On the meteorological interpretation of the chemical composition of monthly precipitation samples[1]

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ABSTRACT

A methodology is presented for studying the influence of synoptic weather patterns on the chemical composition of monthly precipitation samples. The data selected for illustration are the sulfur and chloride monthly depositions at two stations in southern Sweden, Plönninge (coastal) and Flahult (inland), the observations extending from 1951 to 1969.

The monthly values have been grouped in various ways into subsets of about 24 members, and the median has been used as an index of central tendency in each subset. An initial grouping according to monthly precipitation amounts yielded curvilinear relations between deposition and precipitation. Another grouping by 2-year time periods revealed a marked increase in sulfur deposition at both stations in the early 1960's: chlorides, on the other hand, were highest in the middle 1950's, and the secular variations at Plönninge were not in phase with those at Flahult. The variations in deposition could not be explained by variations in precipitation amounts.

In order to study the influence of meteorological factors, a weather classification was developed based on the direction of the surface geostrophic wind over southern Sweden during periods of precipitation. For sufficiently wide sectors and for medians of large samples of data, this proved to be a useful predictor of deposition, being an index of upwind trajectory. All precipitation events during the 18 years of record were thus classified, and linear relations were established between median depositions and median monthly frequencies of precipitation-bearing SE–SW–NW flows (sulfur) and SSW–NW flows (chloride).

For chloride, most of the secular variations at Plönninge could be explained with this index. The method was not so successful at Flahult, probably because the upwind arc was too wide at that station: the principal source for chlorides is the sea, and SSW winds have not generally had a recent over-water trajectory before reaching Flahult.

For sulfur, the secular variations in the frequencies of precipitation-bearing SE–SW–NW flows were very closely in phase with median sulfur depositions 1951–1969. There was evidence, however, for a residual upward trend in sulfur depositions. A linear regression analysis that included both weather frequencies and time as dependent variables yielded a best estimate for this trend of 2 to 3 % per year, a figure not in disagreement with estimates of the rise in emissions of anthropogenic sulfur.

1. Introduction

The principal chemical constituents in monthly precipitation samples have been measured at a number of locations in northern Europe for about 20 years. Some early results were given by Eriksson (1952) and Rossby & Egnér (1955) while more recent discussions have been presented by de Bary & Junge (1963), Stevenson (1968), Eriksson (1970) and Petrenchuk & Selezneva (1970).

There is considerable public concern about the fact that concentrations of various constituents seem to be rising (Odén, 1968; Eriksson, 1970), although there is uncertainty as to whether this is due to an increase in emissions, changes in the atmospheric general circulation, or both. There have been few studies of the relative importance of the two factors, despite the ecological importance of the question. In

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Fig. 1. Map showing the locations of the Plönninge and Flahult precipitation chemistry sampling stations.

his paper, Nyberg (1970) emphasizes that the second factor must not be overlooked when seeking explanations for secular changes in pollution concentrations.

A paper that should be mentioned particularly is the investigation by Schmidt & Velds (1968) of the winter mean sulfur dioxide concentrations in the air over Rotterdam during the years 1962–68. These authors found not only a decrease in SO_2 content over the years but also a decrease in the frequencies of particular weather patterns conducive to poor air quality. The evidence suggests that meteorological factors contributed significantly to the observed reduction in SO_2 levels.

The purpose of the present contribution is to present a methodology for examining the influence of prevailing synoptic weather patterns on the chemical composition of monthly precipitation. The analysis is restricted to two sampling stations in Sweden, and to two constituents, sulfur and chloride, for the period 1951–1969. A new methodology was required because precipitation events have a time scale of a day or so at most, whereas the available deposition data are monthly totals.

Meteorological indices averaged over one-month intervals are likely to obscure non-linear effects, even if depositions are in fact strongly weather-dependent on the shorter time scales.

In Section 3 we obtain curvilinear relations between median monthly depositions and median monthly precipitation amounts. In Section 4 we determine the secular variations in deposition over the period 1951 to 1969, and we show that secular variations in precipitation amounts cannot be used to explain these patterns.

A weather classification system is developed in Sections 5 and 6, based on the direction of the surface geostrophic wind during periods of precipitation. This system seems capable of explaining the main secular variations in chloride depositions (Section 7). For sulfur, however, there is a residual upward trend in values (Table 3, Section 6), the magnitude of which is estimated in Section 8 from a linear regression analysis.

2. Sources of data

The chemical sampling methods have been described recently by Eriksson (1970) and will not be repeated here. We have used the values of monthly precipitation in millimeters and deposition of sulfur and chloride in milligrams per square meter at two Swedish stations, Flahult and Plönninge. The locations are shown in Fig. 1. Flahult is in the inner part of southern Sweden while Plönninge is about 5 km from the southwest coast.

The period of record is from July 1951 to October 1969 inclusive, with the following months missing:

Flahult: Mar. 1960 (Cl), Jan. 1963, Mar. 1964, June 1965, Oct. 1965 (S), June 1967–June 1968 inclusive, Nov. 1968 (Cl).

