Pollution of the Arctic Troposphere: Northeast Greenland 1990 - 1996

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Data sheet

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Summary

Measurements of atmospheric pollution have taken place at Station Nord in Northeast Greenland since 1990. Weekly samples have been collected for analysis of sulphur dioxide, sulphate in particles, total gaseous and particulate phases of reduced and of oxidised nitrogen. In addition concentrations of a considerable number of elements in aerosols have been determined by the PIXE method.

The results show that although the levels of all pollutants are generally very low there are large and recurrent seasonal variations where concentrations rise to considerable heights, similar to observations at other High Arctic sites. The periods of high concentrations fall in different seasons, primarily in winter, dependent on the type of pollution and the source type responsible. Winter concentrations of sulphur have decreased in the last few years, possibly caused by reduced emissions in the northern part of Russia.

A receptor model is used for identifying the natural and anthropogenic source types most important at Station Nord, for apportioning concentrations to these sources and for determination of the seasonal variation of the source strengths. The recurrent influence of remote sources on the air quality in the High Arctic indicates that large scale meteorological mechanisms, similar from year to year, are responsible for the high concentrations..

For the sulphur compounds this hypothethis is confirmed by model calculations. The results obtained with an Eulerian hemispheric model show that a significant atmospheric pollution transport from very distant sources in industrial areas in Europe and Russia takes place in winter. This transport often occurs in episodes The deposition is however not very high.

Measurements of ozone reveal a striking pattern in spring of sudden ozone depletion lasting from a few hours to a couple of days. The phenomenon is believed to be related to the Polar sunrise and the return of daylight that may initiate a photochemical activity involving the ozone destructing bromine, the origin of which remains unclear.

1 Introduction

Atmospheric research
in Greenland

The Danish atmospheric research in the Arctic has naturally been centred on Greenland. Since 1990 the National Environmental Research Institute of Denmark (referred to by its Danish acronym DMU) has operated an atmospheric research station at Station Nord in Northeast Greenland. Data from this site has also since 1994 been used for the purposes of the Arctic Monitoring and Assessment Programme, AMAP.

Measurements
and models

The atmospheric programme at Station Nord consists of an experimental part and a modelling part. The experimental programme consists of continuous sampling of a number of atmospheric pollutants in gaseous and particulate form. The purpose is to determine the atmospheric levels and the likely origins of these pollutants that recurrently occur in the High Arctic. In the numerical part of the programme a Eulerian hemispheric model has been developed. It is used for studies of transport mechanisms and chemical transformations that are responsible for the occurrence of the air pollution that is found in the High Arctic. The model is under constant development to encompass a growing number of chemical compounds and processes.

Observational coverage

The observational basis consists of data on several atmospheric pollutant concentrations measured since the beginning of the programme in the summer of 1990 to the end of 1996. The limitation of this dataset is that the data only originate from one location and therefore cannot be representative for the whole of Greenland. On the other hand it does contain observations of a considerable number of atmospheric pollutants. In addition the observations are believed to be representative for a large part of the High Arctic region around the North Pole.

Model coverage

The model calculations are based on a much larger database. Geographically the model covers the major part of the Northern Hemisphere and the meteorological data used in the model extend over several years and cover the period from Autumn 1990 to Summer 1996. The limitations of the model results are in particular that at present the model only handles one type of pollutants, the gaseous and particulate phases of sulphur and that all emissions are not up to date.

Interaction between
measurements and
models

The experimental data and the model results are mutually independent and supplement each other, and some of the shortcomings of one set is compensated by the other. The agreement between the model results and the measured data on sulphur allows the interpretation of the data to be extended considerably in both time and space. Hence the above conclusion that the measuring site at Station Nord is quite representative of the high latitudes and more so than of the more southern parts of Greenland.

2 The Arctic Atmosphere

2.1 Climatological characteristics

The Polar Front

The Arctic atmosphere over the central polar area of the High Arctic and the adjoining tundra plains and boreal forests contains the cold and dry and naturally clean air north of the Polar Front. The Polar Front separates the Arctic atmosphere from the temperate and more humid air masses at middle latitudes and it is characterised by strong gradients in i. a. temperature, pressure, and water vapour content. These gradients represent a very large reservoir of potential energy that to some extent is released in the strong westerly jetstreams aloft. The Polar Front and the pattern of jetstreams form a wavy circumpolar barrier along which cyclonic low pressure systems accompanied by stormy conditions and frequent precipitation alternate with high pressure anticyclonic systems. This is illustrated for the 500 hPa surface in Figure 2.1.
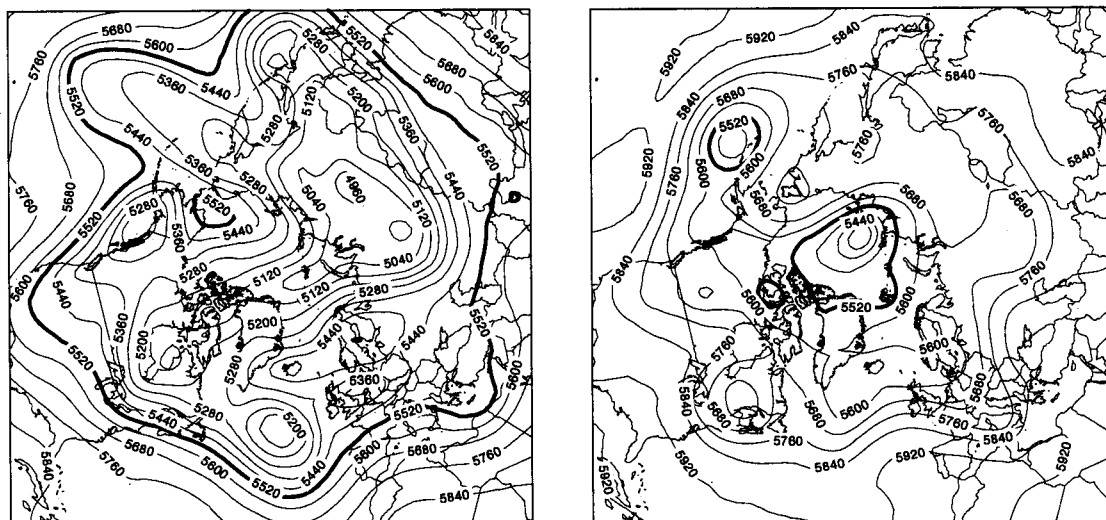
Fig. 2.1. The heights of the 500 hPa surface for 22. February 1994 (left) and 22. July 1993 (right). The bold contour line is the 5520 m height, and in winter it indicates the location of the Polar Front.

Polar Front waves

Over short time periods the waves of the Polar Front move eastward out of North America with increasing amplitudes and decreasing velocity so that with time the wandering cyclones tend to catch up with the high pressure anticyclones. Eventually this leads to a breakdown of the pattern and the Polar Front is re-established in its original form. As the Polar Front ages the high pressure systems may thus block the way for the moving lows. This happens frequently in winter over land bordering on the Barents Sea. When a low pressure system is blocked close to a high pressure area the cyclone deepens and in the case of a westerly Low and an easterly High a strong northward flow of air is established (see section 4). Since the air circulated around the cyclone has a southerly origin this constitutes an

injection of middle attitude air into the Arctic. The proximity of the anticyclone lends vertical stability to such a flow.

Polar Front movements

Because the position of the Sun changes over the year the Polar Front also moves on seasonal time scales. It retracts northwards in summer and moves south in winter. In summer the Arctic atmosphere is therefore isolated more or less north of the Polar Circle whereas in winter the Polar Front may as seen in Fig. 2.1 encompass a major part of the Euro-Asian landmass and induce southerly airflows from large continental areas.

Arctic Climate

The climate of the Arctic is characterised by the prolonged light and dark periods with scarce precipitation in the cold season. It is determined by a balance between the net loss of energy through radiation and the gain by convergence of the atmospheric and oceanic energy transport. The extreme cold produces a very pronounced stratification of the lower atmosphere and the Arctic climate is to a large extent controlled by conditions in a very shallow boundary layer where *e.g.* the temperature in the lower few hundred meters rises dramatically from very low surface values through tens of degrees. These conditions also govern the atmospheric transport along and to the surface. The position of this layer is critically close to the border of Arctic snow and ice and small changes may have large effects. The Arctic climate is therefore believed to be considerably more sensitive to disturbances than at lower latitudes.

Global implication

Since the Arctic region occupies an essential position in the atmospheric circulation system that dominates the Northern Hemisphere and in the corresponding chemical, radiative, and heat balance systems *there is a strong coupling between the Arctic and the Global climate.* Therefore even small changes in the Arctic atmosphere, induced *e.g.* by pollution, may have global impacts.

2.2 Environmental Phenomena

Arctic Haze

Over the last 15 years investigations in the Greenland, Norwegian, Russian, American, and Canadian Arctic have shown that even in this remote area the atmosphere is recurrently burdened with a significant pollution load of distant anthropogenic origin (Heidam 1984, 1990; Barrie & Barrie 1990; Beine *et al.* 1996). In winter the major part of the pollution, known as Arctic haze, apparently originates from industrial and other anthropogenic activities in the Euro-Asian region, including in particular central Europe, northern Russia and the Ural region. This is believed to be a result of a series of southerly injections of the type described above. In winter the Polar Front is already in a southerly position and so the injections may well have collected air over major industrial centres and pollution sources, see Fig. 2.1. Because of the stabilising influence of the anticyclone and the scarcity of precipitation in winter air pollutants injected into the Arctic atmosphere at this time of the year have a long residence time. The phenomenon of Arctic Haze is very pronounced in Northeast

Greenland, but is has also been observed in Northwest Greenland and in general it decreases towards the south.

Sulphur and Metals

Arctic Haze consists mainly of sulphur-containing aerosols (sulphuric acid, sulphates) and is often and to a varying degree accompanied by a gaseous component of sulphur dioxide. It is observed to occur in the lower few thousand metres of the troposphere where it may seriously affect the normally very good visibility. It can therefore be feared that it may also affect other aspects of the atmospheric radiation balance. Since aerosol particles act as condensation nuclei this enhanced occurrence of aerosols may also lead to changed patterns of cloud and precipitation formation. Finally deposition of sulphur containing compounds could lead to acidification of the Arctic ecosystems. In the winter season the atmospheric aerosols over Northeast Greenland have also during short episodes been observed to contain a minor component of heavy metals that seem to originate in the northern part of the Urals.

Polar Sunrise

A considerable number of air pollutants have thus been observed in the Arctic atmosphere in unnaturally high concentrations at the end of the dark season. A similar accumulation can therefore also be expected for other and possibly strongly reactive pollutants that have not yet been investigated. Upon the return of sunlight a fierce photochemical activity may therefore be taking place in the Arctic atmosphere. Little is known, however of these processes at 'polar sunrise' but various halogenides seem to play a key role.

Global change

Because of the earlier mentioned feedback mechanisms and the sensitivity of the Arctic atmosphere it is generally believed that the Arctic region constitutes a 'signal area' where the effects of anthropogenic induced changes in the atmospheric composition will appear first and with maximum strength. The results of many Global Circulation Models, constructed to simulate climate responses to the increased Greenhouse effect, confirm this and show that the rise in atmospheric temperatures will be largest in the Arctic.

Other pollutants - other media

Enhanced levels of persistent toxic organics and heavy metals, in particular the volatile metal Mercury have been found in the Arctic food chains and in human blood and tissue (Bjerregaard and Weihe, 1997). One of the path-ways for these compounds is certainly in the atmosphere. These volatile toxins appear to take part in a global scale 'distillation process' of emissions and repeated depositions and re-missions due to evaporation. This complex of processes moves the pollutants down the global temperature gradient until they finally accumulate in the Arctic environment. This is all the more serious since in the cold and dark Arctic region the breakdown and turn-over processes of pollutants in the environment are much slower than in more temperate zones.

3 Measurements of Arctic Atmospheric Pollution in Greenland

3.1 Location and logistics

Northeast Greenland: Clean and polluted air

The Danish atmospheric measurements under AMAP take place at Station Nord in the north-east of Greenland, located as shown on the map in the Fig. 3.1(a). The reasons for choosing this location are partly logistic and partly scientific. From a logistics point of view Station Nord is attractive since it is not only the most easily accessible place in the Northeast Greenland but also contains the necessary technical facilities for the operation of an atmospheric observatory. From a scientific viewpoint Station Nord is interesting as this remote area normally is influenced by katabatic winds from the ice cap, *i.e.* by typical Arctic background air. But in winter Station Nord is also recurrently exposed to episodes of long-range transported air pollution from Euro-Asia. Both of these features are believed to be characteristic of the High Arctic.

Station Nord

Station Nord at the position 81°36'N, 16°40'W and about 20 m above sea level is a Danish military station under the jurisdiction of the Ministry of Defence. Station Nord is therefore a small enclave in the vast natural park of Northeast Greenland. It can only be reached by air and all supply and transport to and from the station is the responsibility of the Royal Danish Air Force. The use of the remote station is therefore somewhat limited but regular admittance to the area under certain conditions has been obtained. At Station Nord the necessary electrical power is available and access to workshops and transport vehicles is also possible. The permanent staff at Station Nord comprises five military persons with some technical expertise.

Measuring sites

Since the start in 1990 the measurements have taken place north of the central complex of buildings, at the not quite ideal location marked 'LW hut' on the map in the Fig. 3.1. From the spring of 1995 the main activity of the experimental programme has been moved to a new observatory. This station, named 'Flyger's Hut' (FH) has been erected by DMU with support from the Danish Environmental Protection Agency at the position shown on the map in Fig. 3.1(b). The location is inside the National park of Northeast Greenland, approximately 3 km south of the central complex of buildings, right outside the military area and has been chosen so as to minimise influence from any local air pollution. Flyger's Hut is supplied with electricity and heat and is used as the main base for the AMAP Air Monitoring Programme. However, the original measurements at the 'LW' position have been maintained for reasons of continuity, comparability and quality control, and for studies of representativeness of the two sites.
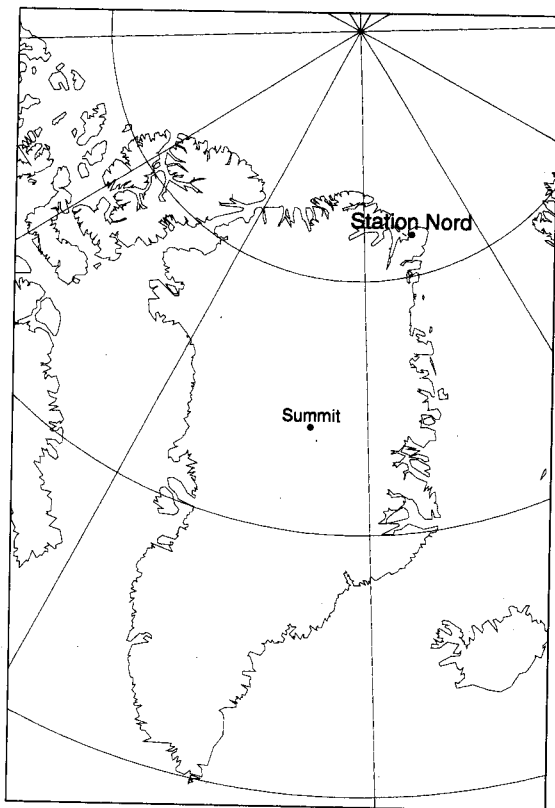
Fig. 3.1(a). Greenland with the location
of Station Nord and Summit.
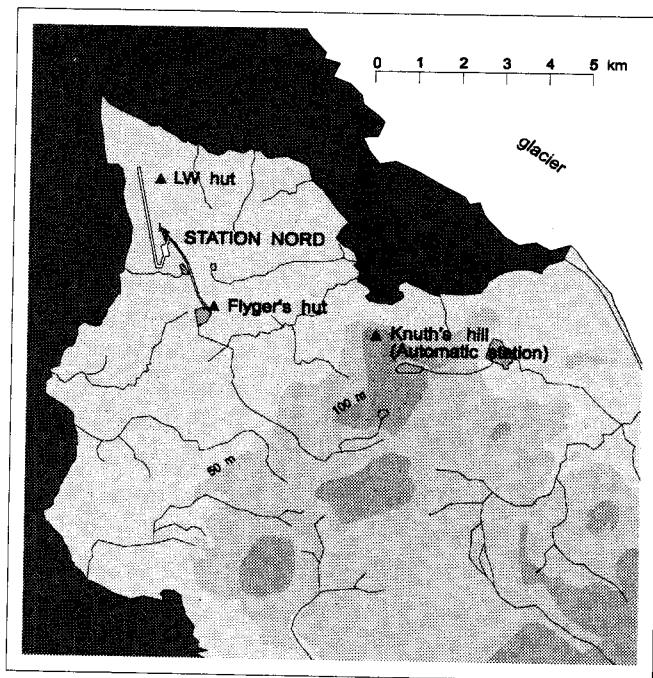
Fig. 3.1(b). Station Nord. Measuring sites and
surroundings.

Instrument supervision

The daily operation of the instruments is carried out by the personnel at Nord. They also change all filters and return exposed samples to DMU utilising all available flights. Maintenance and calibration of the instruments is carried out at two annual field visits by DMU. The field visits are also used for exchange of information and experience in instrument field performance between the laboratory and the station personnel.

3.2 Measurement programme

Pollutants measured

The measurement programme comprises collection of filter samples on a weekly basis and some gaseous measurements on a ½ hourly basis.

The filters are subsequently analysed in the laboratory at DMU for the concentration of the following atmospheric pollutants:

Acidifying compounds - Arctic Haze:
- Gases: SO_2, sulphur in sulphur dioxide
- Aerosols: SO_4^{2-}, sulphur in sulphates
- Total phase (gases (g) and particles (p)) of oxidised and reduced nitrogen:
  $[HNO_3(g)+NO_3^-(p)]$ and $[NH_3(g)+NH_4^+p)]$.

