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Interelement and multi-station concentration evidence for large scale aerosol sulfur transport across Sweden

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ABSTRACT

The concentrations of sulfur and several more elements were measured in a network of six sites in southern Sweden. High time resolution samples were taken using a continuous filter sampler and analysed by particle induced X-ray emission (PIXE). Simultaneous increases in the sulfur concentrations were seen along the network due to the inflow of polluted air masses. High sulfur concentrations generally occurred during south-westerly to easterly air flow. Some of the episodes, distinguished by their shorter duration and their elevated vanadium and nickel concentrations, are suggested to be of local origin.

1. Introduction

Interest in the possible long range transport of air pollution over distances greater than 1000 km has focused on sulfur in the form of gaseous SO₂, sulfuric acid and sulfates (Sweden's case study 1971, Rodhe et al., 1972; Brosset 1973). In the OECD study on long range transport of air pollutants (OECD, 1977), an estimate of a European budget for the total deposition of sulfur in 1974 has been made. The results show that large amounts of sulfur pollutants are transported over long distances under certain meteorological conditions. Furthermore, countries like Finland, Norway and Sweden receive considerably larger amounts of air pollution from abroad than are emitted within these countries (Ottar, 1977).

A comparison of chemical and meteorological data ideally should be made using aerosol sulfur concentration measurements with a time resolution comparable to the time variations in air flow pathways. The frequently employed strategy of sampling suspended particulate matter for 24-h periods often averages concentrations over different meteorological conditions of possible importance to pollution transport. Consequently, a time

resolution of less than 24 h for aerosol sampling may be a desirable improvement. The present investigation was undertaken as a field test of such a strategy.

It is important to distinguish between contributions from nearby pollution sources and the larger scale transport of pollutants from more distant sources. A short time resolution, such as employed in this study, may permit the identification of periods when concentrations are influenced by plumes from local air pollution emissions. A complete investigation of air pollution sulfur transport, of course, should include measurements of both gaseous and particulate forms of sulfur. In this investigation, however, only the aerosol was sampled for elemental analysis.

2. Experimental

Six sampling sites in southern Sweden were chosen for this investigation. These sites, with locations shown on the map (Fig. 1), are among those chosen for the precipitation sampling network operated by the International Meteorological