Plönninge: Mar. 1960, Feb. 1961 (Cl), Feb.–Mar. 1962, Oct. 1962, Feb. 1963, Mar. 1964, Jan. 1966 (S), Apr. 1966 (S), Oct 1967 (Cl), Feb. 1968.

In many of these cases, there was either no precipitation or too small an amount to undertake a chemical analysis.

The Flahult and Plönninge precipitation values are monthly totals only, and no information is given on the daily distribution. For the meteorological analysis of Section 5, therefore, the precipitation data for Jönköping and Halmstad have been used. Jönköping is about 8 km north of Flahult while Halmstad is 12 km southeast of Plönninge.

A final source of data was the 0600 GMT daily surface weather maps published by the Swedish Weather Bureau.

3. The effect of precipitation amount on deposition

Even if the sources of sulfur and chloride were uniformly distributed around a sampling station, the deposition would be expected to vary from month to month because of differing precipitation amounts. Conversion to concentration per litre of water is supposed to normalize for this effect. In a single rainfall, however, the concentration of contaminant normally decreases with time, a fact that can be explained by the washout processes (e.g., Makhon'ko, 1967). Furthermore, a monthly precipitation total arises from a number of separate precipitation events: for the same monthly total rainfall and air quality, the distribution of precipitation events must have a considerable effect on deposition. Finally, because the rain gauges are exposed during dry as well as during wet weather, the measured monthly concentrations in precipitated water must include an amount due to dry deposition. For all these reasons, the existence of a linear relation between monthly deposition and monthly precipitation is not obvious. We have therefore attempted to establish empirical relationships for the Flahult and Plönninge sampling stations.

Deposition values are close to being log-normally distributed (Eriksson, 1970). The median was therefore selected as an appropriate and convenient index of central tendency. Alternatively, the geometric mean might have been used but for sufficiently large samples, the two indices are highly correlated. Preliminary tests showed that about 24 deposition values were required in order to produce a stable median, i.e., stable in the sense that an additional two or three values would make a difference of less than 5 mg/m^2 in the median. For samples of only 12, on the other hand, the two central values sometimes differed by more than 20 mg/m^2, confounding the subsequent analysis. The precipitation data were therefore stratified into non-overlapping subsets of about 24 cases, each subset consisting of months with precipitation amounts within designated class intervals. Medians were then calculated of both the precipitation and the deposition in each subset. The results are shown in Figs. 2–3.

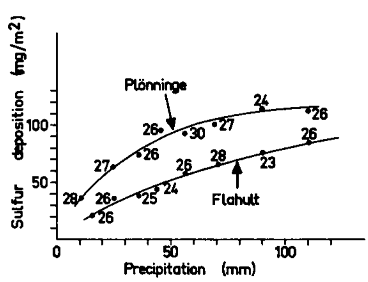

Fig. 2. Median values of monthly sulfur deposition as a function of monthly precipitation. The numbers indicate the number of months within each subset.

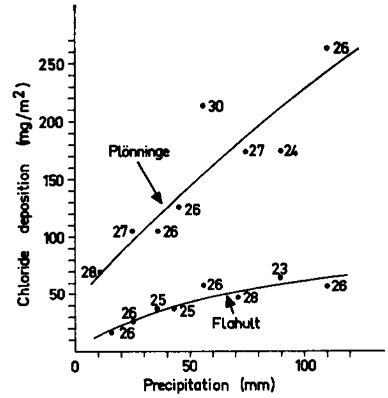

Fig. 3. Median values of monthly chloride deposition as a function of monthly precipitation.

Median depositions increase with increasing precipitation but not linearly. No attempt has been made to obtain a mathematically best-fitting curve because the precise form is not essential for the subsequent analysis. However, curved lines have been sketched by hand. Note should also be made of the fact that although the medians reveal a strong relation with precipitation amount, there was a considerable scatter within each subset, and individual values were as high as 729 and 1 345 mg/m^2 for sulfur and chloride, respectively.

Dry deposition is presumably given by the y-intercept of the curves in Figs. 2–3. The lines cannot be extrapolated accurately but it seems that median dry depositions must be only a small fraction of the corresponding median wet depositions.

The oceans have long been recognized as major source regions for atmospheric chlorides. This undoubtedly accounts for the fact that median values of chloride are much higher at Plönninge, a coastal station, than at Flahult.

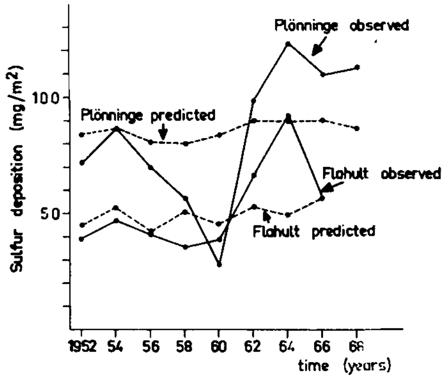

Fig. 4. Observed and predicted median values of monthly sulfur deposition as a function of time. The prediction is based on the curvilinear relations of Fig. 2.