Radiatively Important Trace Species - RITS:
- O_3 - Ozone
  ½ hourly mean concentrations of ozone have been started in 1995.

Elements in aerosols, including Heavy Metals and Sulphur, listed by chemical abbreviation and atomic number:
  Al 13, Si 14, S 16, Cl 17, K 19, Ca 20, Ti 22, V 23, Cr 24, Mn 25, Fe 26, Ni 28, Cu 29, Zn 30, As 33, Se 34, Br 35, Rb 37, Sr 38, Zr 40 and Pb 82.

The measurements listed above fulfil a considerable part of the monitoring requirements in AMAP.

Measurements not included

AMAP Measurements not included at Station Nord.
The Danish monitoring station is not classified as an AMAP master station and therefore a full AMAP programme is not implemented. With reference to the parameters labelled 'E: Essential' in the programme (AMAP,1993) the following measurements are not performed at the Danish station:
- POP;
- Metals: Mercury, Hg;
- Radionuclides;
- RITS: CO_2, N_2O, CH_4, and CFC's;
- Arctic Haze: PAN;
- NO_2 - gas.
  The sampling of NO_2 on separate impregnated glass filters, initiated in 1994 was terminated in 1995 for reasons given below.

3.3 Sampling, analysis and quality control

Weekly sampling

The acidifying gas and aerosol compounds are collected weekly on 4 stacked filters in a filterpack collector. The first filter is used for collection of particles less than about 15 μm diameter, a value somewhat dependent on the wind speed. The subsequent 3 filters are specifically impregnated to catch the various gas phases of sulphur and nitrogen. These instruments require attendance once every three weeks for change of filters, reading of collected air volumes etc.

Experimental limitations

However, since the aerosol at Station Nord is often rather acid it is quite likely that in such instances a considerable part of the gaseous nitrogen is converted into particulates on the first filter, either as nitrates or ammonium-salts. During less acid circumstances some of the nitrogen may degas from the first filter to be catched on the subsequent filters. For this reason no distinction is made between gaseous and particulate nitrogen, instead the nitrogen content in the sums of the gaseous and particulate phases is reported. These components are designated as (NH_3 + NH_4)-N for reduced nitrogen and (HNO_3 + NO_3)-N for oxidised nitrogen and they are referred to as Total ammonium or TNH_4 -N and Total nitrate or TNO_3 -N, respectively.

Analysis and
Quality Control

The acidifying components are analysed according to the methods acknowledged and prescribed by the international environmental programmes in which DMU's Department of Atmospheric Environment participates. The foremost of these is EMEP, the European Monitoring and Evaluation Programme established under the UN_ECE Convention on Transboundary Air Pollution in Europe (EMEP Manual 1995). Normal quality control procedures are applied to all the measurements mentioned above. This includes among others analysis of extra control samples and maintenance of calibration by means of standards. In general the quality objective is to attain a 10 - 15 % accuracy but that may not be attainable when the concentrations are very small.

Elements in particles

The elemental contents of the aerosols sampled on the particle filters are analysed by means of the PIXE method. This Proton Induced X-ray Emissions spectroscopy is a sensitive multi-element method, where all elements heavier than Al which are present in amounts above the detection limits of the method can be determined. Samples from Greenland normally contain the elements listed above.

Ozone

Half-hour mean concentrations of ozone have since the spring of 1995 been measured by an ozone-monitor at Flyger's Hut. In addition a PC has been installed to control the Ozone monitor and to store and retrieve the data.

Experimental problems

The efficiency of the sampling of NO_2 on filters impregnated with KI and arsenite has been investigated. The purpose was to evaluate the suitability of this method, originally designed for measurements on a 24 hours basis in EMEP, for continuous sampling over a week under Arctic conditions. Unfortunately it turned out that the method apparently underestimates the NO_2-concentrations severely. These data have therefore been excluded from the evaluation and the sampling has been terminated.

Database Storage

After analysis and quality control the approved results are transferred to DMU's databases. Approval follows the normal QA-procedures of the department's other monitoring programmes.

4 Experimental results

4.1 Gases and aerosol ions

Annual mean
concentrations

The concentrations of the acidifying compounds measured on a weekly basis are summarised as annual means since 1991 in Table 4.1. The values are arithmetic means in $\mu g \cdot m^{-3}$. For comparison the corresponding mean values for the same components measured at two Danish rural stations, Tange and Keldsnor, in 1994 are also presented.

Table 4.1. Annual arithmetic mean concentrations at the LW-site at Station Nord in Northeast Greenland and in Denmark

$\mu g \cdot m^{-3}$	Nord 1991	Nord 1992	Nord 1993	Nord 1994	Nord 1995	Nord 1996	Tange 1994	Keldsnor 1994
SO_2-S	0.169	0.177	0.198	0.168	0.072	0.088	1.01	1.76
SO_4-S	0.136	0.175	0.215	0.193	0.117	0.140	1.31	1.64
TNH_4-N	0.054	0.045	0.061	0.056	0.036	0.040	3.39	3.42
TNO_3-N	0.024	0.014	0.016	0.013	0.011	0.017	0.99	1.36

Sulphur concentrations

It can be seen that the average sulphur values in both the gaseous and particulate phases are about 10-20 times lower in Greenland than in Denmark whereas the concentrations of the nitrogen compounds are lower by a factor of about 100. It is noteworthy that the average ratio of primary gaseous sulphur to secondary particulate sulphur is about 1:1, even after several days of transport in the atmosphere. That points to a very low oxidation efficiency in these cold regions.

Seasonal variation

These annual averages cover a very considerable variation through the year. This can be seen in Figs 4.1 - 4.2 which show the individual concentrations over the whole period. The concentrations are all high in the winter periods but in the summer period they fall to such low values that the air at Station Nord must be considered as truly representative of global background air. In the summer, the concentrations of particulate sulphur are about 100-200 times lower than in winter and especially sulphur dioxide falls to such low values as to be virtually absent.

High winter concentrations
of sulphur

In winter the situation is drastically different. Every winter the sulphur concentrations rise to very high values in the period January-April. It can be seen from Fig. 4.1, that the maximum winter values in Northeast Greenland are in fact of the same magnitude as the annual averages found in Denmark and quoted in Table 4.1. Such high values can only be reached if there is a considerable atmospheric transport from remote sources. Both the maximum concentrations and the mid-winter means (December-February) of total sulphur peaked in 1993 and have since then shown a downward tendency. The mid-

winter means have in fact decreased by a factor of 2. This may be an accidental meteorological effect but model calculations indicate that it may in fact be a real trend caused by reduced emissions (see chapter 4 on model calculations).

Agreement among sites

The levels and the variations at the two measuring sites agree very well in the period when both are active. The results from the more than 80 simultaneous samples covering well over a year show that the total sulphur concentrations are highly and significantly correlated with a correlation coefficient above 0.95. The same is true for the subcomponents SO_2 and SO_4.

Nitrogen

The concentrations of reduced and oxidised nitrogen are shown for the LW-site in Fig. 4.2. The levels at the FH-site are similar and the correlations between the two sites are also high and significant with correlation coefficients in the range 0.83 - 0.90. For this reason the much more numerous results from the LW-site have been chosen for presentation. The nitrogen concentrations in Northeast Greenland are very low and do not in any way approach the levels found in Europe, not even in winter. However, the nitrogen concentrations also vary considerably but relatively less than sulphur. The ratios of winter to summer concentrations lie between 20 for oxidised nitrogen and 50 for reduced nitrogen.

Correlation of sulphur and ammonium

It can be seen that there is a very good correlation between sulphate and total ammonium. At both sites the correlation coefficients are in fact 0.89 and highly significant. The total ammonium and nitrate are as mentioned the sum of the gaseous and particulate phases of reduced and oxidised nitrogen that cannot be separated because of suspected transformations on the filters. But it is believed that these phase sums to a great extent represent predominantly particulate phases in the atmosphere. This is especially true for total ammonium since the gaseous NH_3 is highly reactive and quickly transforms into an ammonium salt.
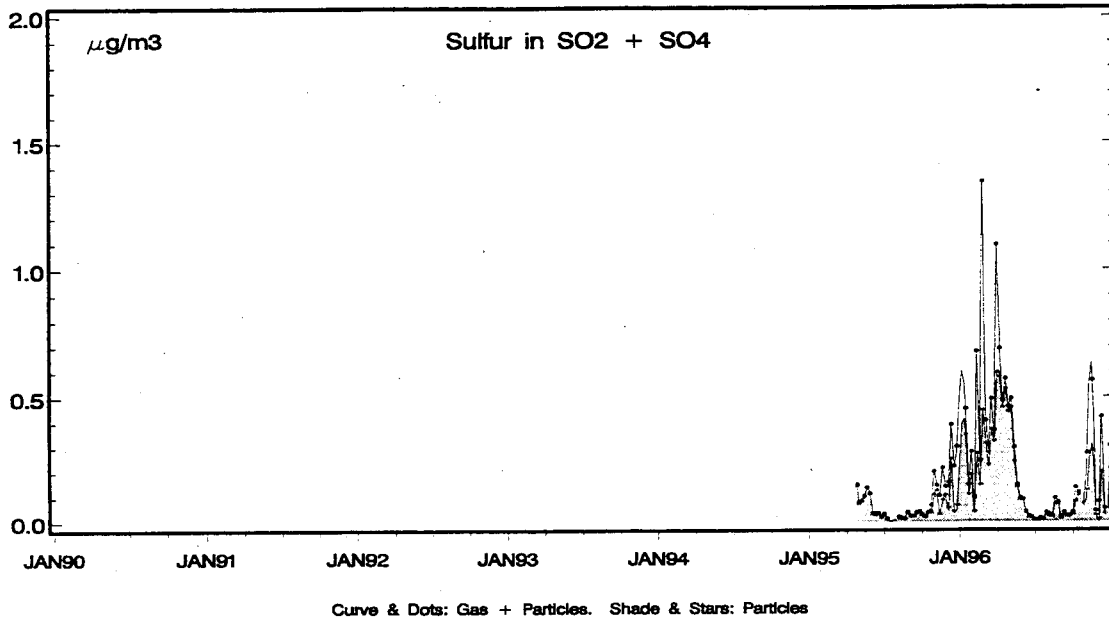
Stochiometry

The high correlations suggest that ammonium is present in some form of ammonium-sulphate. In that case it will signify that sulphuric acid to some degree has been neutralised by ammonia. At Station Nord ammonium is measured by analysis of the particle filter in the filterpack sampler, while ammonia is collected and analysed on an impregnated filter placed after the particle filter. The measured ammonia concentrations are very low compared with the concentrations of ammonium, and probably the measured ammonia is an artefact due to degassing from the particle filter. The degree of neutralisation is shown in Fig. 4.3 where TNH_4-N, is plotted against SO_4-S. Also shown are the stochiometric ratios corresponding to ammonium sulphate (($NH_4)_2SO_4$) and ammonium bisulphate (($NH_4)HSO_4$). It can be seen that the degree of neutralisation is approximately 25% of the full neutralisation as represented by $(NH_4)_2SO_4$. This is very low compared to the situation in Denmark, where sulphuric acid is most of the time fully neutralised by ammonia, because as shown in Fig. 4.4 a large excess of reduced nitrogen is found in the atmosphere as

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Weekly concentrations in air 1990—1996

STATION = NORD/FH

Curve & Dots: Gas + Particles.   Shade & Stars: Particles

STATION = NORD/LW

Curve & Dots: Gas + Particles.   Shade & Stars: Particles
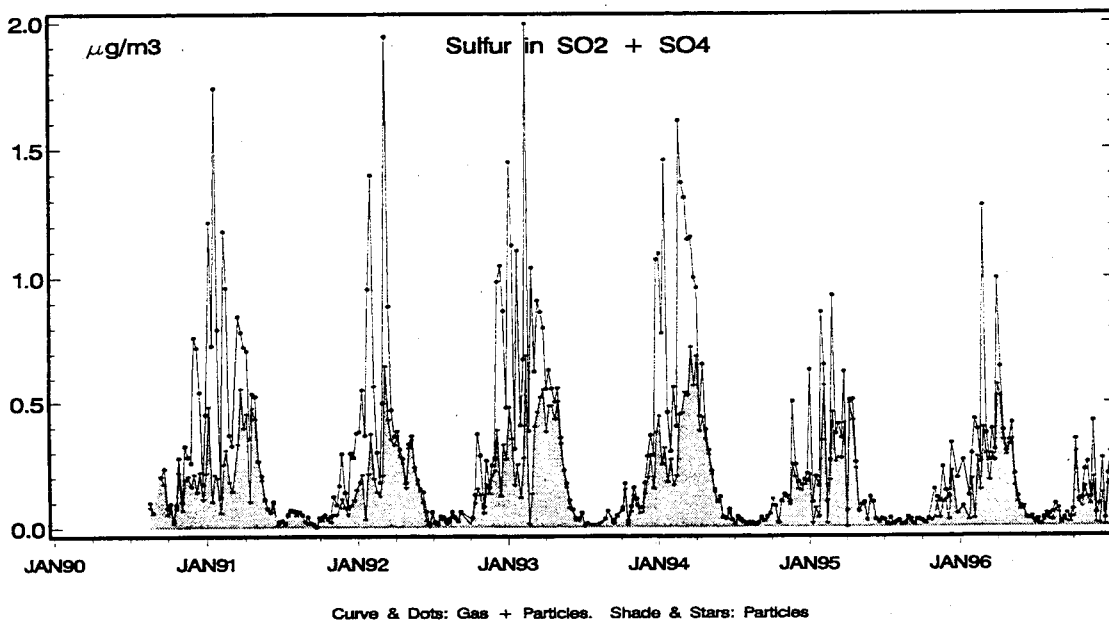
min. 99 % data

nzh: 18AUG97 14:58

Fig. 4.1. Results for sulphur concentrations in the particulate and gaseous phases at the two measuring sites FH and LW at Station Nord.

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Weekly concentrations in air 1990 – 1996

STATION = NORD/LW

Curve & Dots: Gas + Particles.

STATION = NORD/LW

Curve & Dots: Gas + Particles.
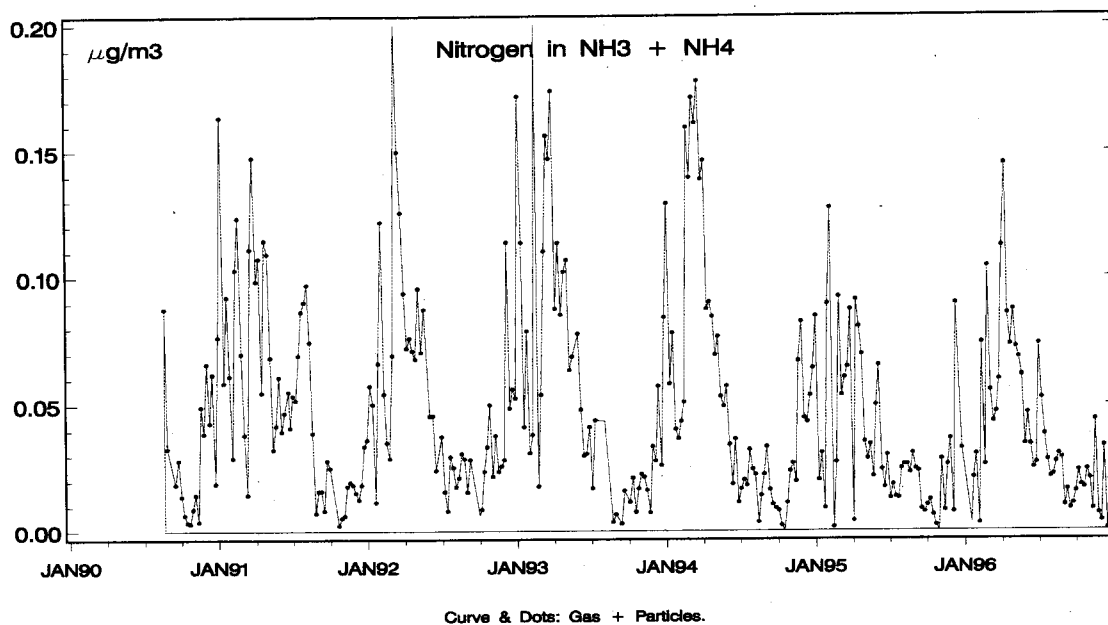
Fig. 4.2. Results for nitrogen concentrations in the total reduced and oxidised phases at the LW-site at Station Nord.

a free gas and as ammonium nitrate. This could mean that at most 25% of the sulphur shares origin and transport history with reduced nitrogen. For the most part these compounds probably originate in different source areas and arrive in Northeast Greenland by different transport pathways.