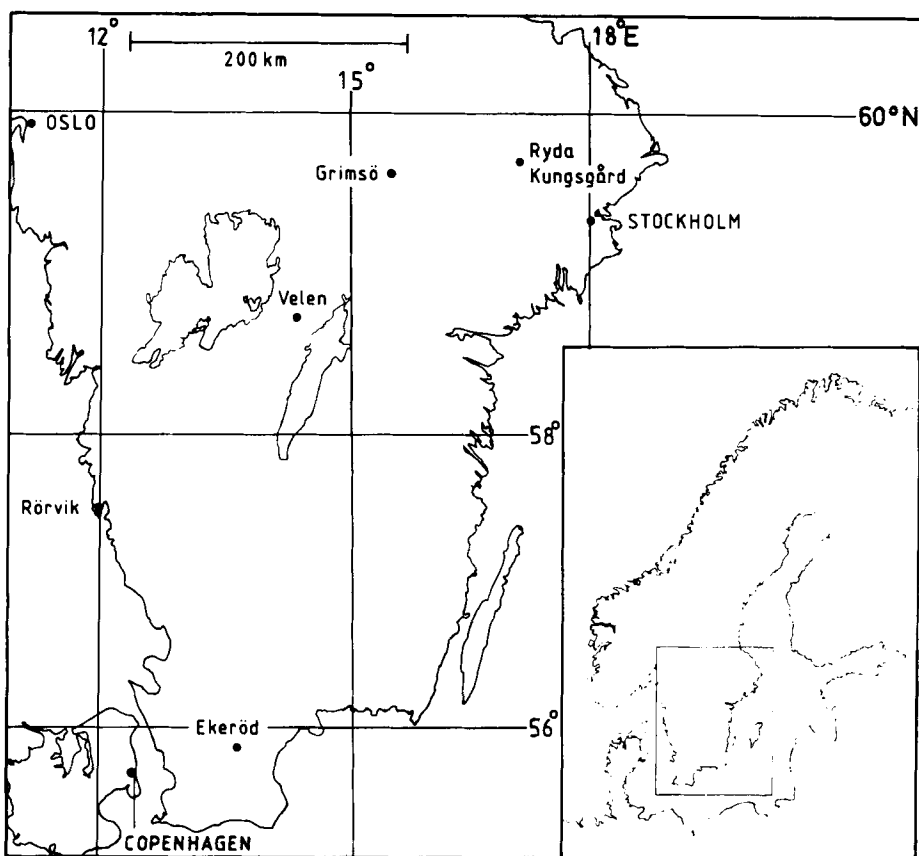


Fig. 1. Map showing six aerosol sampling locations in Sweden at Stockholm, Ryda Kungsgård, Grimsö, Velen, Rörvik and Ekeröd.

Institute in Stockholm (IMI-network) and are fully described elsewhere (Granat et al., 1977).

The sampling was generally carried out several meters above ground, at locations with negligible obstructions in the neighborhood. The samplers used were of a special continuous time sequence design (Nelson et al., 1976). These "streaker" samplers consist of an orifice which moves with a constant speed along a Nuclepore filter strip. Air is drawn through the orifice at a rate of 0.8 l/min. Hereby a 5-mm-wide streak of aerosol deposit is left on the filter. Consecutive 2-mm spots of the streak are analysed, resulting in a time resolution of approximately 2.4 h of sampling time. The uncertainty in the absolute time determinations of single spots are less than ± 1 spot = 2.4 h.

Particle induced X-ray emission, PIXE (Johansson et al., 1975; Johansson & Johansson, 1976), has been used for the multi-elemental

analysis of the streaker filter samples for sulfur and other elements ranging in atomic number from silicon to lead. In this investigation the elements Si, Cl, K, Ca and Fe in addition to sulfur, were usually seen above their detection limits in the samples. The analysis was performed by placing a filter strip, representing 8 days of sampling time on a single strip, into a vacuum chamber of the Van de Graaff accelerator at Florida State University and analysing successive steps by detecting X-rays generated during bombardment by 5 MeV protons. The X-ray spectrum from each analysis was recorded electronically during the approximately 1 min of proton bombardment time per step and later resolved into elemental constituents by computer procedures (Kaufmann et al., 1977).

The quality of the PIXE analysis is ensured by analysing standards during each accelerator run. Aerosol samples have been analysed repeatedly

revealing no changes in the composition of the elements reported here. However, recent data (Hansen et al., 1980) points out that in pre-concentrated samples losses of volatile sulfur species and losses induced by the proton irradiation can occur. These effects seem to be most serious for some sulfites. Atmospheric aerosol samples collected at a remote location on Nuclepore filters and analysed by PIXE have been compared with samples collected simultaneously on Acropore filters and analysed by the Thorin method at the Department of Meteorology, University of Stockholm. The results show an agreement between elemental sulfur from the PIXE-analysis and sulfate analysed wet chemically within $\pm 10\%$ in 75% of the samples (within $\pm 5\%$ in 50% of the samples). Since the X-rays emitted from sulfur atoms are relatively soft, self-absorption problems have to be considered. In this study the maximum aerosol deposit on the filter was 0.1 mg/cm^2 causing a negligible self-absorption of sulfur X-rays (Johansson et al., 1975). Large aerosol particles can also cause self-absorption losses, e.g. for a $5\text{-}\mu\text{m}$ diameter particle the self-absorption would be approximately 5%. The pollution-derived sulfur-containing particles are found in the accumulation mode with a mass median diameter of $0.2\text{--}0.4 \mu\text{m}$ (Whitby, 1978). This implies that except for sea spray-derived sulfur-containing particles (larger than $2 \mu\text{m}$) no absorption effects can be expected. The detection limit for sulfur was set primarily by the thickness and composition of the filter material and averaged about 150 ng/m^3 . Since concentrations observed in this study ranged from several hundred to several thousand ng/m^3 , sulfur was detected in all samples. However, certain other elements of interest, including vanadium and nickel, were only occasionally found above their detection limits.