4. Secular variations in median deposition: 1951–1969

Median depositions for the two constituents have been determined for consecutive two-year periods beginning July 1951 (the solid lines in Figs. 4–5). As indicated in Section 3, subsets of about 24 values are required to obtain a stable median. Thus, a two-year period is the shortest unit of time that can be examined. Even then, some of the medians did not quite satisfy the stability criterium especially in the case of chloride, due mainly to the fact that some of the subsets did not contain 24 members. Because of the 13-month break (1967–68) in the Flahult observations, median values are not given for that station after 1967.

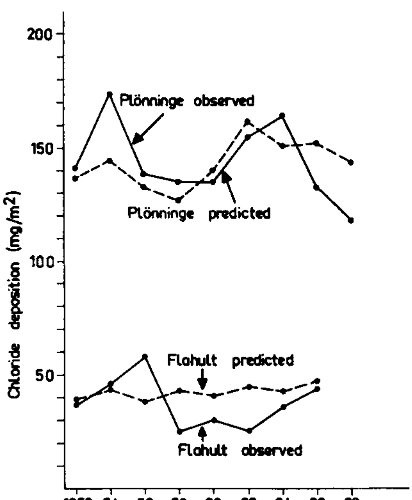

Fig. 5. Observed and predicted median values of monthly chloride deposition as a function of time. The prediction is based on the curvilinear relations of Fig. 3.

For sulfur (Fig. 4) there was a peak in the middle fifties and a larger one in the middle sixties, the fluctuations being in phase at the two locations. This behaviour is in agreement with that found by Eriksson (1970) for the entire Swedish network of stations, using the geometric mean rather than the median.

For chloride (Fig. 5), there was a peak in the middle fifties, although slightly out of phase at the two stations. In contrast with the major sulfur peak in the middle sixties, however, there was no rise at all in median chloride deposition at Flahult, and only a secondary peak at Plönninge. This lack of agreement in chloride variations at the two stations will present interpretative difficulties (see Section 7).

To see whether the patterns in Figs. 4–5 could be explained by precipitation variability alone, the following procedure was adopted. For each two-year period, the median monthly precipitation was determined, and the corresponding depositions were obtained from the curves in Figs. 2 and 3. The resulting values are plotted and joined by dashed lines in Figs. 4–5. The difference between the solid and the dashed lines in these figures is that part of the secular fluctuations caused by factors other than variations in the monthly total precipitation. The differences are substantial.

The analysis in this section confirms what is already known about secular fluctutations (Eriksson, 1970; Odén, 1968) and shows that precipitation variability cannot be invoked as an explanation.

5. A search for a relation between monthly deposition values and meteorological factors

Precipitation in the Plönninge-Flahult area occurs with many different synoptic patterns and air-flow trajectories. Some storms may be rich in sulfur or chloride while others may contribute little to the monthly loading. We therefore restricted our attention in the first instance to those months in which the deposition was "relatively" low, i.e., well below the

Table 1. *Percentage frequencies of surface synoptic patterns causing precipitation in the Flahult–Plönninge area of Sweden with associated relatively low sulfur and chloride monthly deposition amounts (1951–1969)*

The frequencies for the year 1963 are given for comparison

Weather type	Months with relatively low S (%)	Months with relatively low Cl (%)	All months (1963) (%)
N to NE winds	25	26	10
E winds	19	21	5
SE to S winds	20	32	38
Warm SSW to W winds (ahead of cold front)	13	4	22
Cold SSW to WSW winds (behind cold front)	10	11	9
W to NW winds	7	1	12
Light variable winds (mainly with cold low over Sweden)	5	6	3

values given by the curves in Figs. 2 and 3 (thus removing the effect of varying monthly precipitation). This methodology permitted examination of synoptic precipitation patterns that did *not* produce relatively high sulfur or chloride. To begin with high deposition months, on the other hand, would have led to interpretative difficulties because not all the precipitation was then necessarily rich in sulfur or chloride.

To make it more likely that the effects we were studying were of a synoptic-scale and not local character, we required that the deposition (of either sulfur or chloride) be well below normal (as given by Figs. 2 and 3) at both the Plönninge and Flahult stations. We also removed all months in which the total precipitation was less than 20 mm at both locations. The resulting subsets consisted of 18 and 24 months of low sulfur and low chloride, respectively. The associated precipitation amounts, averaged over the two stations, ranged from 24 mm (January 1964) to 120 mm (September 1957).

The next step was to develop a system for classifying the precipitation periods within the selected months, using the synoptic weather charts. Since the advent of meteorology as a science, the search for universal weather classifications has been a popular pastime, and we make no apology for adding to the list of proposals. After some trial and error, we developed the classification outlined in the left-hand column of Table 1. This seemed appropriate for Southern Sweden and for the present purposes, although we are not suggesting that it be adopted elsewhere where the rain-producing synoptic patterns or the source distributions for sulfur and chloride may be different.

