact, semi-permanent features. The central values of pH fluctuate in magnitude from month to month and the positions of the centers shift slightly, but on the whole the pattern is remarkably persistent. The alkaline region of the northern interior (Norrland) does, however, show a distinct annual cycle; the pH is minimum there in late summer and is maximum in spring (compare Figs 2 and 3).

The monthly mean values for the entire network are shown plotted on the graph of Fig. 4. The solid curve applies to the values from the 19-station net for 1953—54, while the short dotted curve represents the means for the first two months of operation of the expanded 44 station net (November and December 1954). A distinct annual cycle is indicated, with a maximum of acidity (pH minimum) in the late fall and winter and a minimum acidity in the late spring. It is to be noted that, except for the month of May, the precipitation over Sweden as a whole is definitely more acid than the CO_2 equilibrium alone would permit; the neutral point is just reached in May. It is unfortunately true that the sampling in the alkaline north is sparse compared with the generally more acid south, so that allowance must be made for this in the interpretation; however, the curve would not be affected too strongly by the addition of more stations in the north because of the low winter precipitation there. The summer values would, however, be shifted upwards by the inclusion of more Norrland data. The two values for the new net (which has better northern coverage) show that the shift in the autumn means produced by doubling the number of stations is smaller than the month-to-month fluctuation.

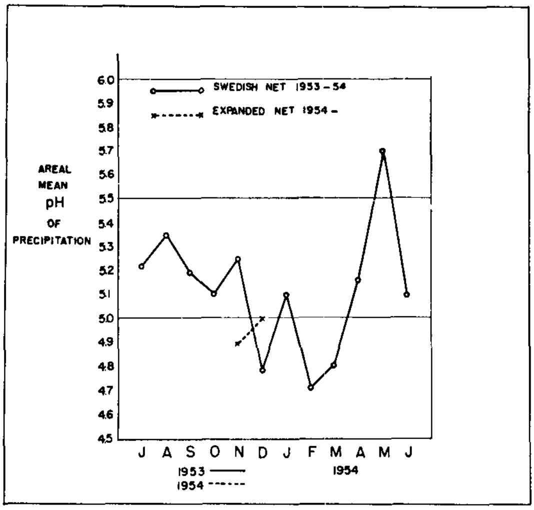

Fig. 4. Areal Mean of Precipitation pH vs. Time July 1953—June 1954 and Nov.—Dec. 1954.

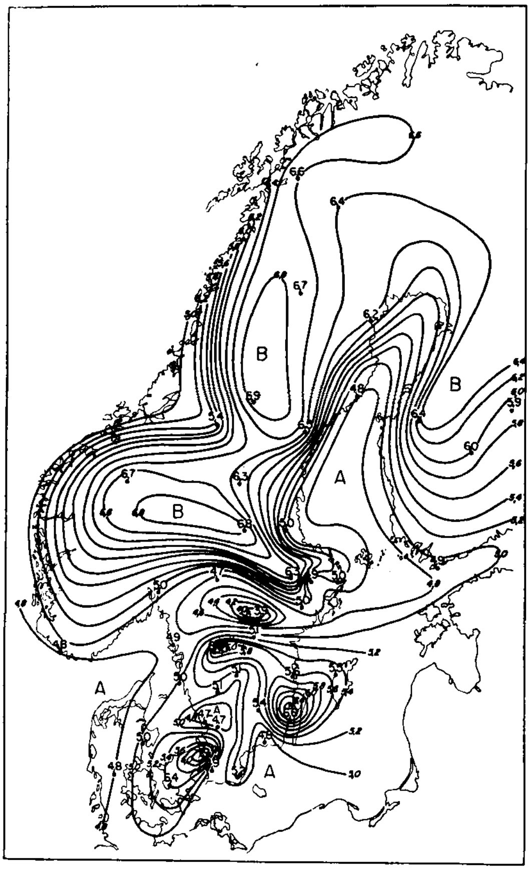

Fig. 5. pH of Precipitation—Expanded Network, November 1954.

Figs 5 and 6 show the pH distribution for the expanded network for the months of November and December 1954. It can be seen that the distribution is very much the same as for the smaller network; the acid character of most of the maritime regions and the alkaline character of the inland area are clearly illustrated. The acidity at the station in central Finland compared to the west Finnish station in the same latitude is, however, an anomalous feature.