Oxidised nitrogen

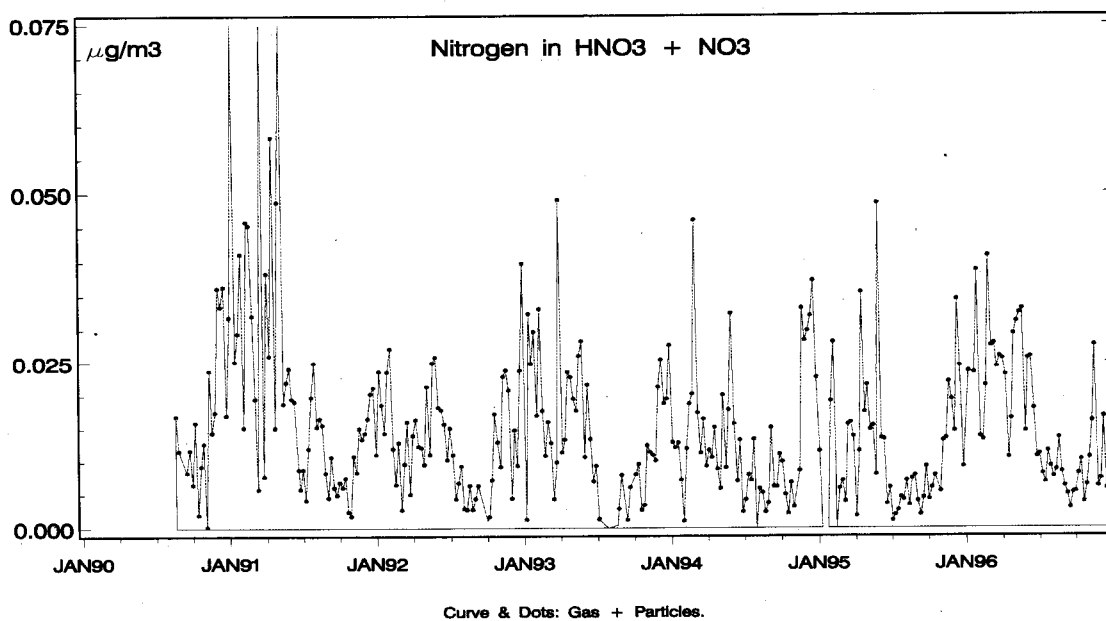Also for oxidised nitrogen the large variations are taken to signify that in winter this component has arrived in Northeast Greenland as a result of atmospheric transport from remote sources. But the correlation with sulphate is much poorer as can be seen from the figures. The correlation coefficients are around 0.55 and the levels are also extremely low. It can therefore be suspected that oxidised nitrogen in Northeast Greenland is only the remains of what once was emitted in distant source areas and that the remainder has been deposited during transport.
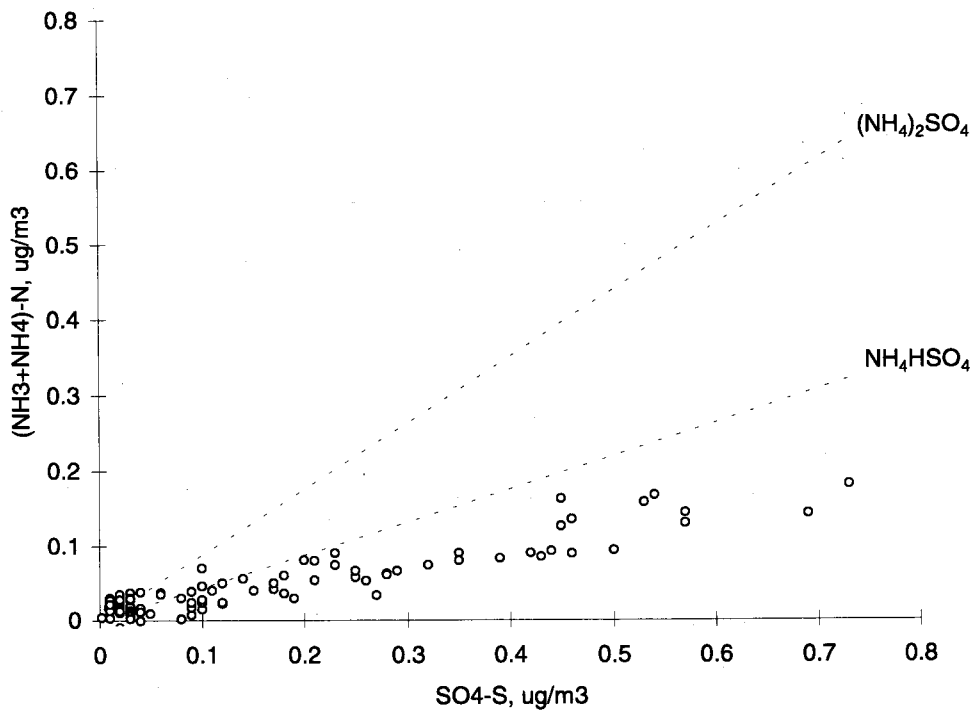
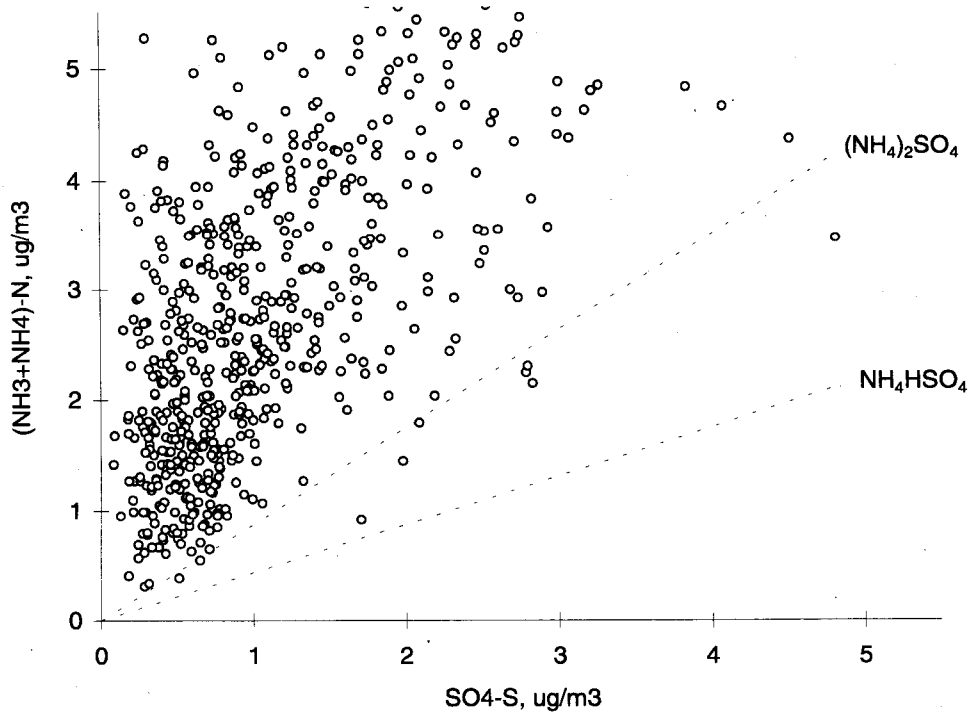Fig. 4.3 Measured concentrations of TNH_4-N at Station Nord in the period 1994-95 plotted against SO_4-S.

Fig. 4.4 Measured concentrations of TNH_4-N, at Tange in Jutland in 1994 plotted against SO_4-S.

4.2 Elements

4.2.1 Data overview

Annual mean
concentrations

The concentrations of aerosol elements sampled at Station Nord in 1994 and 1995 and analysed by PIXE (Proton Induced X-ray Emission) are summarised as annual arithmetic mean values in ng/m^3 in Table 4.2. The volumes are scaled to STP conditions. Also shown for comparison are the concentrations measured in 1994 at the Danish rural station Tange. It can be seen that the concentrations as a rule are 5-20 times smaller at Station Nord than at Tange. For reasons explained later chlorine (Cl) could not be measured at Station Nord. Owing to special conditions in the Arctic spring, the annual mean concentration of filterable bromine (F-Br *i.e.* bromine collected on filters even if gaseous) at Station Nord is comparable to the value in Denmark.

Table 4.2. Annual arithmetic mean values of elements in aerosols at Station Nord and in Denmark.

ng/m^3.		Nord 1994	Nord 1995	Tange 1994
Al	Aluminium	39.00	29.00	223.00
Si	Silicon	155.00	124.00	693.00
S	Sulphur	181.00	111.00	1305.00
Cl	Chlorine	-	-	4180.00
K	Potassium	26.00	26.00	193.00
Ca	Calcium	29.00	29.00	161.00
Ti	Titanium	3.20	3.10	13.00
V	Vanadium	0.30	0.17	3.20
Cr	Chromium	0.11	0.08	0.60
Mn	Manganese	0.49	0.52	7.50
Fe	Iron	36.00	31.00	220.00
Ni	Nickel	0.17	0.17	1.20
Cu	Copper	0.41	0.39	2.10
Zn	Zinc	1.40	0.88	29.00
Ga	Gallium	0.03	0.02	-
As	Arsenic	0.20	0.08	1.20
Se	Selenium	0.03	0.02	0.60
Br	Bromine	3.40	2.40	3.60
Rb	Rubidium	0.18	0.14	-
Sr	Strontium	0.38	0.25	2.10
Zr	Zirconium	0.12	0.15	0.90
Pb	Lead	0.77	0.56	9.70

Seasonal variation

Although the annual mean values are substantially lower at Station Nord than in Denmark, the seasonal distribution is very uneven. There is almost no air pollution in the summer, while the concentrations of anthropogenic components in winter and spring ("Arctic haze") are comparable with conditions in Denmark.

4.2.2 The receptor model

Because of the large number of elements the information content in these data are very great. This information is extracted by the use of a receptor model which apportions the measured aerosol concentrations at the receptor point to likely sources (Wåhlin, 1993).

Mathematically, the model

$$x_{ij} \cong \sum_k a_{ik} f_{kj} \quad (X \cong AF)$$

expresses the measured concentrations x_{ij} as linear combinations of constant source profiles a_{ik}. The coefficients f_{kj} represent the source strengths found in the individual samples. Index i refers to the chemical elements, index j to the samples and index k to the sources. An iterative method is used in which the elements of the F matrix and selected elements of an initial A matrix are fitted by turns, and the model is confined to permit only non-negative elements of A and F. Those elements of A which are not allowed to change are marked with zeros in a form matrix with the same number of rows and columns as A (*ibid*). The reference values of Sverdrup *et al.* (1942) have been used in the sea profile, while the composition of the soil source and the combustion source are allowed to change freely except for Zn and Pb, which in the soil profile are fixed to Si in the very small ratios (here essentially zero) found in igneous rock (Kaye and Laby, 1959).

The model has a hybrid character. It can be characterised as a chemical mass balance model with a built-in ability to fine tune known source profiles. On the other hand, if all elements of A are allowed to adjust freely (permitting a confusion of more or less mixed-up sources), the method has resemblance to factor analysis. The uncertainties of the measurements, s_{ij}, are handled in an appropriate manner in the fitting process, in which the chi-square statistic,

$$\chi^2 = \sum_j \sum_i \frac{(x_{ij} - \sum_k a_{ik} f_{kj})^2}{\sigma_{ij}^2},$$

is minimised within the limits imposed by the constraints. This also allows data below the detection limit to be put on a par with other data.

4.2.3 Aerosol sources

The receptor model is used to apportion the measured aerosol at the receptor point to its likely sources. This is accomplished by using the different characteristic contents of chemical substances and elements in the emissions from natural and anthropogenic sources. An important advantage of using a receptor model is that a lot of informa-tion can be expressed in a reduced and more transparent form. To some extent the data reduction will smooth away the scatter in the data, which makes the apportioning easier.

No local sources

In the context of source apportioning it should be noted that local sources, *i.e.* emissions from Station Nord itself are normally negligible. Only very few episodes of substantial local air pollution (caused by waste burning) have been noticed since the start of aerosol measurements at Station Nord in 1990.

Four source types

In all other instances the measured concentrations at Station Nord for all elements except S, Cl and Br can be expressed as combined contributions from only 4 types of sources:

- A marine salt source (sea)
- A crustal source (soil)
- A prominent anthropogenic source (combustion)
- A additional anthropogenic source (metal)

Seasonal variations

The seasonal distribution of impacts from different sources is shown in Figs. 4.5-4.9, where the individual measurements at Station Nord in 1994-95 of PIXE elements are shown as squares at the sample start dates. The source contributions to the individual samples are shown as thin or dotted lines whereas the complete model fits are shown as bold full-drawn lines.

Crustal elements

The elements Al, Si, Ti and Zr, shown in Fig. 4.5, are of almost pure crustal origin. It can be seen clearly that the seasonal variation is very much the same, and that it can be fitted with the same soil source time signal with peaks in spring and late summer.

Marine elements

The elements Ca, K and Sr, shown in Fig. 4.6, are abundant in sea water and in aerosols created by sea spray. The elements, which also have considerable crustal and combustion contributions, are arranged after increasing influence by the sea source. The sea signal has peaks in the winter half-year showing the influence by ocean storms at Station Nord.

Combustion elements

The elements Fe, Mn, Ga, V, Cr, Se, As and Pb, shown in Figs. 4.7 and 4.8, are arranged after increasing influence by the combustion source compared to the soil source. The last three elements Se, As and Pb in Fig. 4.8 have almost the same seasonal variation showing the pure combustion time signal with peaks in the winter and almost total absence in the summer, which is typical for "Arctic haze".

Metallic elements

The elements Zn, Ni and Cu, shown in Fig. 4.9, exhibit episodic winter peaks not found in the common anthropogenic combustion signal. These deviations are ascribed to an additional anthropogenic source involving particularly high emissions of these metallic elements. The elements are arranged after increasing influence by the metal source.
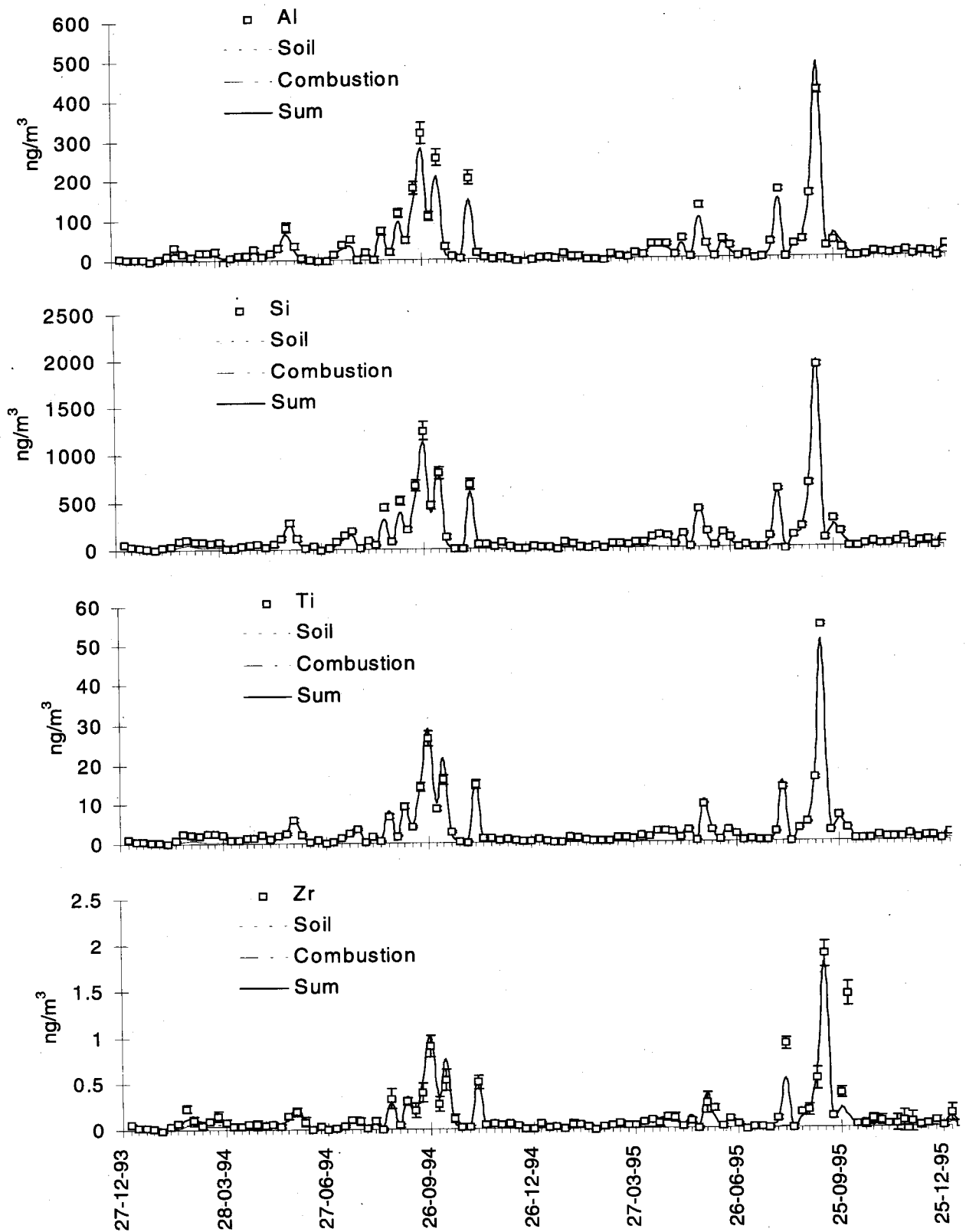
Fig. 4.5 Seasonal variation of Al, Si, Ti and Zr in 1994 and 1995 at Station Nord compared to receptor model results with a dominant soil contribution

Fig. 4.6 Seasonal variation of Ca, K and Sr in 1994 and 1995 at Station Nord compared to receptor model results. The elements are abundant in sea water and in aerosols created by sea spray. The elements, which also have considerable crustal and combustion contributions, are arranged after increasing influence by the sea source.