We recognize that precipitation scavenging often encompasses a rather substantial fraction of the troposphere but there are two reasons why surface flows are useful predictors of deposition.

1. On many occasions the upper-air and surface trajectories are within the same class sectors.

2. Part of the deposition is due to washout within the surface boundary layer. A correlation must exist, therefore, between surface directions of flow and the deposition values.

The specific details of the procedure that led to the results given in Table 1 are as follows:

(*a*) The two subsets (18 and 24 months) were merged in advance so that the classifier (REM) had no clue as to whether a particular month was one with low sulfur or low chloride, thus removing one source of bias.

(*b*) The 12-hour precipitation totals for 0600–1800 GMT and 1800-0600 GMT (listed on the reverse side of the daily weather maps) were scanned. Whenever there was at least 1 mm

Table 2. *Percentage frequencies of surface synoptic patterns causing precipitation in the Flahult–Plönninge area of Sweden with associated relatively low sulfur and chloride monthly deposition amounts*

The frequencies for the years 1951–1969 are also given

Weather type	Months with relatively low S (%)	Months with relatively low Cl (%)	All months (1951–1969) (%)
N, NE, E and light variable winds	49	53	29
SE to S winds	20	32	25
Warm SSW to W winds	13	4	21
Cold SSW to NW winds	17	12	26

of precipitation at either Jönköping or Halmstad, the amount was recorded. The error introduced by using precipitation values at Jönköping and Halmstad instead of Flahult and Plönninge is believed to be small.

(*c*) For each precipitation period, the surface pressure pattern was classified according to the scheme listed in Table 1. In about 70% of the cases, the classification could be made with high confidence, e.g., when there was a stationary depression over the Baltic causing showers in southern Sweden. In another 10 to 20% of the cases, there was uncertainty about which of two adjacent classes should be selected, e.g., whether the rain had come with S or SSW winds. The remaining 10 to 20% of the cases, mainly associated with rapidly-moving depressions whose centres passed over southern Sweden, were very difficult to classify.

(*d*) For each month, the total precipitation in each class, averaged over the two stations, was summed, and percentages were obtained for each of all classes.

(*e*) The monthly percentages in each class were then averaged over the entire subset; this ensured that low-precipitation months would be given the same weight as those with high rainfall.

(*f*) The year 1963 was selected as a comparative control, yielding the percentages in the right-hand column of Table 1. Admittedly, this was a year in which sulfur deposition was higher than usual (Fig. 4), but we shall provide a more broadly-based comparison in Section 6.

Inspection of Table 1 reveals relatively large differences in the frequencies of precipitation weather patterns amongst the three subsets. For both low sulfur and low chloride months, the frequencies of N, NE and E winds are much higher than in the year 1963. The reverse is generally true for winds from the southsouthwest to northwest. Finally, there is a relatively large deficit (18%) of SE to S flows in low sulfur months as compared with 1963, but only a small deficiency (6%) in low chloride months.

These patterns are consistent with our genneral understanding of the regional sources of sulfur and chloride. It is well known, for example, that the only important chloride source is the sea: thus chloride values should be low in the Plönninge-Flahult area in months when there are few rain-bearing winds from the southwest to northwest. The sea is also a source for sulfur but in addition, anthropogenic sulfur originates regionally to the southwest, south and southeast of the sampling stations. Rain-bearing winds from the north through east, on the other hand, should be rather low in sulfur and chloride, as indeed is indicated in Table 1.

6. Extension of the weather classification concept to the entire period of record

Encouraged by the results summarized in Table 1, we decided to classify all precipitation events occurring between July 1951 and June 1969, inclusive. The same procedure was followed as in the preparation of Table 1 but only four airflow classes were used, namely,

(*a*) N, NE, E and light variable winds,
(*b*) SE to S winds,
(*c*) Warm SSW to W winds,
(*d*) Cold SSW to NW winds.

In the discussion of Table 1 in Section 5, we noted that 1963 was characterized be relatively high sulfur depositions and therefore was not a representative control. When the entire 18 years of records are used, the results are as shown in Table 2. Again for low sulfur months there is a large deficit of SE–S–SW–W–NW flows while for low chloride months, there is a substantial deficiency of SSW to NW cases.

Up to this point, the emphasis has been on those months with unusually low sulfur and chloride depositions. To see whether more general relations could be found between weather-classification frequencies and deposition values, we adopted a procedure similar to that used in the preparation of Figs. 2 and 3. Considering chloride first, and assuming that this constituent is associated mainly with SSW to NW flows, we subdivided the monthly frequencies of such winds into non-overlapping subsets of about 24 cases, each subset consisting of months with frequencies within designated class intervals. Medians were then calculated of both the weather-pattern frequencies and the associated depositions in each subset. The results are shown in Fig. 6.