Discussion

The data have shown that, on the whole, the precipitation over Sweden tends to be more acid than pure water in equilibrium with the carbon dioxide of the atmosphere. Furthermore, this excess acidity tends to be maximum at coastal stations and in the southern peninsula of Sweden, while the inland and northern regions tend to be neutral or slightly basic with respect to CO_2 equilibrium. The data from the larger network justify the extension of this picture to all of Scandinavia. The question of the source of the acid arises immediately. Examination of the anion analyses is not exceedingly helpful, since one cannot decide how much sulfate, for example, was collected as sulfuric acid and how much was picked up as neutral salts. One source which comes immediately to mind is combustion acids, primarily sulfuric acid, produced in densely populated and industrial regions. There is no particular difficulty in ascribing the acid tongue which enters Sweden from the south to this source, since the prevailing flow of air into this region is from the industrialized area of Central Europe during most rainy periods. The acid corridor across the southern peninsula of Sweden may also be attributed, at least in part, to such industrial acid. The acid region of the Sea and Bay of Bothnia may probably in part be due to the cellulose industries locates along the coasts in Norrland and Finland. One of the stations in the new network (Kvarntorp 1) is located in close proximity to a shale-oil plant; the pH values for this station are among the lowest recorded.

It appears difficult, on the other hand, to explain the high acidity of the precipitation on the south coast of Norway, the west coast of Sweden, the south coast of Finland and to some extent the coasts of the Sea and Bay of Bothnia as being caused by combustion products. It appears, therefore, that one must look to the sea itself as a source of acids. Provided that such a source can be found in the sea, the decreasing acidity with distance from the coast which is observed in areas free of pollution is readily explainable as a result of washing out of the acids by the precipitation, possibly coupled with addition of alkaline aerosols from the soil in snow-free months.

The next question is whether the sea can provide a source of volatile or easily-dispersed acid, and the chemical nature of this acid. Three possibilities immediately come to mind. The first of these is the possibility that organic acids which are products of biological activity may be concentrated in the thin surface film of the sea and dispersed from thence into the air by evaporation and/or the mechanical action of foaming and bubble breaking. This

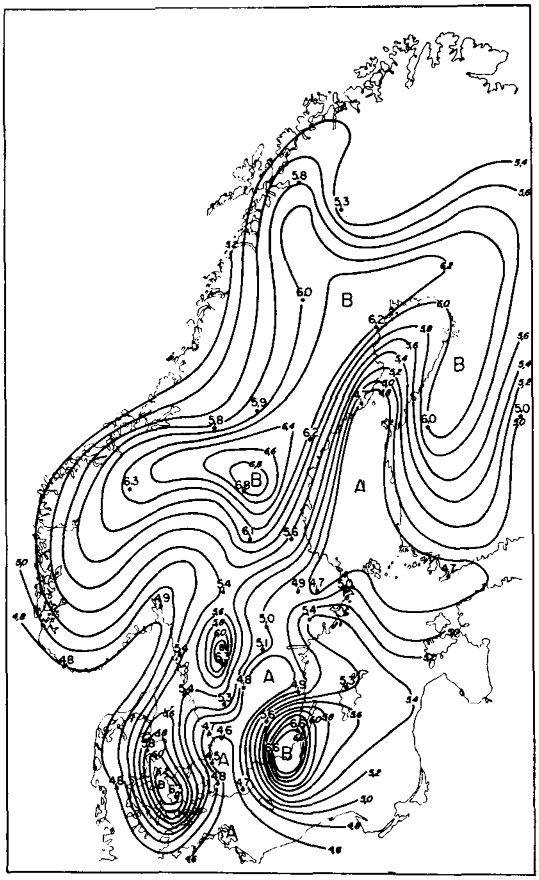

Fig. 6. pH of Precipitation—Expanded Network, December 1954.

possibility is amenable to experimental testing. Exactly the same argument applies to the hydrogen sulfide formed by biological action. This gas should be rather rapidly oxidized to SO_3 photocatalytically and by ozone, and would provide a supply of sulfuric acid. Unfortunately no data are apparently available on the rate of emission of H_2S from the sea, although it is known to occur. Presumably the gas is oxidized rather quickly, at least in daylight, and so the analyses of the air for sulfide would greatly underestimate the actual production. It remains to be determined whether or not this source strength is great enough to account for the observed acidity of the rainfall in coastal regions.

A third possible maritime source of acid may be sought in the ionic separation which has been observed to occur as a concomitant of the foaming of the sea surface (CAUER 1949, KÖHLER and BÅTH 1953). It is conceivable that the fine spray which ultimately becomes the source of many of the condensation nuclei is enriched in anions at the time of formation. This hypothesis is difficult to test, especially since the trapping and analysis of the smaller particles for anion-cation balance is no easy matter.