Fig. 4.7 Seasonal variation of Fe, Mn, Ga and V in 1994 and 1995 at Station Nord compared to receptor model results. The elements are typical crustal elements but the anthropogenic influence by the combustion source in late winter is evident, especially or Ga and V.
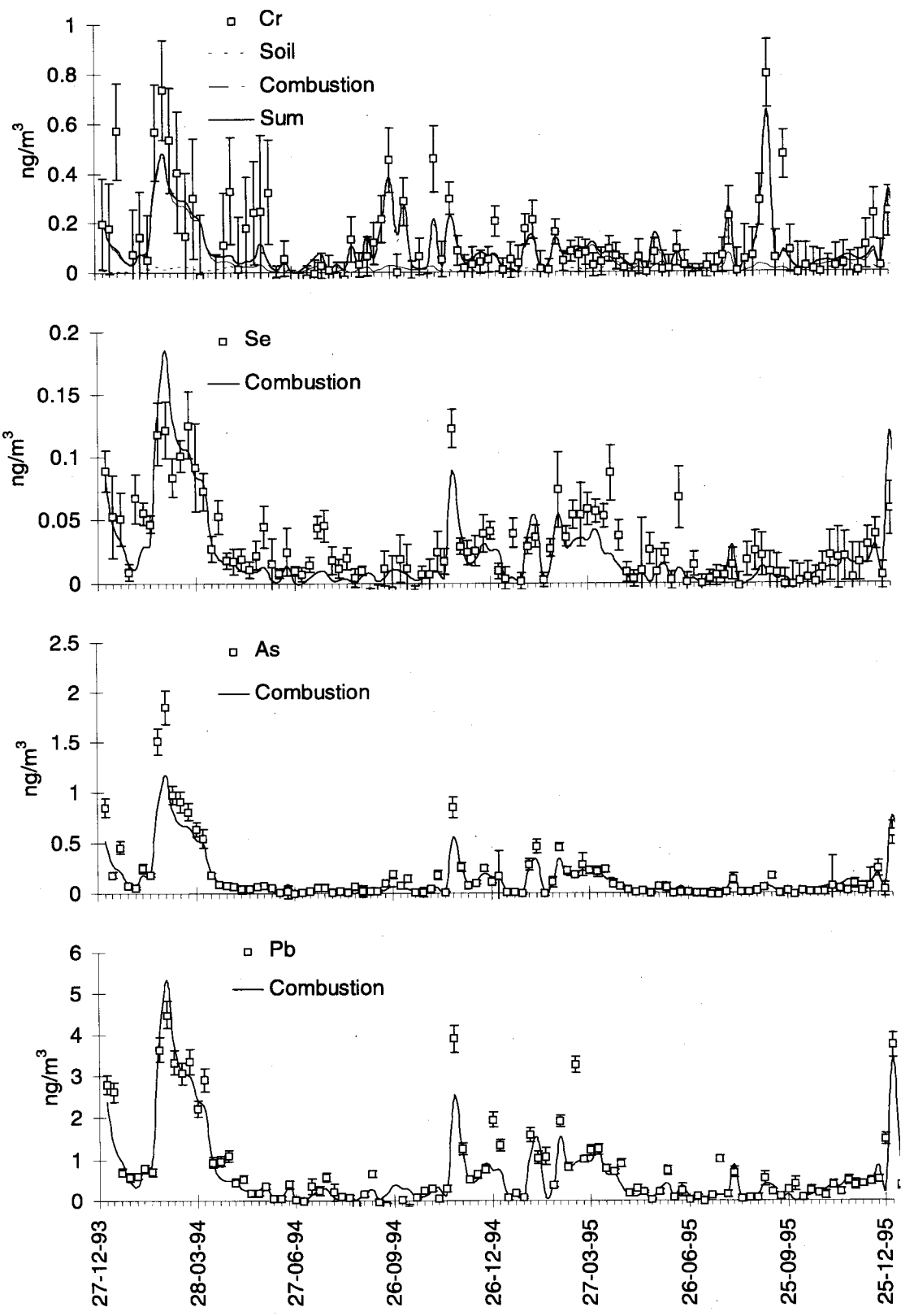
Fig. 4.8 Seasonal variation of Cr, Se, As and Pb in 1994 and 1995 at Station Nord compared to receptor model results. The elements are typical anthopogenic pollutants emiited in various combustion processes. Only Cr also has a crustal origin.
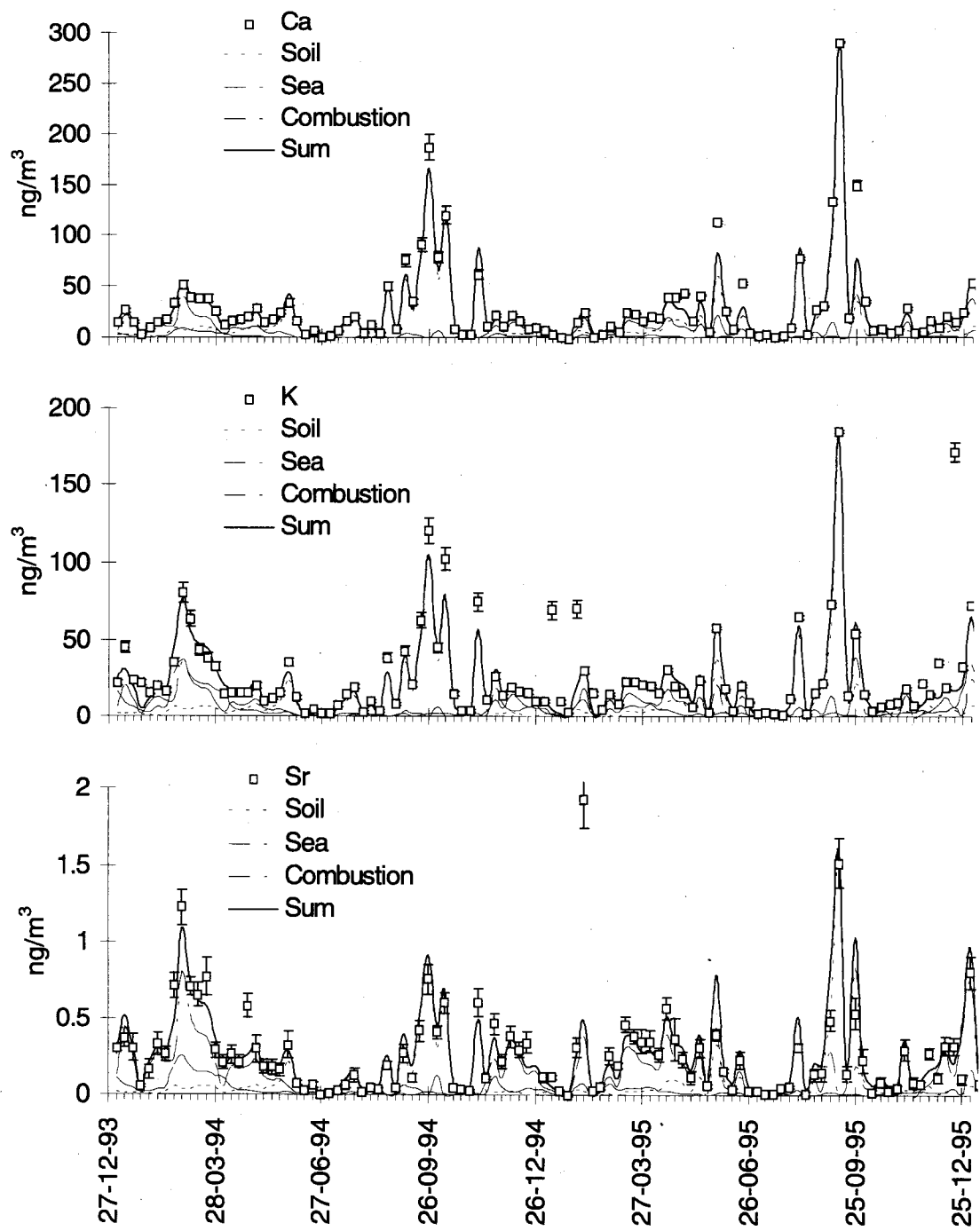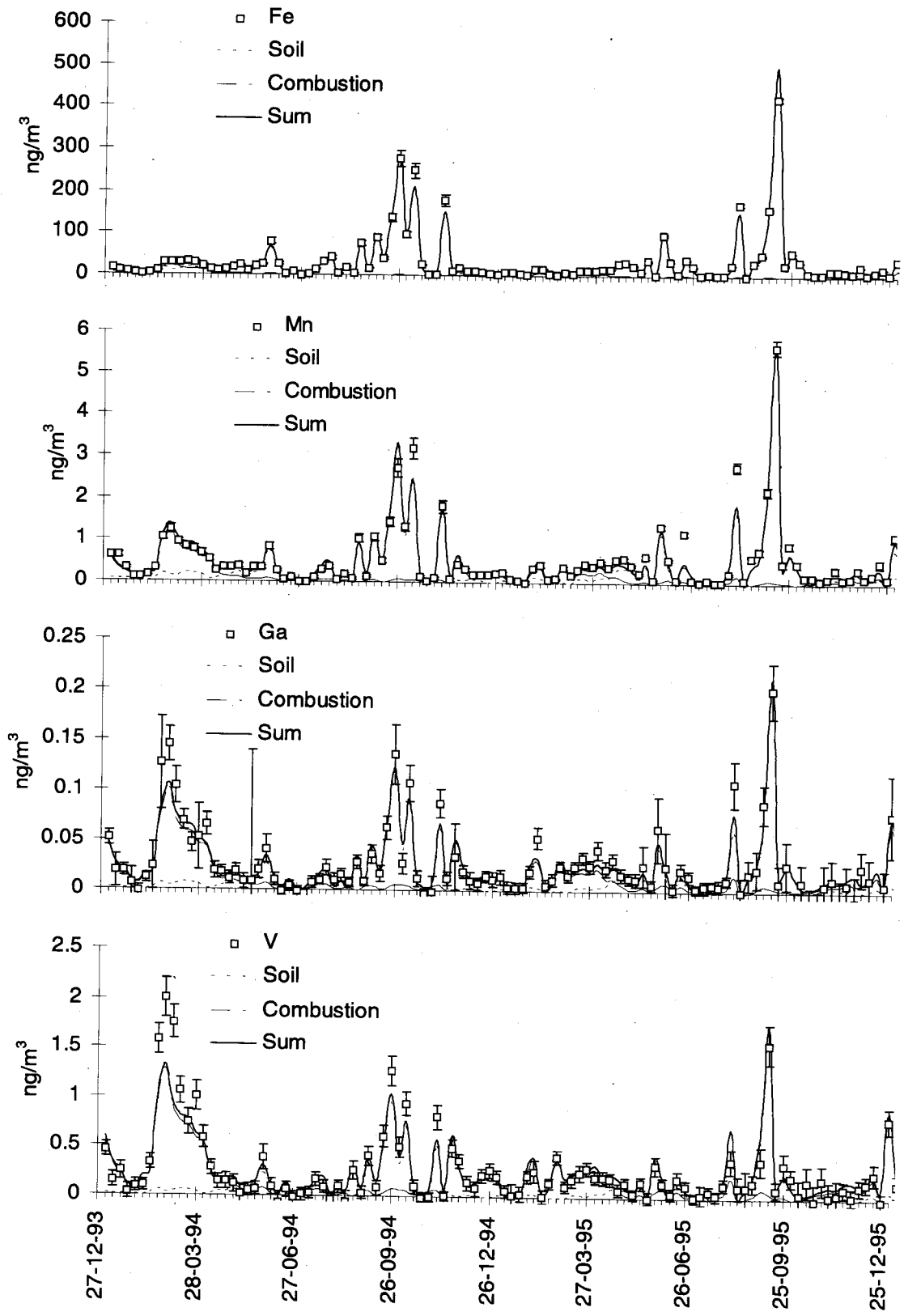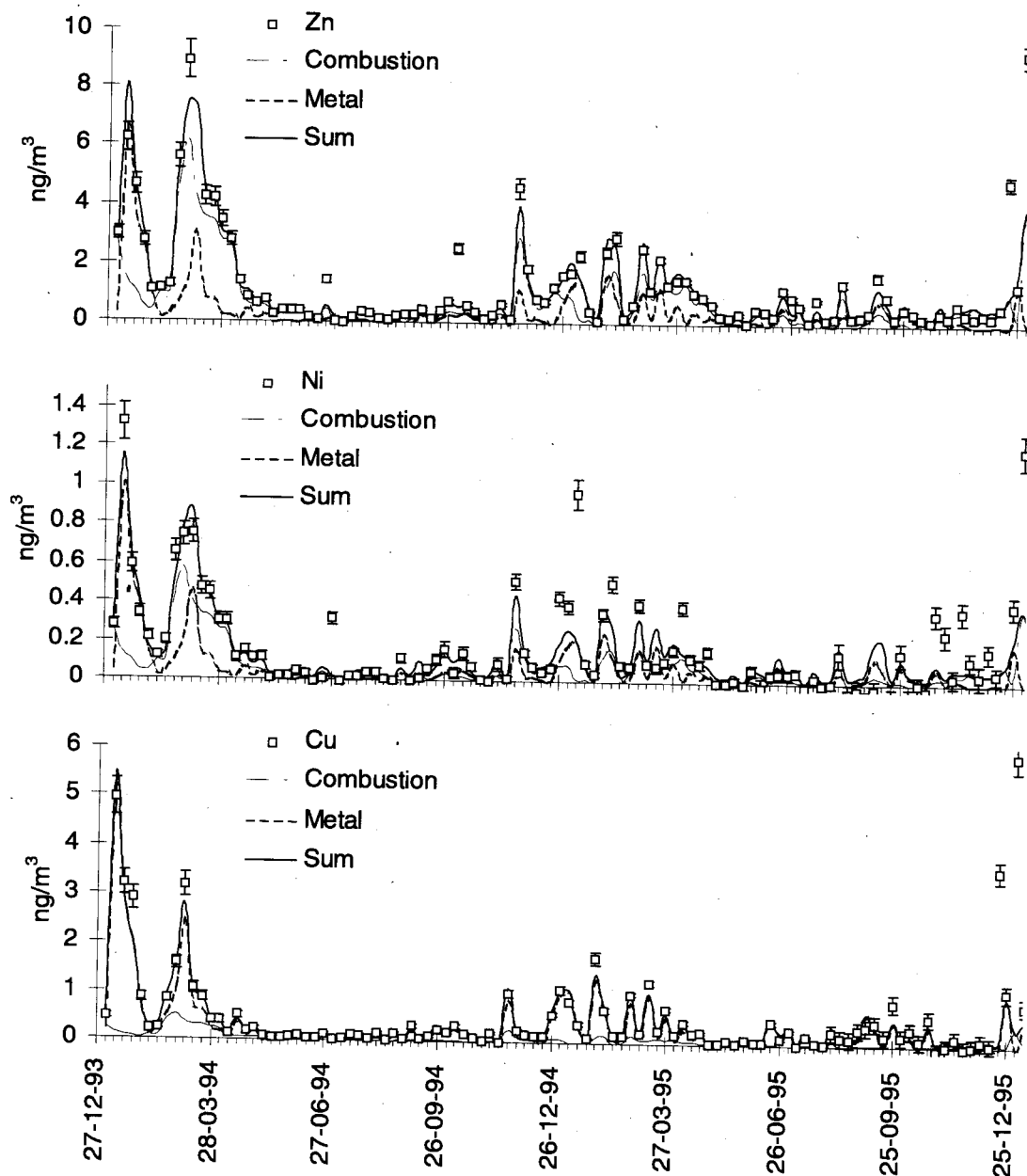
Fig. 4.9 Seasonal variation of Zn, Ni and Cu in 1994 and 1995 at Station Nord compared to receptor model results. The elements are typical antrhopogenic pollutants, only partly attributed to combustion and the influence of a special metal source is evident, in particular for Ni and Cu.

4.2.4 Problematic elements

Chlorine and Bromine

The elements Cl and Br (Fig. 4.10) are highly abundant in sea water and in sea spray aerosols. The measured concentrations are compared in the charts with the sea signal, which has been scaled to the calculated sea salt contributions of K, Ca and Sr in the ratios found in average sea water. It can be seen that almost all the expected Cl is missing. Halogen depression associated with volatilisation by the effect of sulphuric acid in filters from sea level sampling sites in the Arctic has been reported by several authors (cf. Shaw, 1991). The measured concentrations of Br are in the same manner compared

with expected sea salt contributions. A pronounced rise in Br concentration, which can not be related to sea salt, is observed in the spring. High spring Br has previously been observed in the Arctic and comes possibly from marine sources (Barrie and Barrie, 1990) cf section 4.3. The destruction of tropospheric ozone at Polar Sunrise has been connected with the appearance in the spring of particles containing non-sea-salt bromine (Bottenheim et al., 1990).
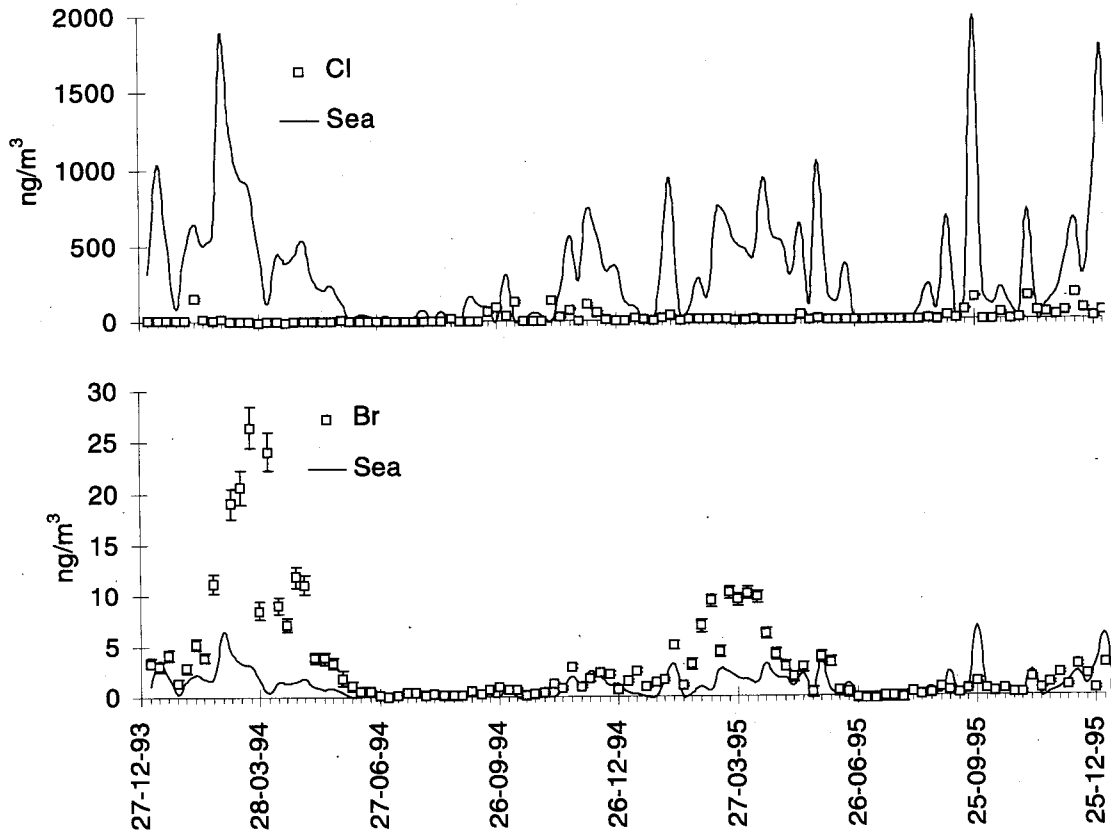
Fig. 4.10. Seasonal variation of Cl and Br in 1994 and 1995 at Station Nord. The influence by the crustal source and the anthropogenic source is minimal.