Fig. 6 reveals that linear relations (sketched by hand) are appropriate and that extrapolation to the zero and 100% frequencies can reasonably be made. For a hypothetical subset of months in which precipitation never occurs with SSW to NW winds, median depositions of about 40 and 10 mg/m² are to be expected at Plönninge and Flahult, respectively:

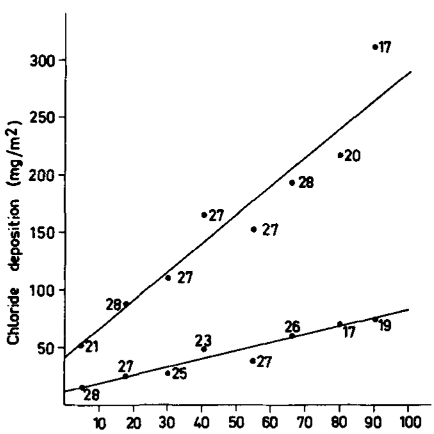

Fig. 6. Median values of monthly chloride deposition as a function of frequency of rain-bearing flows from SSW–NW. The numbers indicate the number of months within each subset.

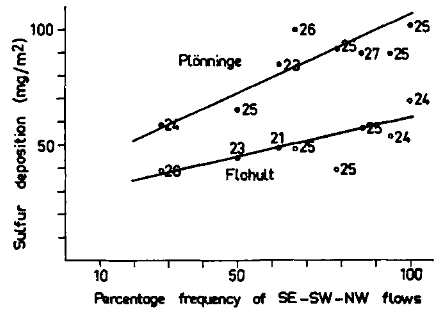

Fig. 7. Median values of monthly sulfur deposition as a function of frequency of rain-bearing flows from SE–SW–NW.

the larger value at Plönninge is probably due to the larger dry deposition at this coastal station, and the fact that rain-bearing flows from the south may contribute significanty to the chloride deposition at Plönninge but not at Flahult (see Fig. 1). Not such a clear linear relation could be established for sulfur. Several combinations of weather classes were tried but in all cases there was more scatter than was found for chloride. Fig. 7 shows the median sulfur deposition values for eight classes of frequencies of airflows from SE clockwise through NW. We believe that at least part of the scatter in Fig. 7 can be explained, and we introduce Table 3, which was derived in the following way. For each subset of airflow frequencies (for winds from the SE through NW) we determined the median date (year and month). Separately for Plönninge (columns 2 and 3) and Flahult (columns 4 and 5), we then counted the number of deposition values smaller than the subset median that occurred before the subset median date (columns 2 and 4) and after the subset median date (columns 3 and 5).

For chloride, the numbers in columns 2, 4 are about the same as in columns 3, 5, respectively, indicating that the weather classification has produced subset distributions that are independent of time. For sulfur, on the other hand, the subsets are biased, with significantly larger numbers of low values in earlier than in later years. We believe, in summary, that Table 3 and Figs. 6–7 indicate that, (*a*) chloride and sulfur de positions are both weather-dependent, and (*b*) there is an additional time-dependent component of sulfur deposition,

Table 3. *Analysis of time trends of sulfur and chloride depositions associated with airflows from the SE clockwise through NW*

Airflow median frequency	Plönninge: No. of observations with depositions smaller than the median deposition for the subset		Flahult: No. of observations with depositions smaller than the median deposition for the subset	
	Before median date	After median date	Before median date	After median date
Sulfur, %				
0	9	3	6	4
6	8	3	6	6
14	9	3	10	2
22	7	4	7	5
33	9	4	7	4
39	8	2	7	3
50	7	3	5	6
72	5	6	8	4
Total	62	28	56	34
Chloride, %				
0	6	6	8	4
6	6	6	5	7
14	6	7	7	5
22	4	7	4	7
33	6	7	6	5
39	6	4	6	4
50	4	6	5	6
72	7	6	6	7
Total	45	49	47	45

presumably due to an increase in regional anthropogenic emissions over the years (see Section 8).

7. Secular variations in median chloride deposition: A meteorological interpretation

For each consecutive 2-year period beginning July 1951, the median frequencies of precipitation-bearing SSW–NW flows have been determined. The lower curve in Fig. 8 gives the secular variations, and a comparison should be made with the solid curves in Fig. 9 (observed median deposition at the two stations: replotted from Fig. 5). Qualitatively, there is reasonable agreement between the Plönninge depositions and the median frequencies of SSW–NW flows, with peaks in the middle fifties and middle sixties. The variations at Flahult, however, do not correspond. This is perhaps surprising, in view of the linear relation found in Fig. 6. To test whether the disagreement was caused by uncertainty in the determination of the Flahult medians, the subsets were increased from 24 to 36 consecutive monthly values. Although the medians became more stable, their secular fluctuations still showed no correspondence with those of the median frequencies of SSW–NW flows, determined in this case over 3-yearly periods.

The extent of the disagreement is shown in another way in Fig. 9. The dashed lines have been constructed using a procedure rather similar to that employed in Figs. 4 and 5. Using the 2-year median frequencies of SSW–NW flows (Fig. 8), the subset median depositions were obtained from the straight lines in Fig. 6. For Plönninge, the predictions are rather good but for Flahult, little of the variation is explained.