Although a decrease in acidity inland is to be expected as a result of the progressive washing-out of the (presumably maritime) acid contaminants as a precipitating air mass moves inland, it does not seem possible to account for pH values greater than about 5.7 in this way. In the mean, to be sure, the highest pH reported is 5.77 at Ås in central inland Sweden; however, the monthly values at the northern and inland stations are frequently above 6.0 and in a few cases above 7.0. It thus seems necessary to postulate the presence of alkaline aerosols of terrene origin. Examination of the concentrations of the various ions shows that many of these high pH values are associated with high calcium contents or a high ratio of calcium to sulfate; this suggests that aerosols of limestone are responsible for the alkalinity in the northern inland regions.

The two alkaline regions of Southern Sweden apparently result from a combination of pollution effects. The southeastern region coincides closely with the maximum area of surface limestone in Sweden; the Baltic islands of Gotland and Öland and the nearby Swedish coast possess considerable deposits of this mineral. The southwestern region, which also extends over eastern Denmark, is, in contrast to the area just mentioned, characterized by a high percentage of ammonium ions in most cases. The source of this ammonia is probably to be found in the extensive dairy farms of Denmark as a product of biological activity. However, a calcium pollution source exists at the southwest tip of Sweden in the form of a large cement factory; this point source frequently results in an anomalously high pH and calcium content at one or both of the two observing stations in this region. One may conclude, therefore, that the southwestern alkaline cell is clearly a result of human activity, in contrast to the southeastern cell and the northern inland.

The annual cycle of the network mean pH,

Fig. 4, is interpretable as a combination of effects. The minimum in February-March coincides rather well with the time of maximum combustion of fuel. At the same time the prevailing air flow during rain periods is from the south. In May the situation is reversed; the combustion decreases and the prevailing air flow is from the north and northeast in connection with the blocking anticyclone over the British Isles and the North Sea. In summer the blocking breaks down and the rain-bearing air may arrive from any direction; the maritime and industrial acids which are brought in from southerly and westerly areas bring the pH down from the spring maximum of 5.7 to intermediate values of around 5.2.

It is admitted that the making of such generalizations on the basis of only one year's data is slightly presumptuous. The conclusions are therefore put forward as tentative suggestions, subject to later revision when several years of data have been accumulated.

It would be highly desirable to attempt to relate the pH of precipitation to the region of origin of the associated air mass and to the past history of the air mass. It is unfortunately impossible to accomplish this in an unambiguous way if one is constrained to use total monthly samples of precipitation. One may attempt to relate the pH distribution to the mean isobaric pattern for the month and so obtain characteristic charts of pH distributions associated with air flows from various directions. These may, however, be somewhat misleading, since the precipitation samples represent, for particular stations, only a fraction of the days in the month. Furthermore, it sometimes happens that all of the rainfall at the station occurs on one or two days with completely atypical flow patterns. The monthly mean pressure pattern can therefore only be used for correlation studies when an examination of the daily charts shows that most of the precipitation did indeed arrive with wind patterns closely resembling the mean flow. A more satisfactory approach (although much more laborious) is to calculate precipitation-wind roses for each station and, by a study of the daily synoptic charts, to estimate trajectories of the air for each rain day and each station. In this way the fraction of the total precipitation which derives from a particular source region may be computed for each station.

A much better approach to the problem of correlation of precipitation properties to air masses would be to equip some stations (in regions free of local pollution) with large-aperture precipitation collectors and to analyse the samples collected at such stations during a single rain period. This procedure is contemplated, and it is expected that more reliable correlations between precipitation chemical composition and air masses will be obtained thereby. In the meantime the monthly mean isobaric patterns provide the only readily calculable information for correlation studies, but they must be used with caution.

REFERENCES

CAUER, H., 1949: Ergebnisse Chemisch-meteorologischer Forschung. *Arch. f. Meteor., Geophys. u. Bioklimat.*, Ser. B, **1**, 221—256.

EGNÉR, H., and ERIKSSON, E., 1955: Current data on the chemical composition of air and precipitation. *Tellus* **7**, 134—139.

KÖHLER, H., and BÅTH, MARKUS, 1953: Quantitative chemical analysis of condensation nuclei from sea water. *Nova Acta Reg. Soc. Sci. Ups. Ser. IV, vol. 15, no. 7.*

ROSSBY, C.-G., and EGNÉR, H., 1955: On the chemical climate and its variation with the atmospheric circulation pattern. *Tellus* **7**, 118—133.