Sulphur: Gas and particles

Sulphur is the most abundant element in Arctic Haze. It originates mainly in combustion processes and is emitted to the atmosphere in the form of sulphur dioxide gas. Under normal atmospheric conditions sulphur dioxide is oxidised to sulphuric acid particles during a day or so. However in the Arctic winter and very far from the sources sulphur is, as already shown in Fig. 4.1, still found as a mixture of both gaseous and particulate phases (see also Barrie and Hoff, 1984). For that reason elemental sulphur was not included in the aerosol oriented receptor model on the 1994 and 1995 data from Station Nord, and so the combustion source strengths were determined by the other measured combustion trace elements (Mn, Ga, V, Ni, Cr, Se, As, Zn and Pb). The calculated combustion source strengths are compared in fig. 4.11 with particulate sulphur concentrations measured as sulphate/sulphuric acid (SO_4-S), and with total sulphur ($[SO_2 + SO_4]$-S) including sulphur dioxide. It can be seen that total sulphur correlates better with the other combustion elements ($r^2 = 0.74$), than sulphate/sulphuric acid do alone ($r^2 = 0.56$).

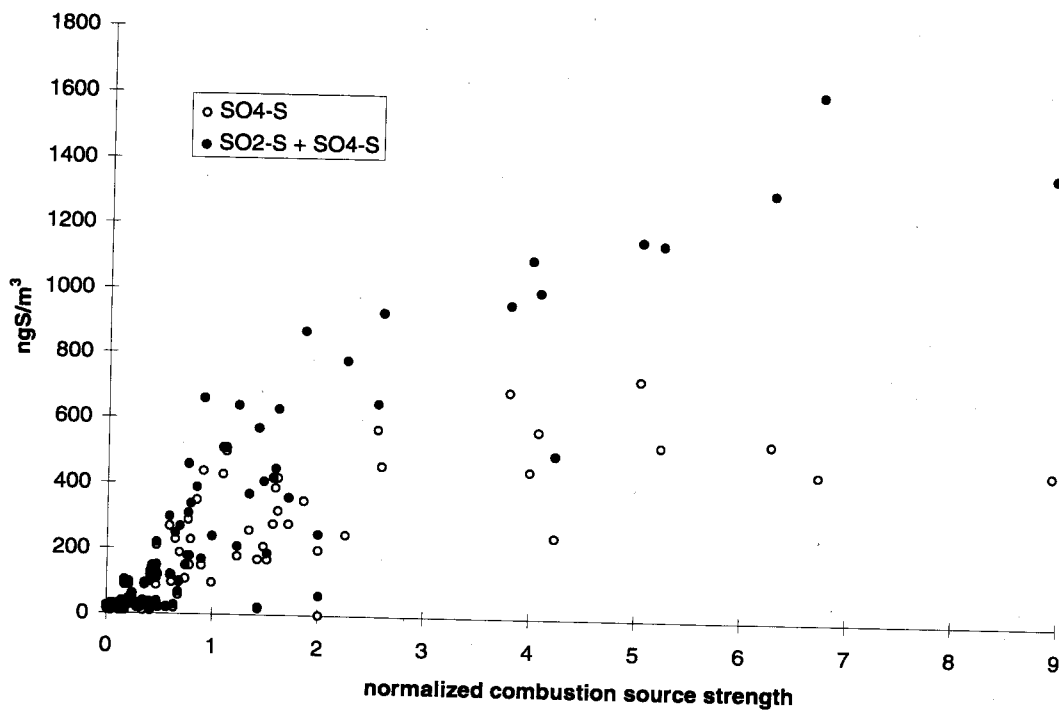Fig. 4.11. Receptor model strengths of the combustion source compared with concentration of sulphur as sulphate/sulphuric acid (SO_4-S), and as total sulphur ($[SO_2 + SO_4]$-S).

4.2.5 Source apportioning

Source strengths

The normalised source strength signals with mean values of unity are plotted in Fig. 4.12. The seasonal variations show that the influences by the sea, the combustion, and the metal sources are much more important in the winter half-year than in the summer half-year. In contrast, the soil source has high peaks in late summer, probably due to local windblown dust raised from the bare ground after the melting of the snow-cover.

Source impacts

The measured mean values in the two-year period 1994-95 are shown in Table 4.3 along with mean source contributions apportioned by the model. It is seen that in most cases the model can account for a major part of the measured values. The source contributions to the individual samples (shown as dotted lines in Figs. 4.5 - 4.11) have been constructed by multiplying the source strengths in Fig. 4.12 by the source mean concentrations in Table 4.3. The model operates with source profiles that are constant for all samples. In the real world there is no reason to expect this to be true, but the general fit of the 4 sources to the 19 elements is nevertheless reasonably good.

Arctic pyrometallic sources

The very low concentrations of both total ammonium and total nitrate compared to sulphate and sulphur dioxide (see table 4.1) indicate that the air pollution detected in Northeast Greenland is emitted from sources that are different from important pollution sources in northern Europe, cf section 4.1. If the main sources are pyrometallurgical non-ferrous metal smelters and other gross sulphur emitters in the Arctic, or close to the Arctic, (*e.g.* Norilsk, the Kola Peninsula and the Ural region), it might be possible to explain both the high

sulphur content, the high fractions of sulphur found in mid-winter as sulphur dioxide (*e.g.* non-oxidised due to the lack of sunlight), and the frequent impacts of copper and nickel (the metal source).
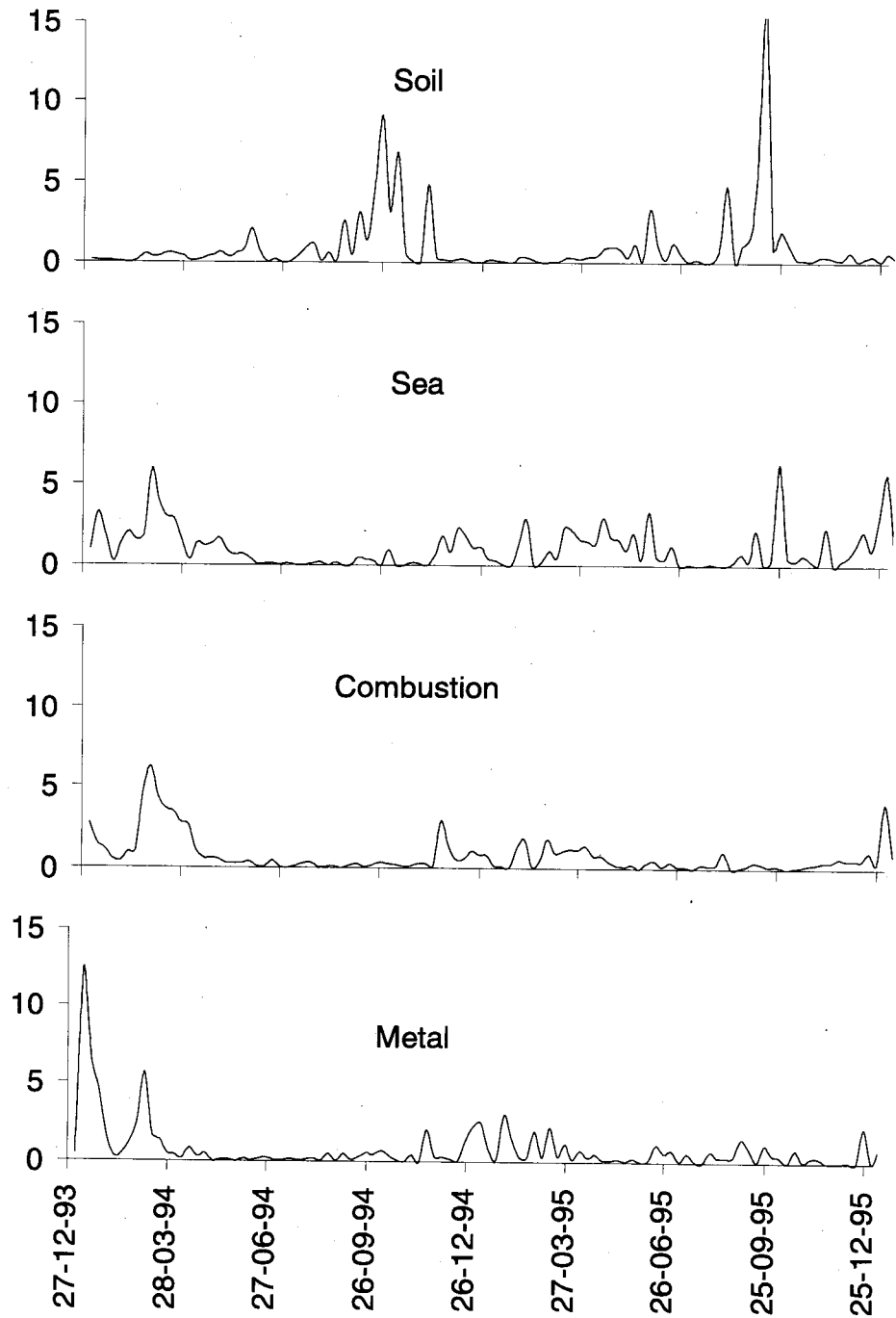

Fig. 4.12 The seasonal variation of the normalised source strengths signals in 1994 and 1995 at Station Nord.

Table 4.3 Mean aerosol concentrations at Station Nord, averaged over the period 1994-1995, with contributions from different sources apportioned by receptor model analysis.

ng ,m^{-3}	Total Measured	Soil	Sea	Combustion	Metal	Other
Al	32.00	29.00	-	1.00	-	-
Si	134.00	117.00	-	8.00	-	-
S	166.00	-	15.00	150.00	-	-
Cl	(20)*	-	321.00	-	-	-
K	26.00	11.00	6.00	4.00	-	-
Ca	28.00	18.00	7.00	2.00	-	-
Ti	3.10	3.10	-	0.10	-	-
V	0.26	0.10	-	0.16	-	-
Cr	0.11	0.04	-	0.06	-	-
Mn	0.53	0.38	-	0.15	-	-
Fe	34.00	30.00	-	3.00	-	-
Ni	0.18	0.01	-	0.07	0.07	-
Cu	0.46	-	-	0.06	0.35	-
Zn	1.35	-	-	0.72	0.45	-
Ga	0.03	0.01	-	0.01	-	-
As	0.16	-	-	0.14	-	-
Se	0.03	-	-	0.02	-	-
Br	3.60	-	1.10	-	-	2.60+
Rb	0.17	0.08	-	0.07	-	-
Sr	0.29	0.10	0.14	0.03	-	-
Zr	0.13	0.11	-	0.01	-	-
Pb	0.75	0.01	-	0.63	-	-

* The low measured value is caused by evaporation of hydrochloric acid from the filter.
+ non-sea-salt bromine.

4.1 Tropospheric ozone

4.1.1 Ozone and other pollutants

Experimental technique

Ozone is measured by two API-400 UV-absorption ozone monitors as 10 minutes mean values which are averaged to half hour values. The detection limit is 1 ppbv (3 times std. on laboratory blank). The uncertainty of the measurements above 10 ppbv is 1.5 % and below 10 ppbv it is 3 % (2 x std. on certified reference standard ozone sources).

Seasonal variations

Ozone concentrations from March 1995 when the measurements started until the end of June 1996 are shown in Fig. 4.13. The missing values at Spring 1996 is due to problems with the PC which overwrote a series of data.. The ozone concentration is observed to vary strongly in springtime during the polar sunrise, notably in episodes of depletion where it falls from about 45 ppbv to below detection limit. After this highly perturbed period the ozone concentration is stabilised in June at about 25 ppbv without any diurnal cycle which is normally observed at lower latitudes. The ozone concentration increases slowly during the following months to reach about 45 ppbv again just before the next polar sunrise in the beginning of March 1996 where a new perturbation period of ozone depletion episodes starts.

The slow build up of ozone which continues in the dark period cannot be explained by in situ chemistry but must be due to transport of ozone from aloft or from lower latitudes to the Arctic region.
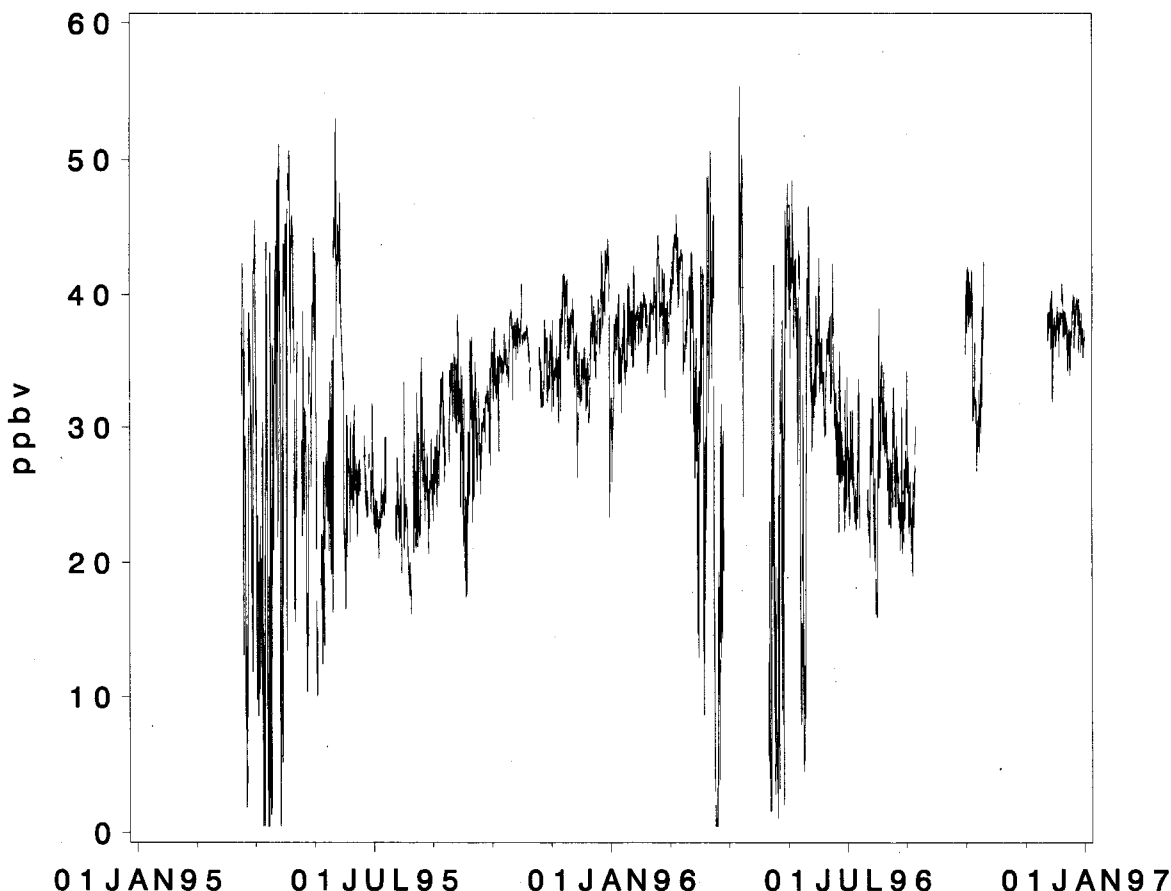
Figure 4.13 Half hour average ozone concentration at Station Nord in Northeast Greenland. Notice the strong perturbation periods during spring.

4.1.2 Processes controlling Arctic ozone

Ozone chemistry

Ozone chemistry in the troposphere is mainly controlled by the concentrations of NOx (NO + NO_2), non methane hydrocarbons and sunlight. However, several authors and latest, Anlauf *et al.* 1994 and Solberg 1996 observed ozone depletion during the polar sunrise in the Arctic MBL (marine boundary layer) which could not be explained by this type of chemistry. Instead of, it was suggested that Br atoms are responsible for the removal of ozone by a catalytical cycle:

$$Br_2 + hv \rightarrow 2Br$$

$$O_3 + Br \rightarrow BrO + O_2$$

$$BrO + BrO \rightarrow Br_2 + O_2$$

netto $\quad O_3 + O_3 \rightarrow 3O_2.$
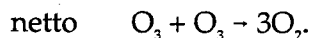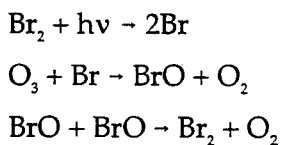
This mechanism is now generally accepted. However, the source of atomic bromine in the Arctic troposphere is still unclear, although several possibilities have been suggested. First Barrie *et al.* (1988) and

Bottenheim et al. (1990) proposed that photolysis of organic bromides and e.g. bromoform could be an important source. However, the authors showed that the observed amount of organic bromide and the known photolysis rates are not sufficient to give high enough levels of Br atoms to account for the observed ozone depletion rate. Heterogeneous formation of BrNO and $BrNO_2$ from NaBr with NO_2 and N_2O_5, respectively, are suggested as sources of Br atoms through fast photolysis. However the concentration of NO_2 in the Arctic is very low during ozone depletion and the reaction of NO_2 is most probably of minor importance (Finlayson and Johnson, 1988, Finlayson-Pitts et al. 1989, 1990, Sturges, 1989).