We conclude that the weather classification scheme was not entirely appropriate for chloride at Flahult, despite the straight-line relation of Fig. 6. Inspection of Fig. 1 suggests a reason for this. With zero or anticyclonic curvature of the isobars, southsouthwest winds at Flahult have not had a recent trajectory over salt water,[1] as is the case at Plönninge. Because this synoptic pattern (with associated precipitation) is not uncommon in southern Sweden, the SSW–NW weather class in retrospect may have encompassed too large a sector to be a useful predictor of chloride at the inland station.

8. Secular variations in median sulfur deposition: An interpretation based on changes in weather frequencies and emissions

The upper curve in Fig. 8 shows the variations in the 2-year median frequencies of precipitation-bearing SE–S–SW–W–NW flows. This should be compared with the median sulfur depositions joined by solid lines in Figs. 10–11. Qualitatively, the agreement is excellent, both curves showing peaks in the middle fifties and larger peaks in the middle sixties.

The method used in Section 7, Fig. 9 for chloride secular variations cannot be applied

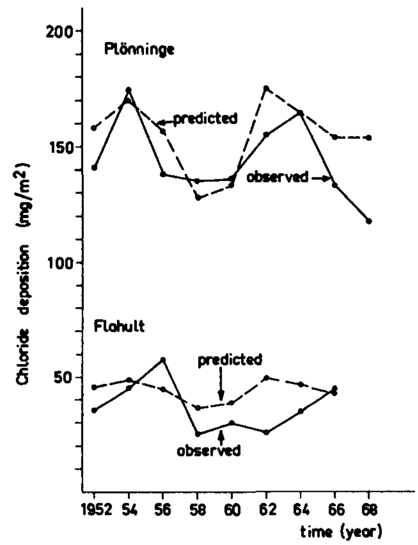

Fig. 9. Observed and predicted median values of monthly chloride deposition as a function of time. The prediction is based on the linear relations of Fig. 6.

in the case of sulfur, because of the possible existence of a time trend in regional anthropogenic SO_2 emissions. Mean values for the increase in source strength might be estimated (see below). Since the relative strengths of the anthropogenic and the natural sulfur sources are not known, however, there is no possibility of inferring *a priori* the expected trend in the "effective" source strength.

An alternate approach is to seek a statistical relation between median 2-yearly deposition (dependent variable) and two independent variables, time and frequency of occurrence of rain-bearing winds in the SE clockwise through NW sector.

The following model was adopted:

$$\ln d_k = \alpha + \beta(p_k - \bar{p}) + \gamma(t_k - \bar{t}) + \varepsilon_k$$

or equivalently,

$$d_k = \alpha' \exp [\beta(p_k - \bar{p})] \exp [\gamma(t_k - \bar{t})] \varepsilon'_k$$

where d_k is the sulfur deposition (median of 24 monthly values) centred on time k,

α (or α') is a constant,

p is the frequency of occurence (in %) of rain-bearing winds in the SE–SW–NW sector,

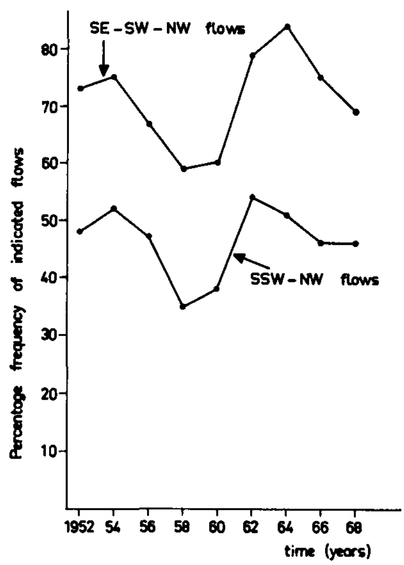

Fig. 8. Frequency of rain-bearing flows from SE–SW–NW and from SSW–NW as a function of time.

[1] The surface waters of the Baltic have a low salinity and do not contribute significantly to atmospheric chlorides.

Table 4. *Results of the regression analysis (see text)*

	Flahult	Plönninge
α	3.91	4.36
β	0.027	0.040
95 % confidence range for β	0.016 to 0.038	0.010 to 0.070
γ	0.029	0.023
95 % confidence range for γ	0.009 to 0.049	−0.019 to +0.065
ε_1	−0.06	0.04
ε_2	−0.03	0.06
ε_3	0.01	0.15
ε_4	0.04	0.22
ε_5	0.03	−0.58
ε_6	−0.01	−0.13
ε_7	0.13	−0.15
ε_8	−0.16	0.05
ε_9	—	0.28
$1/n \sum_1^n \varepsilon_k^2$	0.006	0.059

t is the time (in years),
ε (or ε') is the residual,
β and γ are coefficients describing the dependence of d on p and t, respectively.

The bar represents an arithmetic mean value over the entire set of medians.