The high sensitivity of the PIXE method in combination with the small sample requirements makes this method useful for the analyses of many types of samples. Since only a small sample ($\sim 10 \mu\text{g}$) needs to be collected, light weight and portable sampling devices may be employed, requiring small vacuum pumps with modest electrical power requirements. Depending on the information needed, different combinations of time, particle size and site-to-site distance resolution can be used. In a standard type 12–24 h aerosol sample (total filter or cascade impactor), 10–20 elements heavier than

phosphorus can be resolved in a 1–3 min routine analysis. On the sacrifice of a few elements and size distribution information, a time resolution of a few hours can be achieved. A streaker sampler can operate in rural or remote air with time resolutions from 2 to several hours. Since each streaker filter will contain samples collected over a week or more, its infrequent changing makes this sampler very easy and inexpensive to operate. The streaker sampler with a suitable time resolution, used in conjunction with PIXE analysis, is therefore ideal in many respects for use in air pollution sampling networks.

3. Results

Two sampling periods, each of 8 days' duration, in the spring of 1978, were selected for this study. The meteorological conditions included airflow from both northerly and southerly directions and therefore provided an opportunity to compare the composition of air passing over strong pollution source regions with that from less polluted areas. Fig. 2 shows 96 h back trajectories for air masses at the 850 mbar level, calculated by the Norwegian Meteorological Institute. Surface weather maps from the Swedish Meteorological and Hydrological Institute are shown in Fig. 3. The significance of the weather data is discussed further below in connection with the sulfur concentration data. In Fig. 4 the measured concentrations of aerosol sulfur are shown on a linear scale as a function of time of sampling. In all cases the concentrations varied markedly with time over a total range of up to a factor of 10, with large variations taking place frequently over a few hours. As the following discussion will make clear, some of the high sulfur concentration episodes may be due to local air pollution passing over the sampling sites, whereas other episodes appear to be large scale effects apparently due to sulfur transported over long distances.

One indication of the presence of a local sulfur plume (resulting mainly from the combustion of fuel oil) can be found by examining relationships between sulfur and other trace elements emitted from the same type of sources. Fuel oil often contains vanadium and nickel. The concentrations vary somewhat depending on the origin of the oil. The sulfur emissions are initially mainly in the form