Other processes

It has also been proposed (McConnel et al. 1992) that bromine can be activated not from only sea salt aerosols but also from the snow pack which have received deposition of sea salt aerosols during the winter. The catalytical reaction cycle shown above is interrupted by the reaction of Br atoms with organic compounds with easy extractable hydrogen atoms as aldehydes to form BrH and BrO with OOH to form BrOH which represent an inactive form of bromine. Reactivation of BrH and BrOH is therefore important for the amount of Br atoms available for reaction 1.Several authors also pointed out that meteorological modulation may play a crucial role in the ozone depletion (Gong et al. 1997).

Ozone depletion

The ozone depletion during the polar sunrise observed at Station Nord in the Northeast Greenland is similar to previous observations at Alert, at Narwhal ice floe (Shepson et al. 1996), and at Spitsbergen (Solberg et al., 1996). The abrupt changes in the concentration indicate that the phenomenon is of local origin or alternatively, that the observation is on the edge of an area with large scale destruction of ozone. However, it can be concluded that ozone depletion must be an ubiquitous event in the Arctic, but further studies are needed to clarify if it is due to many small local events or if it is a large scale process covering most of the Arctic.

Possible bromine sources

In the Arctic spring during ozone depletion, filterable (F-)bromine has the same time variation as sulphate and therefore F-bromine has a maximum concentration in the early Spring (Fig. 4.14). At midlatitudes the source of F-bromine is nearly 100% sea spray with anthropogenic emissions of negligible importance. In the Arctic the sea spray source of bromine is only of minor importance (see Fig. 4.10 and Table 4.3) so the major source of F-bromine cannot be identified by the receptor model. The discrepancy is largest in late winter and early spring. The source of bromine in the Arctic may be organic bromides and liberation of bromine from the snow pack. Local sea salt particles cannot be an important sources of bromine in the atmosphere, but in processed air bromine may have been liberated initially from freshly formed airborne sea spray particles before deposition.

Anticorrelation of ozone and bromine

An anticorrelation between daily mean concentrations of F-bromine and ozone has been reported (Barrie et al. 1988). In this study a similar anticorrelation could not be observed most probably because of

the limited number of observations and the low time resolution of 1 week in the filterpack measurements compared to the ½ hour resolution of the ozone measurements. However, the observations here confirm that also at Station Nord ozone depletion occurs during polar sunrise in the presence of high F-bromine concentrations.

Background ozone concentration

The slow build up of ozone during autumn and winter at Station Nord can be explained by transport of ozone rich air from lower latitudes into the Arctic. During the polar sunrise ozone is depleted. It is unknown at present to which degree this depletion is responsible for the observed difference in the ozone level before (45 ppbv) and after (25 ppbv) the polar sunrise or if the different levels shall be explained by the traditional chemistry of VOC, NO_x and sunlight as well as horizontal and vertical advection of air masses. In the northern Hemisphere the photochemical background concentration of ozone in spring is estimated to be 24±6 ppbv in spring (Skov *et al.* 1997) based on measurements in Europe and North America at middle latitudes. Only time will show whether the observed concentration of 25 ppbv at Station Nord is in support of this estimation or whether the agreement is incidental.
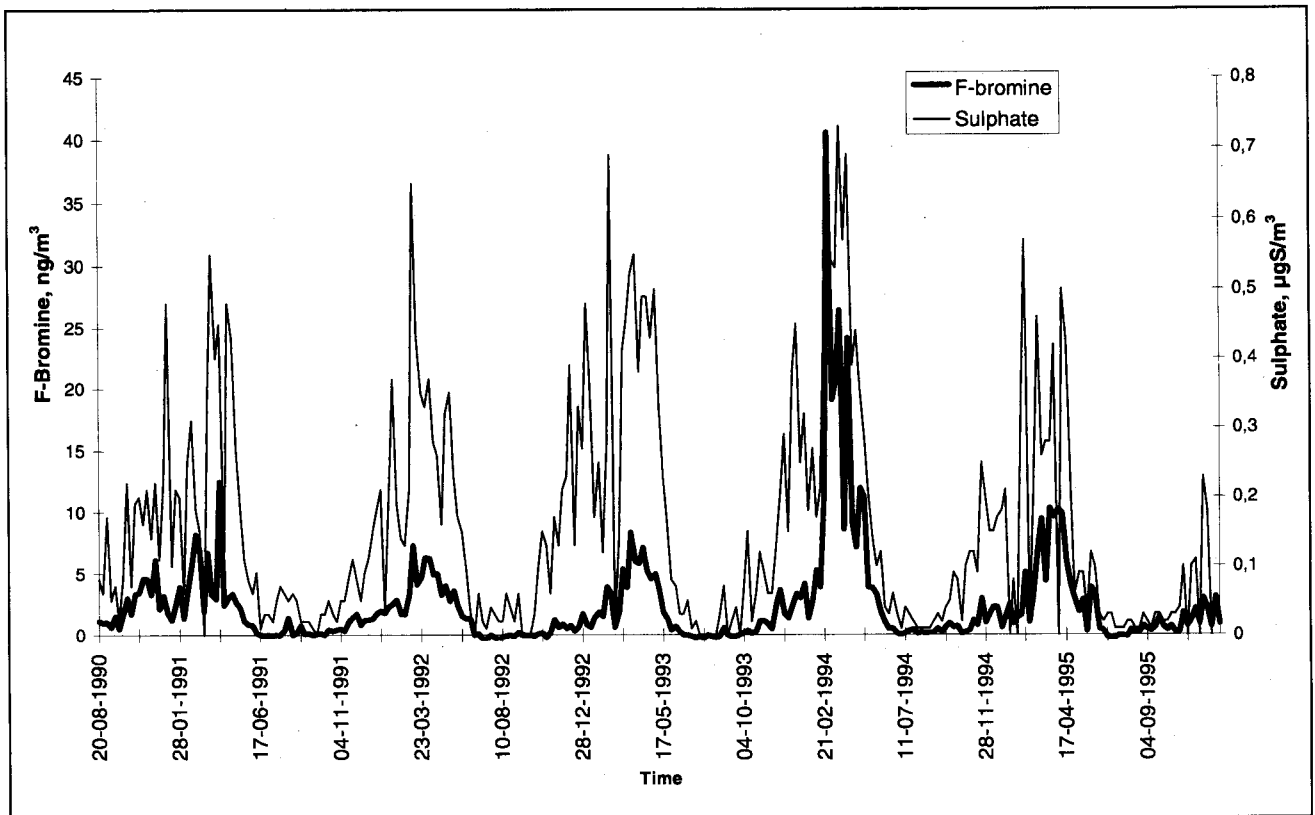

Figure 4.14 Sulphate-S and F-bromine concentration at Station Nord in Northeast Greenland

5 Transport model calculations

5.1 Model principles

Atmospheric processes

A model is a tool for the study of processes and mechanisms, and one of the aims is the reproduction of measurements. This tool should therefore take into account all processes, which the concentrations depend on. The air pollution in the Arctic depends on the emissions from the sources, transport from the emission areas into the Arctic by the wind, dispersion of the pollution by diffusion, chemical transformations during the transport, removal of pollutants due to precipitation and deposition on the surface. A model for the Arctic must take into account all these physical and chemical processes. The different processes must be described very precisely to reduce the uncertainties in the model. It is only possible to handle such a model on a computer, because the processes and the interactions between the different processes are very complex.

Models as tools

There are several reasons why one should use a model. A model is a good tool for improving the understanding of the atmospheric transport pathways to the Arctic. In the development of a model there are strong interactions between measurements and model calculations, where the measurements are used to verify the model. After development the model can be used for interpretation of the measurements, performed in the Arctic, and also to find outliers in the data. A model can be used to normalise the measurements relative to the meteorological factor, *i.e.* estimate the variations in the measurements that are due to changes in the meteorological conditions and variations due to changes in the emissions. Also the contributions from the different sources in the Northern Hemisphere to the Arctic pollution can be estimated by the model. The model can be used together with measurements (which are point measurement) to estimate the distribution in space and time of the air pollution concentrations and depositions. Finally, when the transport part of the model is developed, the model can be expanded to other chemical species, which are not measured in the atmosphere in the Arctic, *e.g.* Persistent Organic Pollutants and Heavy Metals. The only requirement for this purpose is reliable emissions fields.

Hemispheric Sulphur model

The model used for the Danish atmospheric programme under AMAP is a large, comprehensive, three-dimensional mathematical model of Eulerian type. It is referred to as DEHM, the Danish Eulerian Hemispheric Model. The model is presently capable of calculating the transport and transformations of sulphur (as SO_2 and SO_4^{2-}) to the Arctic from all significant anthropogenic and natural sources in the Northern Hemisphere.

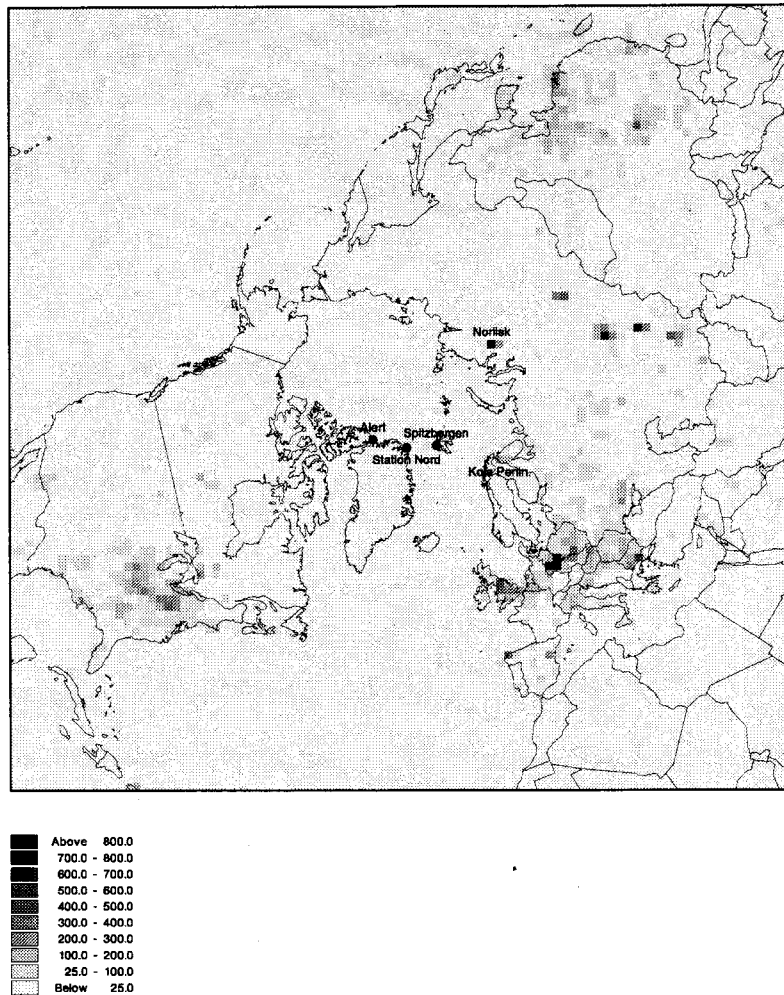|	
■	Above 800.0
■	700.0 - 800.0
■	600.0 - 700.0
▨	500.0 - 600.0
▨	400.0 - 500.0
▨	300.0 - 400.0
▨	200.0 - 300.0
▨	100.0 - 200.0
▨	25.0 - 100.0
☐	Below 25.0

Fig. 5.1. The anthropogenic emissions of Sulphur in ktonnes/ (grid-square*year); 1 grid-square equals 22500 km^2 at 60°N. The locations of Station Nord in Northeast Greenland and several other sites mentioned in the text are indicated on the map.

5.2 Emissions

Anthropogenic emissions

The emissions of anthropogenic sulphur are based on the global GEIA inventory of sulphur emissions, version 1A.1, for 1985 on a 1°x1° grid (Benkowitz et al., 1996) . These emissions are redistributed to the grid used in the model (see Fig. 5.1). The EMEP emissions for 1990 (Sandnes and Styve, 1992) are used for the part of the grid, which is equal to the EMEP grid in Europe. The emissions are distributed evenly up to 800 m above the surface. There are no seasonal variations of the emissions. The important anthropogenic sources for the Arctic are the large industrial complexes at Norilsk and in the Kola Peninsula (see Fig. 5.1), which both have large copper-nickel smelters, and the rest of the emission from the former USSR. The total emissions for 1990 from Norilsk was about 1.2 million tonnes S and for the Kola Peninsula it was about 0.4 million tonnes S, which can be compared to the total emissions in Europe, which was about 22 million tonnes S. It is, however, a big question how representative these emissions are after the economical break down of the former USSR.

Natural emissions

Natural emissions of dimethyl sulphide (DMS) from the open oceans and shelf waters are also included in the model. They depend on the concentrations of DMS in the oceans and the windspeed in 10m (*e.g.* Tarrason *et al.*, 1995, Christensen, 1997). In the summer period, where there is open water in the Arctic and large biogenic activity of phytoplankton, the natural emissions of DMS could contribute to a large part of surface concentrations of sulphur in the Arctic. In the model it is assumed, that 44% of the DMS flux is transformed to SO_2 and 4% to SO_4^{2-} (Hertel *et al.*, 1994).

5.3 Model description

Spatial 3D grid

In the model the Northern Hemisphere is transformed to a plane, using the polar stereographic projection system true at 60° North (Christensen, 1995). The horizontal space of the model is defined on a regular 96x96 grid that covers most of the Northern Hemisphere with a grid-distance of 150 km at 60°N (*i.e.* the horizontal resolution of the emissions is 150km x 150km), and the vertical space is defined on an irregular grid with 12 grid-points, which cover most of the troposphere up to 7 km above the surface.

Meteorological data

Meteorological parameters are obtained from the European Centre for Medium-range Weather Forecasts (ECMWF) in England, ECMWF/TOGA Basic Level III data sets and the supplementary sets on a 2.5°x2.5° grid. All the meteorological data are interpolated to the grid used in the model. The data are given with a time resolution of 6 hours for the cloud cover, wind stress and the heat flux (the last two are accumulated fields) and 12 hours for the other fields, which are 3-d wind, temperature, humidity and geopotential for the upper levels (1000hPa, 850hPa, 700hPa, 500hPa, 400hPa, 300hPa, 250hPa, 200hPa, 150hPa, 100hPa, 70hPa, 50hPa, 30hPa, 10hPa, after 1. January 1992 also 925 hPa data are available) and 10 meter wind, 2 m temperature, 2 m dewpoint, and pressure, temperature, and geopotential for the surface level.

Advection

The transport due to the wind (advection) is a very important process, because it is the wind which is the main reason for the air pollution in the Arctic. The advection is calculated using the 3-d wind fields from the meteorological input.

Diffusion

There is also a small horizontal diffusion in the model to simulate the dispersion of the transported air pollution. This process is not very important. The vertical diffusion is however an important process, because it disperses the emissions inside the planetary boundary layer. The planetary boundary layer is a layer at the surface, which is under influence of the surface and where there is some vertical diffusion. Above the planetary boundary layer the vertical diffusion is small. The vertical diffusion in the boundary layer disperses the pollution within this layer. The height of the planetary boundary layer and the diffusion depend on the windspeed, roughness of the surface, and the heat flux from the surface. In the summer, where the sun heats the surface, there is a large heat flux from the surface, which results in a large boundary layer height and in a large vertical diffusion inside the boundary layer. In the Arctic night the opposite

is often the case, because here the surface is smooth due to the ice/snow and there is a cooling of the surface. This results in a low planetary boundary layer height and a very stable atmosphere with small vertical diffusion. Therefore in the Arctic pollution is often confined to thin layers where it occurs in high concentrations (Arctic Haze).

Sulphur chemistry

The chemistry of SO_2 is rather complex with many non-linear gas- and aqueous-phase reactions, which depend directly or indirectly on the solar radiation. Therefore there is a large difference in the chemistry in the Arctic troposphere between the summer period, where the sun is shining the whole day, and the winter where there is no solar radiation. Since it is not possible to incorporate all this non-linear chemical reactions in the model, it has been assumed that the chemistry can be described as linear, where the oxidation rate of SO_2 to SO_4^{2-} depends on the height of the sun at midday. This spatial and temporal variation of the oxidation rate simulates the variations of OH-radicals in the gas phase and H_2O_2 and O_3 in the aqueous-phase, all depending on the solar radiation. The maximal oxidation rate is about $5.6 \cdot 10^{-6}$ s^{-1}, when the sun is at zenith at midday (life time for SO_2 is about 2 days), and the minimal rate is $0.3 \cdot 10^{-6}$ s^{-1} in the Arctic night (life time for SO_2 is about 40 days).

Removal processes

The atmospheric concentrations in the Arctic depend critically on the removal processes. The reason for this is that the lifetimes of SO_2 and SO_4^{2-} are comparable with the transport time to the Arctic, therefore even small changes in the removal processes (either wet or dry removal) results in large changes of the calculated concentrations. In regional models, *e.g.* for Europe, the concentrations are not so dependent on the removal rates because the transport time is lower than the lifetime due to the removal processes.

Wet deposition

One important removal process for both SO_2 and SO_4^{2-} is the wet deposition process that depends on the amount of precipitation. In the real atmosphere the wet deposition is complex, because aqueous-phase chemistry and cloud physics are involved. But in the model the wet deposition is parameterized through a simple scavenging ratio formulation with two different scavenging ratios: a high in-cloud and a low below-cloud scavenging ratios (Tarrasón and Iversen, 1992; Christensen, 1994, 1995, 1997; Jakobsen *et al.*, 1995). The lifetime for SO_2 at a precipitation rate of 1 mm/h is 3.3 hour for in-cloud removal and 6.7 hour for below-cloud removal, while for SO_4^{2-} they are 1.4 hour and 10 hours, respectively. One big uncertainty is the lack of information about precipitation. Therefore the calculated wet deposition is very uncertain, because the amount of precipitation at a given time at a given place is not known. Instead a condensation scheme is applied. Two parts of the condensation scheme described by Sundqvist *et al.* (1989), the stratiform precipitation and a simple parametrisation of convective precipitation, are included in the model in order to reduce the lack of information about the precipitation. This will give a more physically correct description of precipitation, where transport of humidity and cloud water, lifetime of different types of clouds, evaporation of cloud water or rain drops, are all taken into account (Christensen, 1994, 1995, 1997).