Table 4 shows the results, including the 95 % confidence ranges for the coefficients β and γ. At the outset, we should emphasize that the analysis is based on only 9 median values at Plönninge and 8 at Flahult. However, the "best estimates" of the coefficients agree rather well at the two stations, lending confidence in the analysis, and the residuals are small, particularly at Flahult. Further, the "best estimates" of β and γ are positive quantities as would be expected on physical grounds, with 95 % confidence ranges that remain positive with the exception of that for γ at Plönninge.

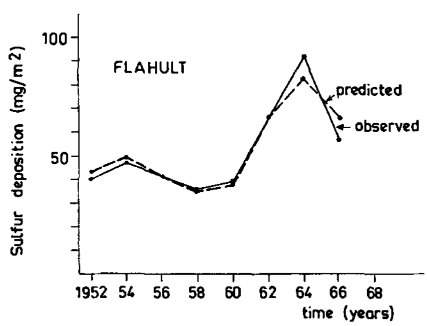

Fig. 10. Observed and predicted median values of monthly sulfur deposition at Flahult as a function of time. The prediction is based on the regression analysis (see text).

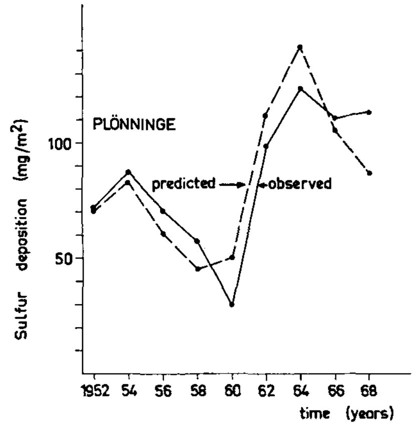

Fig. 11. Same as Fig. 10 for Plönninge.

In Figs. 10 and 11, dashed lines join the median depositions predicted by the regression equation. The fit with the "observed" curve is good. Because the predictions are based on statistical rather than physical principles, however, we do not claim to have "explained" the secular variations in sulfur depositions. Assuming, however, that the γ-values are real with a mean value in or near the interval 0.02 to 0.03, corresponding to an annual increase of 2–3 %, we can draw some conclusions about the relative importance of anthropogenic and natural sources for the sulfur depositions at these two stations.

The total SO_2-emissions from fossil fuel combustion and industrial processes in Sweden have increased with a mean annual rate of somewhat more than 3 % over the years 1951–1969. An exact value for other parts of northern Europe is not known to us but we believe that the average increase has been less than 3 %, rather than more.

If it can be assumed that the anthropogenic sulfur sources affecting the Flahult-Plönninge area have shown a rate of increase of about 3 % and that the strength of natural sources has been more or less constant, we may conclude that a major part—probably more than 2/3 by the middle of the period—of the deposited sulfur at these two stations has been of anthropogenic origin. If, on the other hand, the anthropogenic part had been only a small fraction of the total sulfur, the observed annual increase would have been considerably smaller than 2%. There is of course a possibility that local sources have had a major influence on the measured sulfur deposition and that the observed trends merely reflect the trends in those nearby sources. The significant correlations we have found between deposition values and synoptic weather patterns do, however, indicate that the sulfur transport has a regional character. This reasoning is supported by the fact that the values of the coefficients are similar at the two stations.

Conclusion

Long-term trend in regional pollution may result from either changes in emissions or changes in the atmospheric general circulation or both.

There is a large network of precipitation chemistry stations in northern Europe with data extending back for nearly 20 years. In the present pilot study, we have presented a method for examining the weather dependence of these monthly samples, based on the direction of the surface air flow during precipitation periods. The methods have been used to study sulfur and chloride depositions at two stations in southern Sweden.

The main results may be summarized as follows:

(*a*) There are curvilinear relations between deposition and precipitation amounts (Figs. 2 and 3).

(*b*) Variations in precipitation amounts cannot be an important factor for explaining the observed secular variations in deposition (Figs. 4 and 5).

(*c*) There is a definite correlation between chloride deposition and frequency of rain-bearing flows in the SSW–NW-sector and between sulfur deposition and rain-bearing flows in the SE–SW–NW-sector (Figs. 6 and 7).

(*d*) Secular variations in frequencies of these flows agree rather well with variations in deposition and may be invoked as an explanation for at least part of these variations.

(*e*) There are strong indications of a time trend in the sulfur deposition values. A regression analysis yielded a best estimate for the annual increase of 2–3%.

Finally, some suggestions for additional research should be mentioned. In the first place, a multivariate analysis of all the monthly values, rather than subset medians, might be useful. Secondly, the methods should be applied to other chemical constituents and to data from other stations. Thirdly, the approach employed in this paper should be complemented by studies of deposition measured in daily precipitation samples (or even hourly samples, if possible).

A few individual case studies from a regional network of stations during well-defined synoptic conditions would undoubtedly be rewarding.

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APPENDIX

Derivation of equations used for the regression analysis

Since the method used for the regression analysis may not be considered as standard, the procedure will be described.