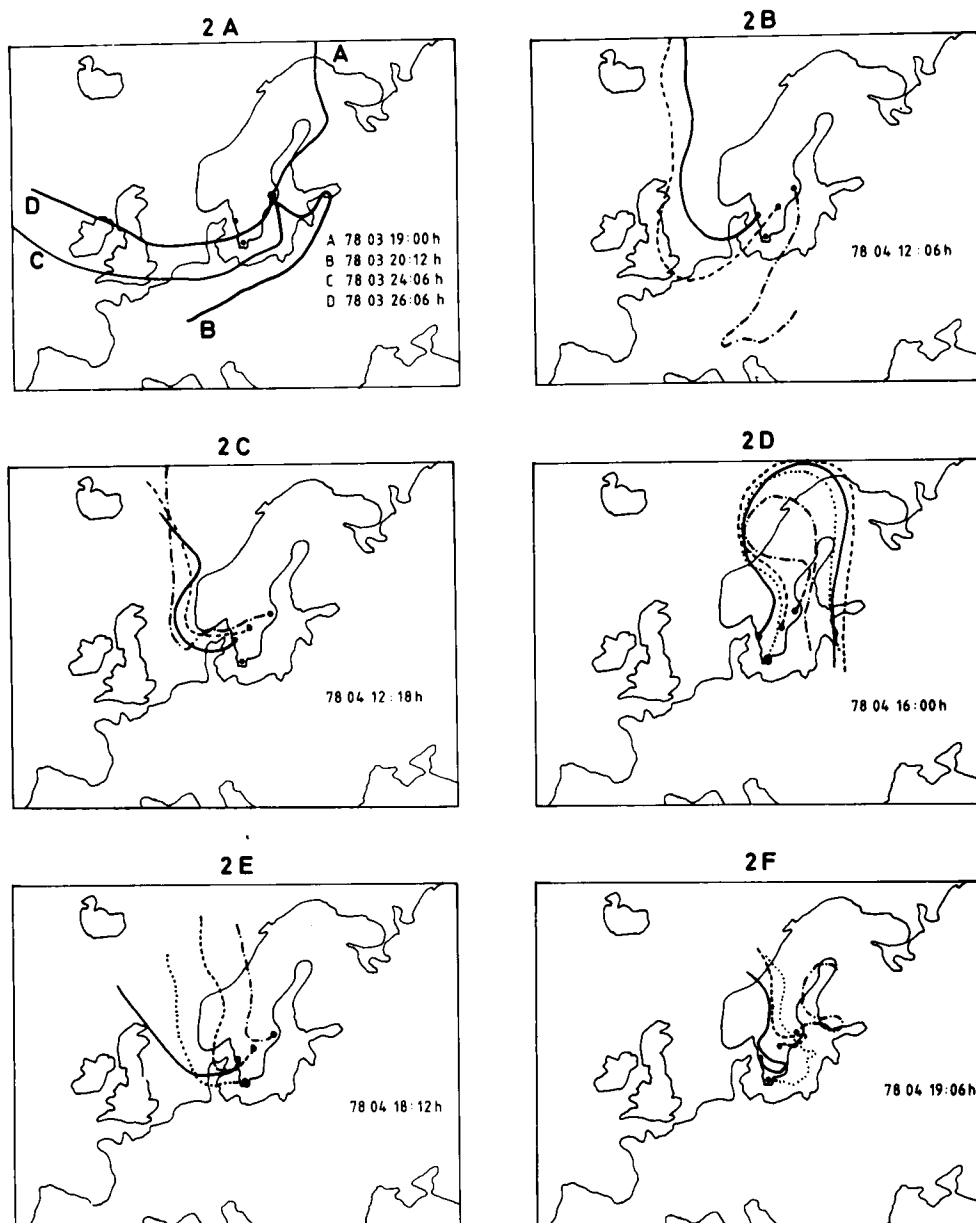


Fig. 2. A-I. Selected (representative) 96-h air mass trajectories at the 850 mbar level. The numbers indicate year, month, day and hour.

of sulfur dioxide gas which is gradually converted to sulfates at a rate depending, e.g. on the pollution level, and typically in the range of 0.1 to 10% per hour (Bouland et al., 1978; Calvert et al., 1978; Harrison et al., 1975). Vanadium and nickel are

already at the point of emission in particulate form. Unpublished data from a study undertaken by Lannefors and Hansson in the middle of Sweden, show that sulfur, vanadium and nickel have almost identical particle size distributions with almost all