Dry deposition

The dry deposition is another important removal process for the Arctic area. This only takes place at the surface. The dry deposition depends on the flux through three layers (see *e.g.* Voldner *et al.*,1986).

1. The flux through the lowest turbulent layer that are few meters above the surface to the small laminar layer over the surface (turbulent flux). This flux depends on the turbulence in the layer, *i.e.* the wind speed and the roughness of the surface. The hemispheric model distinguishes between 8 different surfaces: Coniferous and deciduous forest (high roughness), cultivated and grass land (low, depending on season), urban (high), swamp (low, depending on season), ice/snow (low) and open water (depending on wind speed).

2. The flux trough the small laminar layer just above the surface (laminar flux). This flux depends on the windspeed, roughness of the surface and the molecular diffusivity of the species (for particles, *i.e.* SO_4^{2-}, this flux is low and therefore the dry deposition is limited by this flux, except over open water, where the size of the sulphate particles could be changed due to uptake of humidity (Slinn and Slinn, 1980). In this case the deposition is only limited by the turbulent flux).

3. The flux through the surface (*i.e.* the uptake from the surface), which depends on the types of surfaces. For water the flux is assumed to be infinity, *i.e.* the total deposition is only depending on 1 and 2, while for other surface types this flux depends on the stomata activity in ground vegetation. In an urban area the flux is low, and over ice/snow below -2° C the flux is very low for SO_2, *i.e.* the dry deposition of SO_2 to ice or snow is negligible.

Long deposition lifetimes

In the Arctic areas the amount of precipitation is low, which means that the lifetime due to wet removal is long. In the winter the same is true for the lifetime due to dry removal. The atmospheric lifetimes related to deposition processes in the Arctic are estimated to be 14 days or longer.

5.4 Uncertainties in the model calculations

Emission uncertainties

There is a large uncertainty concerning both the natural emissions and the anthropogenic emissions. The natural emissions are perhaps uncertainties with up to a factor 2-3. The uncertainties of the anthropogenic emissions are also large. To each grid-square on 150kmx150km, which *e.g.* for Europe may contain many different sources, there is only one number for the total annual emission. This total annual emission has an uncertainty of up to 30-40%. On a shorter timescale (a month) the uncertainty is even greater. In addition the emission data for the former USSR have not been updated since 1985. Another uncertainty in the model is due to the stochastic behaviour of the atmosphere.

40

Transport uncertainties	After the release of emissions the horizontal transport takes place. The original wind fields are on a latitude-longitude grid on $2.5°\times2.5°$ and for 14 vertical levels from 1000 hPa to 10 hPa with a time resolution of 12 hours between each windfield. In practice it turns out that these 3-d wind fields (both the horizontal and the vertical) are sufficient to describe the transport of a plume over a distance of more than 2000 km.
Removal uncertainties	Precipitation is very efficient in removing SO_2 and SO_4^{2-} from the atmosphere. Therefore uncertainties in the precipitation in the model have a major influence on the concentrations both on short scale (daily mean) and on longer timescale (monthly mean).

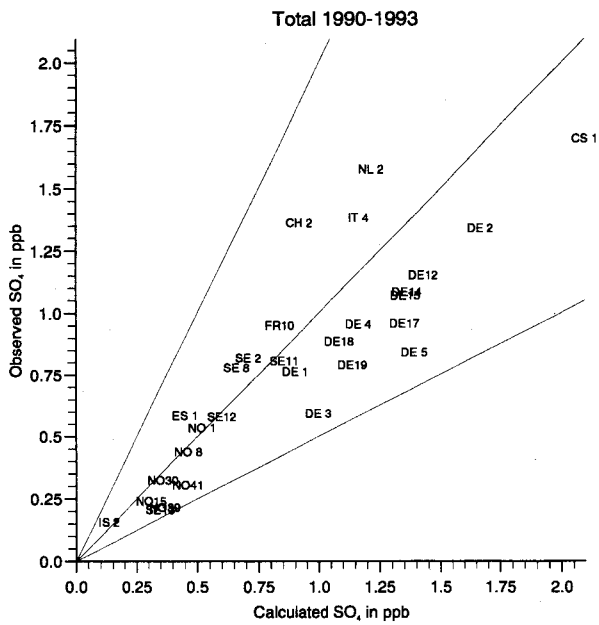## 5.5 Calculated concentration and depositions fields

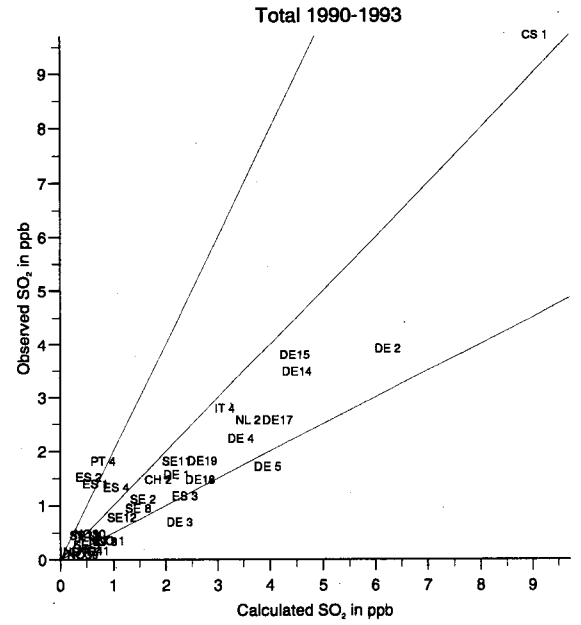|	
Six years	The model has been run from October 1990 to May 1996. All the concentrations are given in ppbV, where 1 ppbV = 1,35 µg S/m^3 at standard temperature and pressure.
Model and measurements in Europa	The calculated concentrations of SO_2 and SO_4^{2-} in the European part of the model have been compared with the European measurements of EMEP. These comparisons show that there is good agreement between the calculated and measured concentrations, both on seasonally, monthly and even daily basis for many EMEP stations (Christensen 1995, 1997). For the wet depositions and precipitation the agreement is not as good as for the air concentrations, mainly because it is very difficult to calculate the right amount of precipitation at the right time. Fig. 5.2 shows two scatter plots with the total calculated and observed mean concentrations of SO_2 and SO_4^{2-} for the period from October 1990 to December 1992 for those EMEP stations, which have measured continuously for the whole period. This figure shows that there is good correlation between observed and calculated mean concentration of SO_2 and SO_4^{2-} in Europe.
Model and measurements in the Arctic	For the Arctic area the model has been compared with measurements from three sites: Station Nord in Northeast Greenland (81° 36′ N, 16° 40′ W) for the whole period (Wåhlin, 1993), Ny-Ålesund at Spitzbergen (78° 54′ N, 11° 53′ E) from October 1990 to December 1993 (Schaug *et al.*, 1992, 1993, 1994; Lövblad *et al.*, 1995), and Alert in Northwest Territories, Canada, (82° 50′ N, 62° 30′ W) for the period from October 1990 to June 1993 and only of SO_4^{2-} (Li and Barrie, 1993). For all three stations there is a reasonably good agreement between the calculated and observed concentrations of SO_2 and especially for SO_4^{2-}, see Fig. 5.3, Fig. 5.4 and Fig. 5.5.

Total 1990-1993 (left plot, Observed SO₄ in ppb vs Calculated SO₄ in ppb)

Total 1990-1993 (right plot, Observed SO₂ in ppb vs Calculated SO₂ in ppb)

NUMBER OF STATIONS IS	29
COMPUTED MEAN	0.91
OBSERVED MEAN	0.81
CORRELATION FACTOR	0.87

NUMBER OF STATIONS IS	31
COMPUTED MEAN	2.28
OBSERVED MEAN	1.74
CORRELATION FACTOR	0.91

Fig. 5.2. Scatterplots for the comparison between the average concentrations from October 1990 to December 1992 of SO_2 and SO_4^{2-} as monitored by EMEP and calculated by DEHM

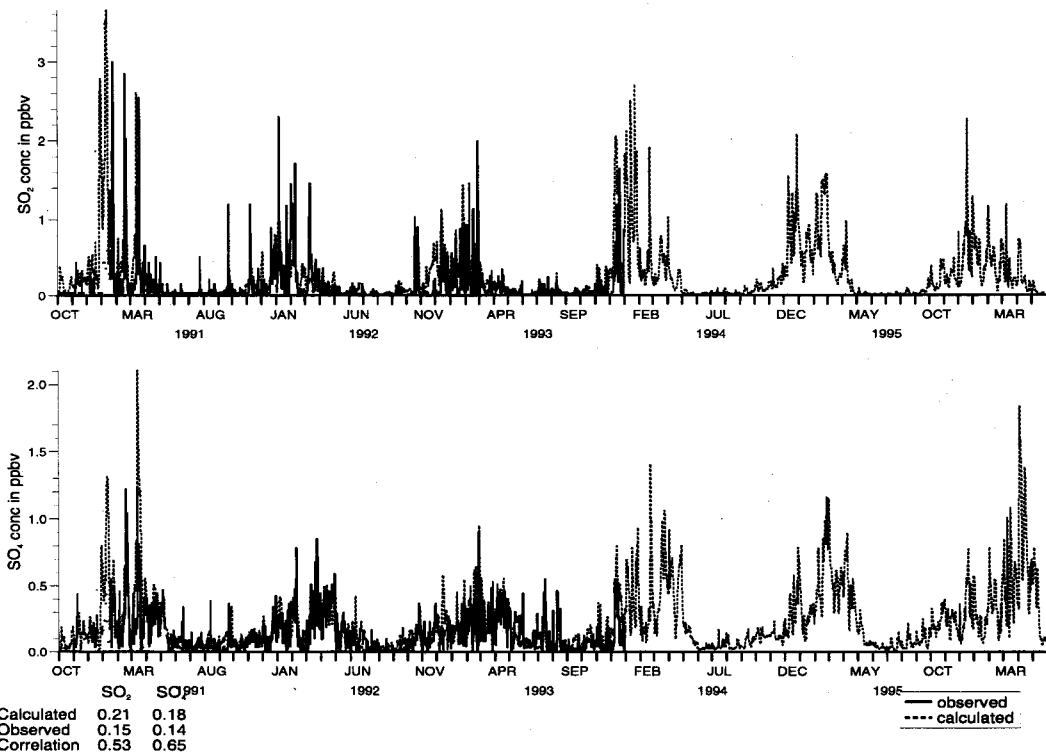|	SO_2	SO_4
Calculated	0.21	0.18
Observed	0.15	0.14
Correlation	0.53	0.65

—— observed
---- calculated

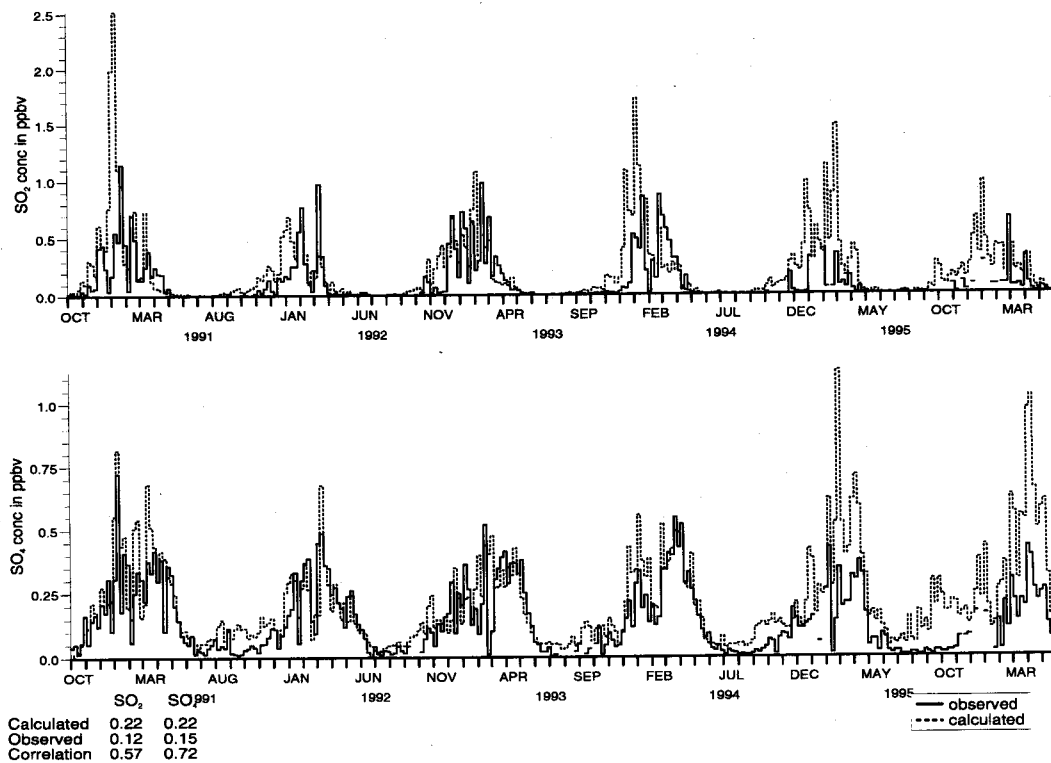Fig. 5.3. Comparisons between observed and calculated daily mean of SO_2 and SO_4^{2-} for Ny-Ålesund at Spitzbergen.

Fig. 5.4 Comparisons between observed and calculated weekly mean of SO_2 and SO_4^{2-} for Station Nord in Northeast Greenland.
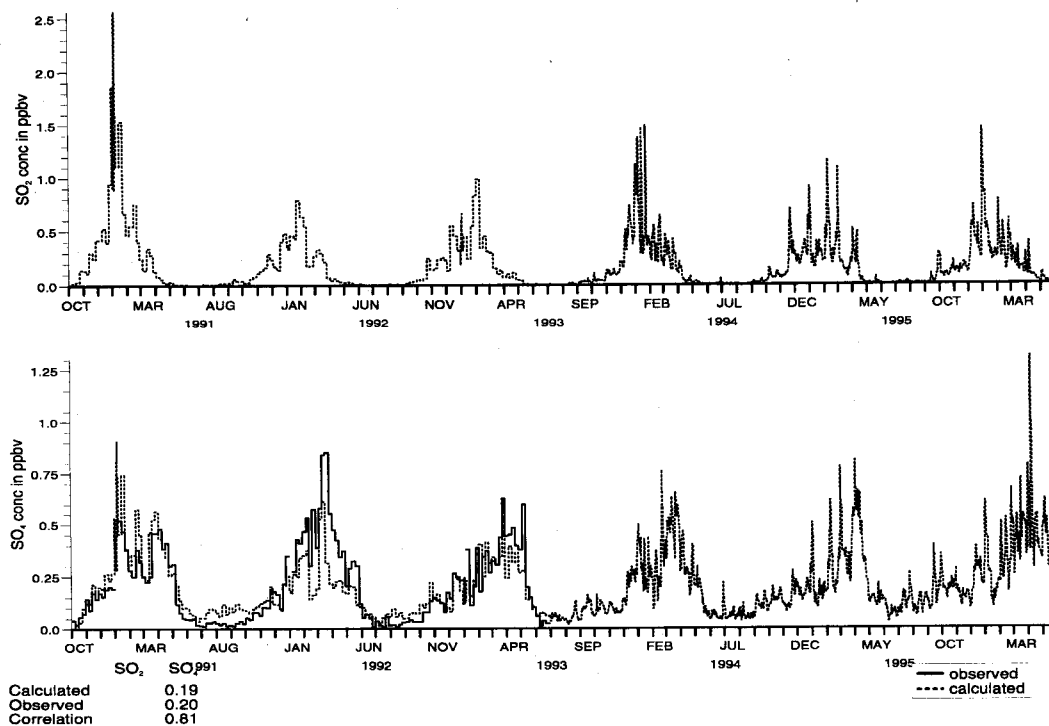

Fig. 5.5. The calculated SO_2 and the comparisons between observed and calculated weekly mean of SO_4^{2-} for Alert, Northwest Territories, Canada.

Overestimated emission

Since the summer of 1994 the model seems to overestimate the concentrations measured at Station Nord by a factor of about 2. There is however still a good correlation of the time variation, especially for SO_4^{2-}. The reason for these discrepancies could be the use of 1985 emissions for the former USSR for the whole period, which may not be correct after the economical break down in USSR.