The model mentioned in the text was the following

$$\ln d_k \equiv y_k = \alpha + \beta(p_k - \bar{p}) + \gamma(t_k - \bar{t}) + \varepsilon_k$$

The coefficients α, β and γ are determined by minimizing

$$Q = \sum_1^n [y_k - \alpha - \beta(p_k - \bar{p}) - \gamma(t_k - \bar{t})]^2$$

With the following notation

$$l_{y,p} = \sum_1^n (y_k - \bar{y})(p_k - \bar{p})$$

$$l_{y,t} = \sum_1^n (y_k - \bar{y})(t_k - \bar{t})$$

$$l_{p,t} = \sum_1^n (p_k - \bar{p})(t_k - \bar{t})$$

$$l_{p,p} = \sum_1^n (p_k - \bar{p})^2$$

$$l_{t,t} = \sum_1^n (t_k - \bar{t})^2$$

we get

$$\frac{\partial Q}{\partial \alpha} = -2n(\bar{y} - \alpha)$$

$$\frac{\partial Q}{\partial \beta} = -2n(l_{y,p} - \beta l_{p,p} - \gamma l_{t,t})$$

$$\frac{\partial Q}{\partial \gamma} = -2n(l_{y,t} - \beta l_{p,t} - \gamma l_{t,t})$$

and the condition

$$\frac{\partial Q}{\partial \alpha} = \frac{\partial Q}{\partial \beta} = \frac{\partial Q}{\partial \gamma} = 0$$

gives

$$\alpha_m = \bar{y}$$

$$\beta_m = \frac{l_{y,p}\, l_{t,t} - l_{y,t}\, l_{p,t}}{l_{p,p}\, l_{t,t} - l_{p,t}^2}$$

$$\gamma_m = \frac{l_{y,t}\, l_{p,p} - l_{y,p}\, l_{p,t}}{l_{p,p}\, l_{t,t} - l_{p,t}^2}$$

The confidence intervals can be estimated by making use of the facts that

$$(\beta_m - \beta)\sqrt{(n-3)\frac{l_{p,p}\, l_{t,t} - l_{p,t}^2}{l_{p,p}\sum_1^n \varepsilon_m^2}}$$

$$(\gamma_m - \gamma)\sqrt{(n-3)\frac{l_{p,p}\, l_{t,t} - l_{p,t}^2}{l_{t,t}\sum_1^n \varepsilon_m^2}}$$

are distributed according to a t-distribution with $n-3$ d.f.

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О МЕТЕОРОЛОГИЧЕСКОЙ ИНТЕРПРЕ ТАЦИИ ХИМИЧЕСКОГО СОСТАВА МЕСЯЧНЫХ ПРОБ ОСАДКОВ

Описана методика изучения влияния синоптических шаблонов погоды на химический состав месячных проб осадков. Для иллюстрации выбраны данные наблюдений с 1951 по 1969 гг. по месячным осаждениям серы и хлоридов на двух станциях в южной Швеции — Пленнинге (побережье) и Флахулт (внутри страны). Месячные величины были сгруппированы различным образом в группы с числом членов около 24 в каждой, и в каждой группе как индекс центральной тенденции использовалось медианное значение. Первоначальное группирование по количеству месячных осадков дало криволинейные соотношения

между осаждением и осадками. Другое группирование по двухлинейным временным периодам выявило заметное увеличение в отложениях серы на обоих станциях в начале 1960-х гг. С другой стороны концентрация хлоридов была наибольшей в середине 1950-х гг., и вековые вариации в Пленнинге не были в фазе с вариациями во Флахулте. Вариации в отложениях не могут быть объяснены вариациями количества осадков. Для изучения влияния метеорологических факторов была разработана классификация погоды, основанная на направлении геострофического ветра у поверхности над южной Швецией в течение периодов осадков. Для достаточно широких секторов и для медианных значений большого числа данных это оказалось полезным предиктором осаждения, будучи индексом траекторий набегающих частиц. Все ситуации с осадками в течение рассматриваемых 18 лет были, таким образом, расклассифицированны и были установлены линейные соотношения между медианными количествами осаждений и медианными месячными частотами потоков с осадками с направлений SE–SW–NW (сера) и SSW–NW (хлориды). Для хлоридов большая часть вековых вариаций в Пленнинге может быть объяснена с помощью такого индекса. Метод был не так успешен во Флахулте, вероятно, благодаря тому, что наветреная дуга была слишком широка для этой станции: главным источником хлоридов является море и ветры с SSW обычно не имели недавних надводных траекторий перед тем, как придти во Флахулт. Для серы вековые вариации осадконесущих потоков с направлений SSW–NW были очень близки по фазе с медианными значениями осаждений серы в 1951–1969 гг. Имеется, однако, указание на остаточную тенденцию к повышению в отложениях серы. Линейный регрессионный анализ, включающий в качестве переменных частоту типов погоды и время, дал в качестве лучшей оценки этой тенденции повышение от 2 до 3% в год. Эта цифра не противоречит оценкам роста в выбросах серы в результате деятельности человека.