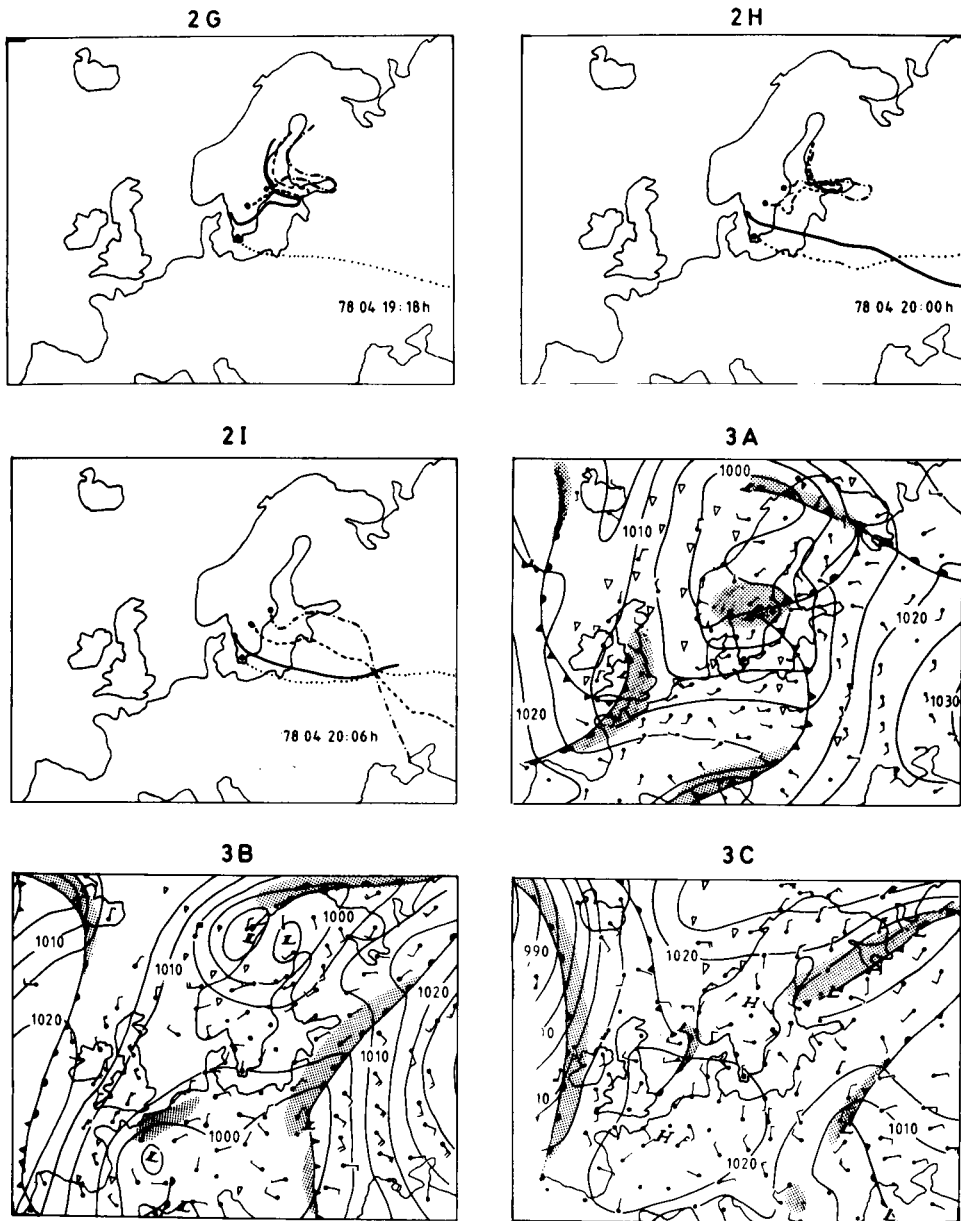


Fig. 3. A-C. Surface weather maps at 0600Z on April 12, 14 and 19, 1978.

the concentration in the accumulation mode. These results are in agreement with those of Charlson et al. (1978) stating coexistence of vanadium, nickel and sulfates on particles in the accumulation mode. Evidently these elements exist on particles having

the same size distribution and maybe also on the same particles. This implies that the sulfate deposition velocity should not differ very much from that of vanadium and nickel. However, since sulfur dioxide is gradually converted to sulfate

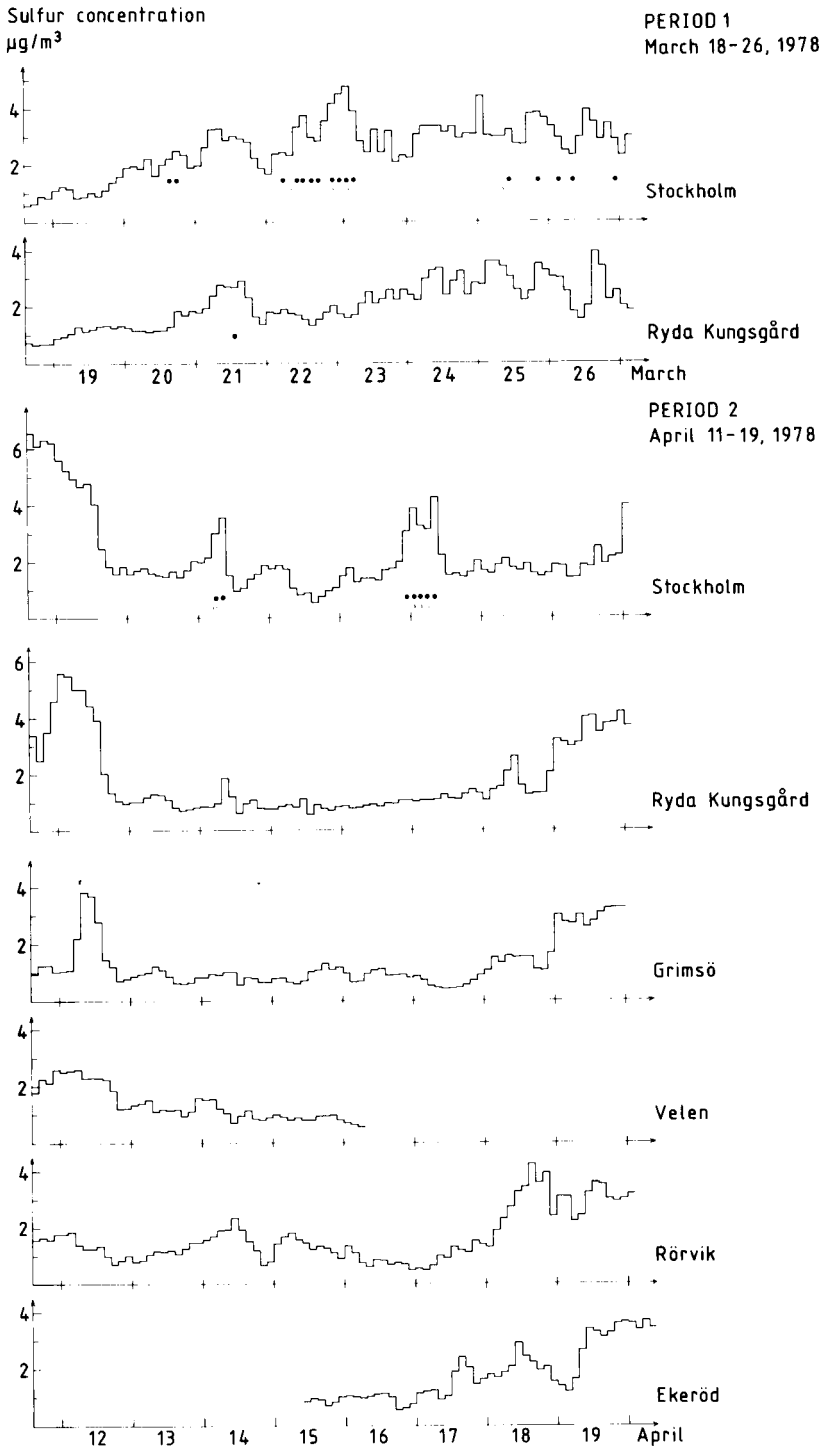


Fig. 4. Time variations of aerosol sulfur concentrations measured every 2.4 h at two sampling sites, March 18–26 and at six sampling sites, April 11–19, 1978. Periods of high V ($>100 \text{ ng}/\text{m}^3$) and Ni concentrations ($>60 \text{ ng}/\text{m}^3$) are indicated by dots (●) for V and circles (○) for Ni.

during the atmospheric transport, the ratio of sulfur to vanadium (or nickel) should increase with the transport distance.

Another indication of influences from local sources is the existence of nonsimilar concentration patterns at different sampling locations.

The Stockholm site and also the nearby Ryda Kungsgård site exhibited short-term sulfur concentration maxima during which significantly increased concentrations of nickel and vanadium were observed. At Stockholm, three pronounced episodes, March 22–23, April 13–14, and April 16–17 1978, were seen during which a correlation of sulfur with vanadium and nickel was found. One of these episodes is illustrated in Fig. 5. Sulfur concentrations reached their highest values during the night and early morning of the April 16–17 episode, when vanadium and nickel also were found substantially above their detection limits. From these results, and by examination of the time

variations at the Stockholm site, it appears that a substantial part of the total observed sulfur concentration during these episodes may be attributed to local plume sources.

Precipitation occurred during several of the sampling days and mostly during March. However, during the 12-h periods when precipitation was recorded, only minor amounts fell (i.e. less than 5 mm and usually also less than 1 mm in 12 h); probably causing only small effects on single elemental concentrations by aerosol particle scavenging. The conclusions made in this study are therefore probably not biased because of effects caused by precipitation.

Because of the frequent use of 24-h sampling routines, it is of interest to calculate from our results the 24-h average sulfur concentration seen on each of the sampling days. These are shown in Table 1 for the six sampling locations. The lowest average sulfur is less than 600 ng/m³ (equivalent to less than 1800 ng/m³ sulfate) and the highest is over 3000 ng/m³ (equivalent to over 9000 ng/m³ sulfate). Individual 2.4 h sulfur concentrations, however, reach as high as 6000 ng/m³ and as low as 400 ng/m³. Therefore, by smoothing over short time fluctuations, the 24-h averages exhibit less variability than is observed over shorter intervals, and episodes when local plumes contributed to the measured concentration may not be recognized.

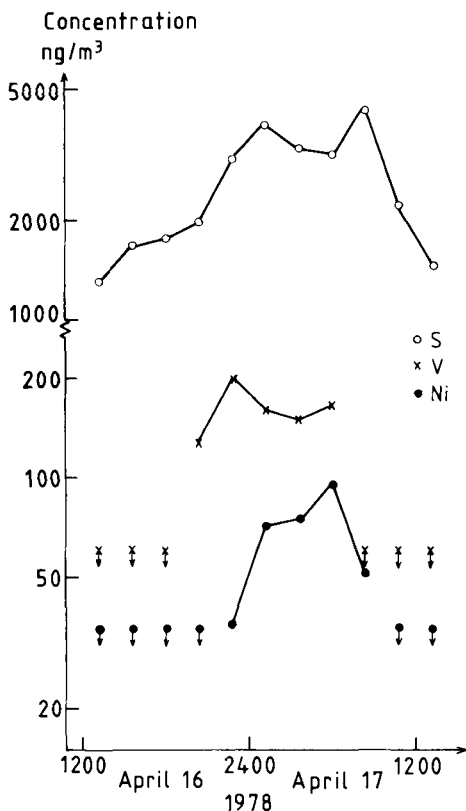


Fig. 5. Concentrations of sulfur, vanadium, and nickel observed at the Stockholm site on April 16–17, 1978. Detection limits are denoted by an arrow.

4. Discussion

By comparing the air mass trajectories an attempt can be made to interpret the observed aerosol sulfur concentrations in terms of atmospheric transport from source regions. In Fig. 4 a striking resemblance is seen in many of the features of the time variability patterns at the different sampling stations in both the March and April periods. Except for the vanadium-related sulfur maxima seen in Stockholm (and also less distinctly at Ryda Kungsgård), the different sites show similarities. In the March 18–26 period at Stockholm and Ryda Kungsgård, concentrations are initially low and later relatively high. According to the air mass trajectories a generally north to northeasterly air flow persisted until noon March 20. A representative trajectory for this period is shown in Fig. 2A. On March 20 and 21 the air masses originated in the northern part of the European Continent and the western part of Russia

Table 1. 24-h mean sulfur concentrations, ng/m³*

Date, March 1978								
Site	19	20	21	22	23	24	25	26
Stockholm	1050	2080	2720	2970	3180	3110	3350	3080
Ryda Kungsgård	1170	1360	2240	1700	2140	2790	3050	2610
Date, April 1978								
Site	12	13	14	15	16	17	18	19
Stockholm	3690	1630	1890	1120	1690	2470	1700	1890
Ryda Kungsgård	3490	986	988	808	896	1160	1613	3560
Grimsö	1870	849	811	912	874	588	1390	2970
Velen	2110	1260	1070	881				
Rörvik	1240	1150	1560	1370	796	1010	2910	3020
Ekeröd				869†	914	1490	2060	2730

* Arithmetic means of 10 observations per 24 h. Sulfate equivalent = 3 × sulfur concentration.

† Based on only six observations

(see Fig. 2A). Higher sulfur concentrations (not related to vanadium and nickel) occurred during these days. Late March 21 the air flow again became north to northeasterly and the sulfur concentrations decreased. A local episode can be discerned in Stockholm on March 22–23. On March 23 the air flow changed to a south to southwesterly direction passing in over the British Isles and the northern part of the European continent (see Fig. 2A). The same flow persists throughout the first sampling period with only minor direction changes in the trajectories. Concentrations of sulfur were generally high but variable. The variations which can be seen at both locations can be accounted for by minor changes in the track of the air masses, sometimes passing in over the northern part of the European continent, sometimes passing over the North Sea (see Fig. 2A). Influences from local sources as well as precipitation scavenging can also help to explain these variations. The results above suggest that southerly flow is associated with higher sulfur concentrations (not related to vanadium and nickel) on a regional scale.

In the April 11–19 sampling period, observations were made at all six sites except for some electrical malfunctions during the first 3 days of sampling in Ekeröd and the last 3 days in Velen. As can be seen from a surface weather map (Fig. 3A) the weather situation on April 12 was dominated

by a circulation around a low pressure center in the middle of Sweden. This created a general inflow of air masses from the Norwegian Sea at the Rörvik sampling site. At the Stockholm, Ryda Kungsgård, Grimsö and Velen sites air masses that had passed over the European continent came in from south to the southwest (see Fig. 2B). As a result increased sulfur levels were seen at the latter sites (especially in Stockholm and Ryda Kungsgård), while the sulfur concentration at Rörvik remained low (see Fig. 4). Late April 12 the air flow changed somewhat not passing over the European continent or the British Isles (see Fig. 2C). This air flow remained until April 18 except for a period on April 15 and 16. During April 15 a flow around a low pressure center situated in northern Scandinavia developed, bringing up old continental air masses to the sampling network (see Fig. 2D). However, no effects can be seen on the sulfur concentrations. During the period April 13 to 18 (including April 15 and 16) the sulfur levels were low except for the two local episodes seen in Stockholm on April 13–14 and April 16–17. The weather maps for April 14 and 17, shown in Fig. 3B and 3C indicate very light winds and clear skies in the Stockholm area, thus reducing mixing and increasing the stability. These conditions are favourable for trapping local emissions, which can be seen as increased sulfur concentrations (related to V and Ni) during the night and morning of April 13–14

and April 16–17. When the first local (V-related) Stockholm episode is broken up, increased sulfur concentrations can be traced at the Ryda Kungsgård site.

On April 18 a complicated flow pattern started to develop. This included first a weak flow from northwest to west (see Fig. 2E) and then during April 19 an even weaker flow mainly from the north but taking different nonstraight paths to the sampling sites (see Fig. 2F). High sulfur concentrations were seen in Rörvik and Ekeröd and could also be traced at Grimsö and Ryda Kungsgård on April 18. Even higher sulfur concentrations (see Fig. 4) were found all over the network on April 19. The weak flow in combination with passages over source areas in Denmark and southern Sweden are possible explanations for those high sulfur concentrations. The accuracy of the calculated air mass trajectories could also be questioned during a complicated meteorological situation.

However, late April 19 and April 20 the situation straightened out and the flow was gradually altering to an easterly flow (see Fig. 2G, 2H and 2I), and the sulfur concentration level became high all over the network (see Fig. 4).

5. Conclusions

This comparison of sulfur concentrations obtained at simultaneously operated sampling sites suggests that large scale features seen in the time variation of the sulfur concentration are the result of long-range transport into Sweden of polluted air masses from a generally southwest to easterly

direction. Superimposed upon this are local emission effects (seen in Stockholm and Ryda Kungsgård), showing vanadium and nickel associations with sulfur, which may be attributed to sources in the Stockholm area. This study illustrates the advantage of combining a network of sampling sites with comparably high time resolution samplers (0.1 day). Good time resolution and multi-element analysis are needed in order to discern local episodes of short duration. Such a time resolution is also needed to study the flow patterns of the air masses at nearby stations. For long-range transport studies with the sampling sites located far apart, with no local sources, a time resolution of 12–24 h appears to be sufficient. Cascade impactors can thus be used, permitting a size classification of the aerosol (Johansson et al., 1976; Lannefors et al., 1977). In combination with multi-element analysis such as PIXE analysis, important information on possible pollution and natural sources can be obtained.

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КРУПНОМАСШТАБНЫЙ ПЕРЕНОС СЕРНЫХ АЭРОЗОЛЕЙ ЧЕРЕЗ ШВЕЦИЮ ПО ДАННЫМ ИЗМЕРЕНИЙ КОНЦЕНТРАЦИЙ РЯДА ЭЛЕМЕНТОВ НА СЕТИ СТАНЦИЙ

На сети из шести станций в Южной Швеции измерялись концентрации серы и нескольких других элементов. Пробы с высоким разрешением по времени брались с использованием непрерывного фильтрового заборника и анализировались с помощью рентгеновской эмиссии, возбуждаемой частицами. Последовательные увеличения в кон-

центрации серы наблюдались на сети станций при притоке загрязненных масс воздуха. Высокие концентрации серы обычно встречались при ветрах с юго-запада до востока. Локальные выбросы серы различались их более короткой длительностью и связью с повышенными концентрациями ванадия и никеля.