Mean Sulphur concentrations

In Fig. 5.6 the mean concentrations of SO_2 and SO_4^{2-} are shown for the surface level calculated for the period from October 1990 to May 1996. The results show, especially for SO_2, how the Arctic area is under influence of emissions from especially Norilsk and the other parts of Russia, and that the influence from the sources in North America is of minor importance. The main pathway for transport of sulphur is from Europe in an easterly direction to Russia and then north into the Arctic. This will be shown later in a discussion about the contribution from the different sources to the Arctic sulphur pollution.
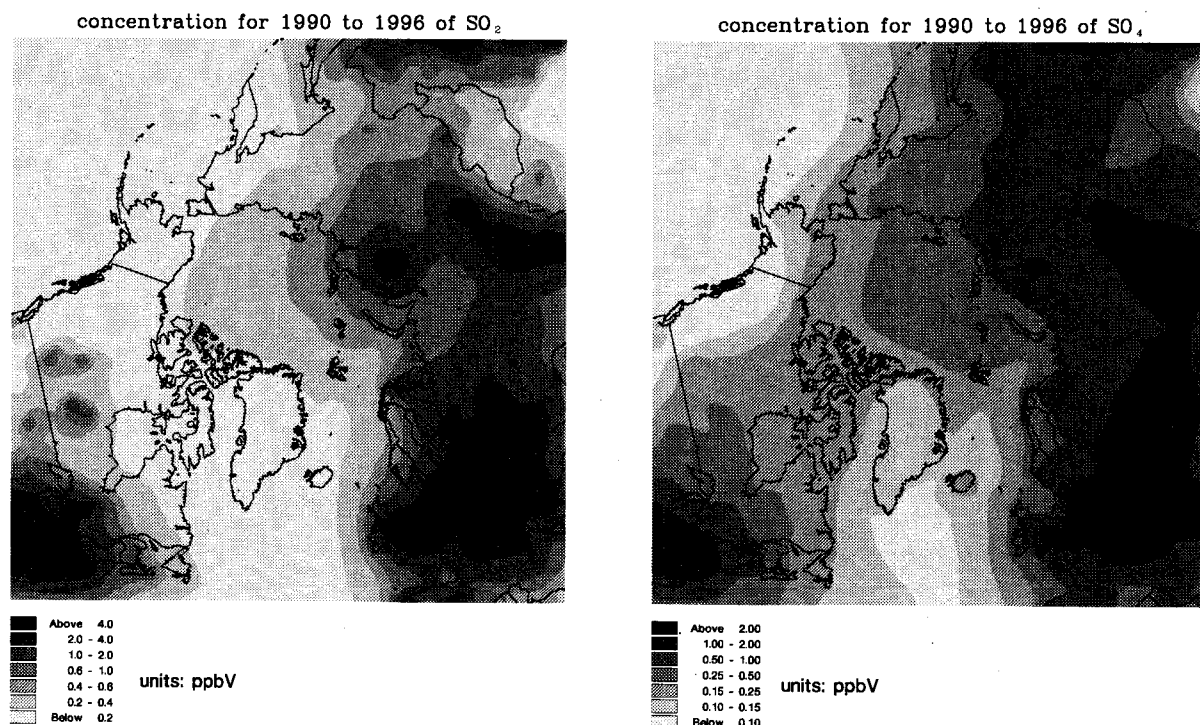
concentration for 1990 to 1996 of SO_2 concentration for 1990 to 1996 of SO_4

Fig. 5.6. The mean distribution from October 1990 to May 1996 of SO_2 (left) and SO_4^{2-} (right) for the surface level in ppbV

Total Sulphur deposition

The total deposition of sulphur for the whole period is shown at Fig. 5.7. This figure shows that the total deposition in the Arctic is relative small, from about 20 mg S m^{-2} ·month^{-1} in the Russian Arctic to less than 4 mg S m^{-2} ·month^{-1} in the Canadian Arctic. This is also the reason for the relatively high concentrations of sulphur in the Arctic troposphere. If the deposition was higher, then concentrations levels would be much lower. There are two areas with depositions larger than 50 mg S m^{-2} ·month^{-1}. These are the Norilsk area and the Kola Peninsula. Close to the smelters the depositions are even higher, but this could not be resolved by the model because of the grid resolution of 150km x 150km. For comparisons the deposition in Denmark is ≈ 100 mg S m^{-2} ·month^{-1}.

Total deposition for 1990 to 1996 of S

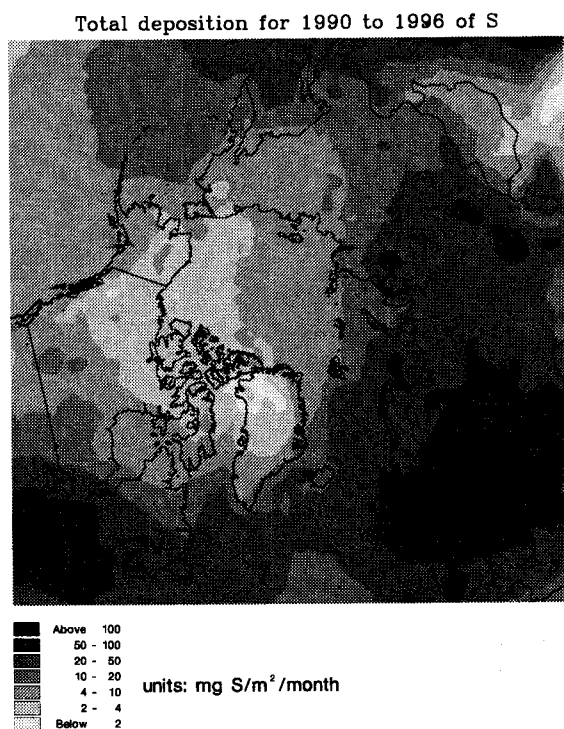|	
Above	100
50 -	100
20 -	50
10 -	20
4 -	10
2 -	4
Below	2

units: mg S/m^2/month

Fig. 5.7. The total deposition of sulphur for the period from October 1990 to May 1996 in mg S m^{-2} ·month^{-1}
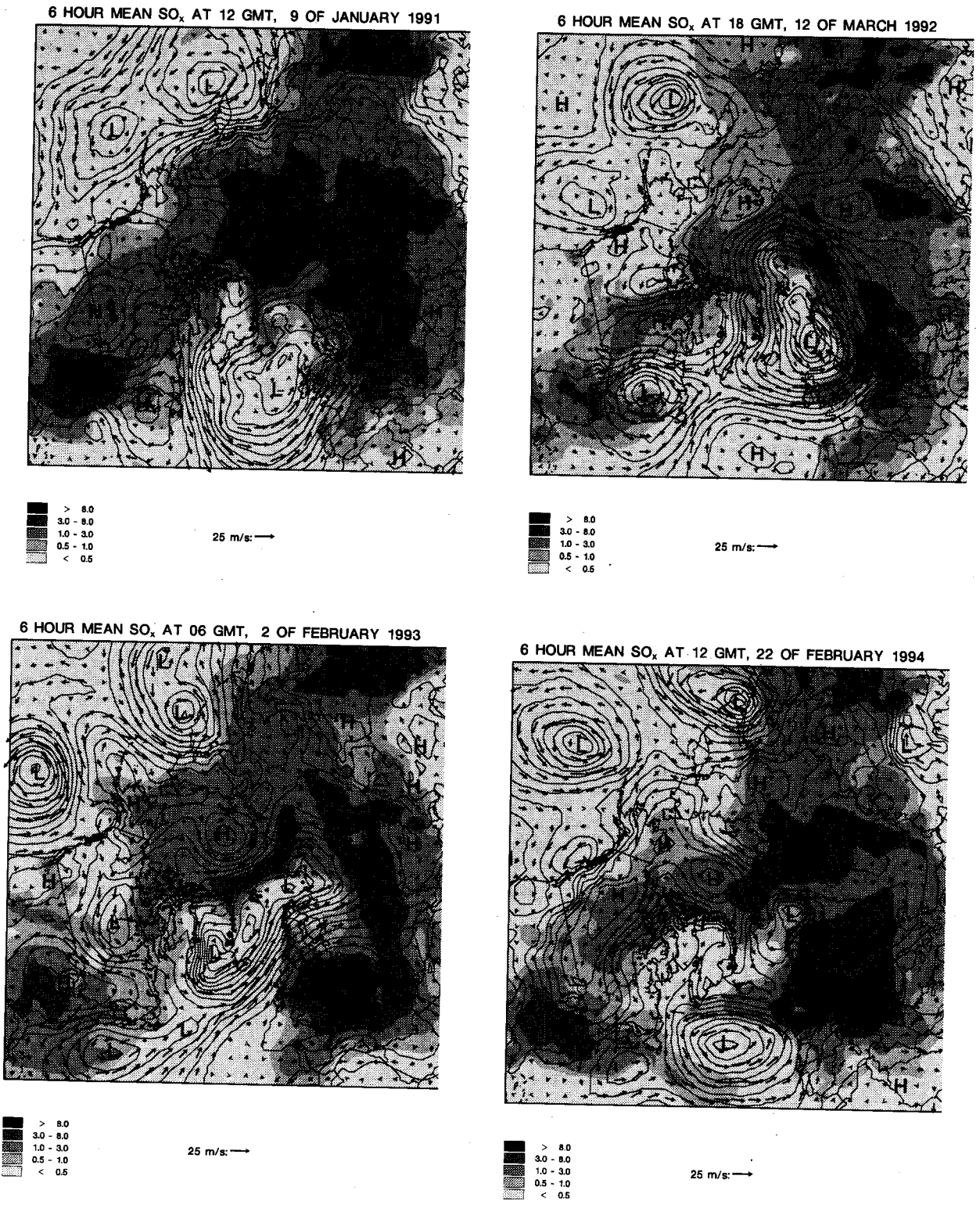
Fig. 5.8. Four examples of transport of SO$_x$ to the Arctic. The concentrations are for the surface level in ppbV, the contour lines are the mean-sea level pressure, and the windfield is at 600 m height.

Episodic winter transport
to the Arctic

There are two necessary conditions for transport of pollution in the surface levels to Arctic. 1) The horizontal wind must have the right directions, and 2) the emissions areas should have nearly the same temperature as the arctic area. Otherwise the warmer air would move above the cold Arctic air. This is equivalent to the requirement that the emissions should originate within the Polar Front. Examples of conditions which obey these two requirements are given in Fig. 5.8, which shows four typical episodes of transport of SO_x ($SO_2 + SO_4^{2-}$), one for each winter period. The figure shows the 6 hour mean concentration of SO_x together with the windfield, contour lines for the Mean-Sea-Level pressure, and L and H for the low and high pressure systems. In the winter a rather persistent high pressure system is built up over Siberia and the East Siberian Sea. These high pressure systems blocks the westerly flow and the low pressure systems from the Atlantic. The episodes typically occur when these low pressure systems stop in the North Atlantic, Norwegian Sea or Barents Sea; this results in the right wind for the transport to the Arctic. Between the low and high pressure systems there is a strong northern flow, which transports pollution into the Arctic. It is interesting to note the similarities and differences between the extreme situations in Fig. 5.8 and the average concentration fields depicted in Fig. 5.6.

Circulation breakdown
in late spring

In the late spring the persistent high pressure systems over Siberia break down. Therefore it is possible for the low pressure systems from the North Atlantic to move further east and north but they are more infrequent and not so deep. This results, together with the higher temperature over the former USSR and Europe in much lower transport in the surface layers to the Arctic. In the summer period transport to the Arctic only takes place at higher altitudes.

Vertical distribution
and sources

The vertical distribution of SO_x concentrations, averaged over the area north of 75°N for the whole period, and the contributions from the different sources are given in Fig. 5.9. The figure shows that the surface concentration is about 0.54 ppbV, the maximal concentration is about 0.60 ppbV at 600 m, and above 600 m the concentrations decreases to 0.06 ppbV at 7000 m. The other part of Fig. 5.9 shows that for the surface concentrations Norilsk and the other part of the former USSR sources (except Kola Peninsula) contribute with about 35% and 40%, while the European sources contribute with about 20%. The contributions from the Kola Peninsula and North America are both about 3%, while DMS emissions and the sources in Asia both contribute with about 1%. At higher altitudes the contributions from Norilsk and Kola Peninsula decreases, because they both are local sources in the Arctic, while the contributions from Europe, North America and Asia increase and the contributions from sources in the rest of the former USSR are nearly the same. Totally the contribution from the former USSR to the concentration of SO_x in the Arctic Boundary layer is estimated to about 78%.

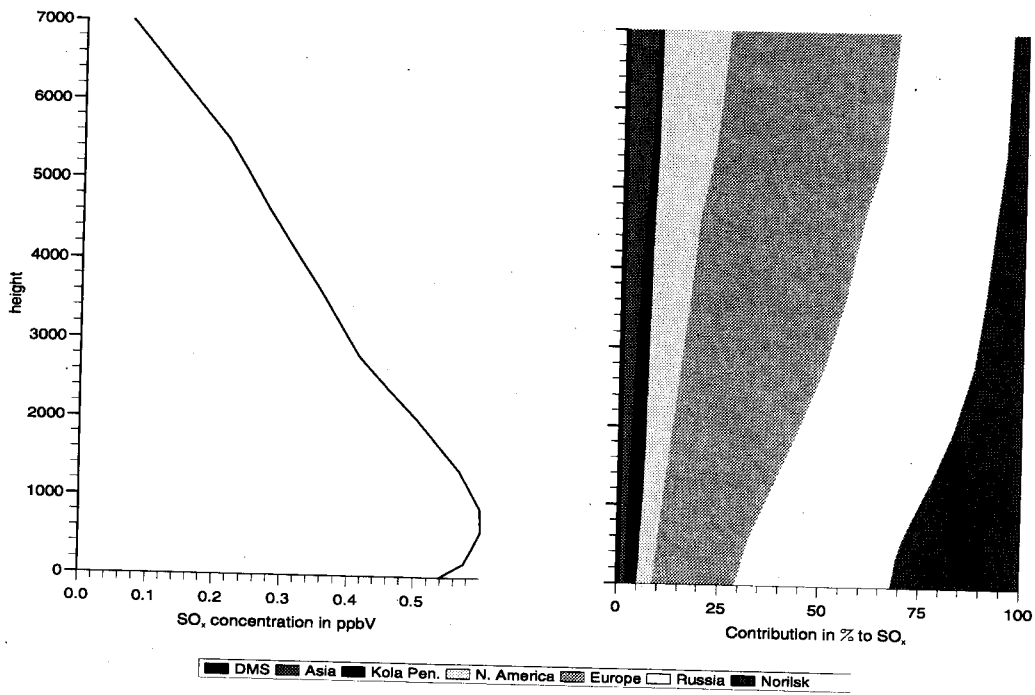Fig. 5.9. Vertical distribution of SO_x in ppbV (left), averaged over the area north of 75°N from October 1990 to May 1996, and the relative contributions from the different sources to the vertical distribution (right).
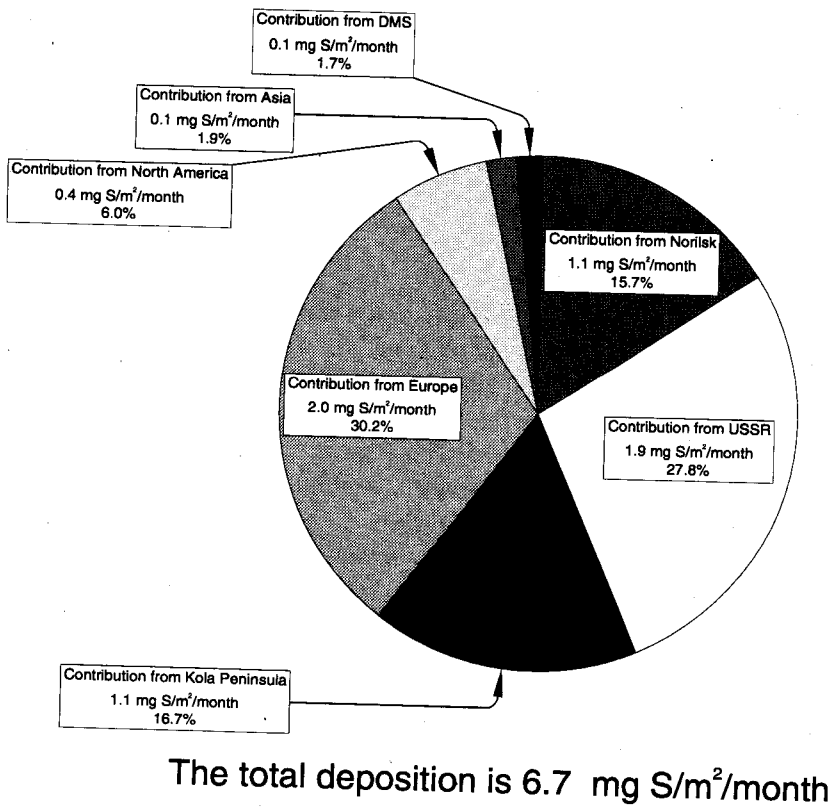

The total deposition is 6.7 mg S/m²/month

Fig. 5.10 The contribution from the different sources to the total deposition, averaged over the area North of 75°N from October 1990 to May 1996.

Deposition and sources

The total deposition of sulphur, averaged over the area north of 75°N for the whole period is about 6.7 mg S/m^2/month. The contributions from the different sources to the total deposition are shown in Fig. 5.10. The figure shows that the rest of the former USSR contributes with 28% and Europe contributes with about 30%, while Norilsk and the Kola Peninsula contribute with about 16-17%. It is quite interesting that although the contribution from the Kola Peninsula to the surface concentration is as low as 3%, the contribution to the total deposition is 17%. It is the opposite for Norilsk. The reason for this is the higher precipitation rate close to Kola Peninsula compared to the Norilsk area.

Seasonal concentrations and sources

The time variation of the monthly mean concentration of SO$_x$ in the Arctic boundary layer, averaged over the area north of 75°N, and the source contributions for different source areas are given in Fig. 5.11. The figure shows that there is a large seasonal variation in the concentrations from 0.1 ppbV in the summer period up to 1-2 ppbV in the winter period. The time variations of the relative contribution from the different sources show that Norilsk seems to have some small seasonal variations, with a smaller contribution in the winter period. The sources from the former USSR have a large seasonal variation from about 15% in the summer period to more than 50% in the winter period, indicating the importance of the sources in this area to the high concentrations in the winter period. This shows that in the winter the Polar Front has moved south and many sources are inside the front. The time variation of the contribution from the European sources show a seasonal variation from 15% in winter up to 40% in summer. The contributions from the other sources have a similar variation from totally 2% in the winter to 25% in the summer.

Seasonal depositions and sources

Fig. 5.12 is similar to Fig. 5.11 but for the total depositions. The total depositions show a much smaller seasonal variation than the concentrations, indicating that in the summer period, the atmospheric transport to the Arctic occurs at higher altitudes. For most of the source areas the seasonal variations of the contributions to the deposition are correlated with the similar variations in the concentrations, except for the sources on the Kola Peninsula.

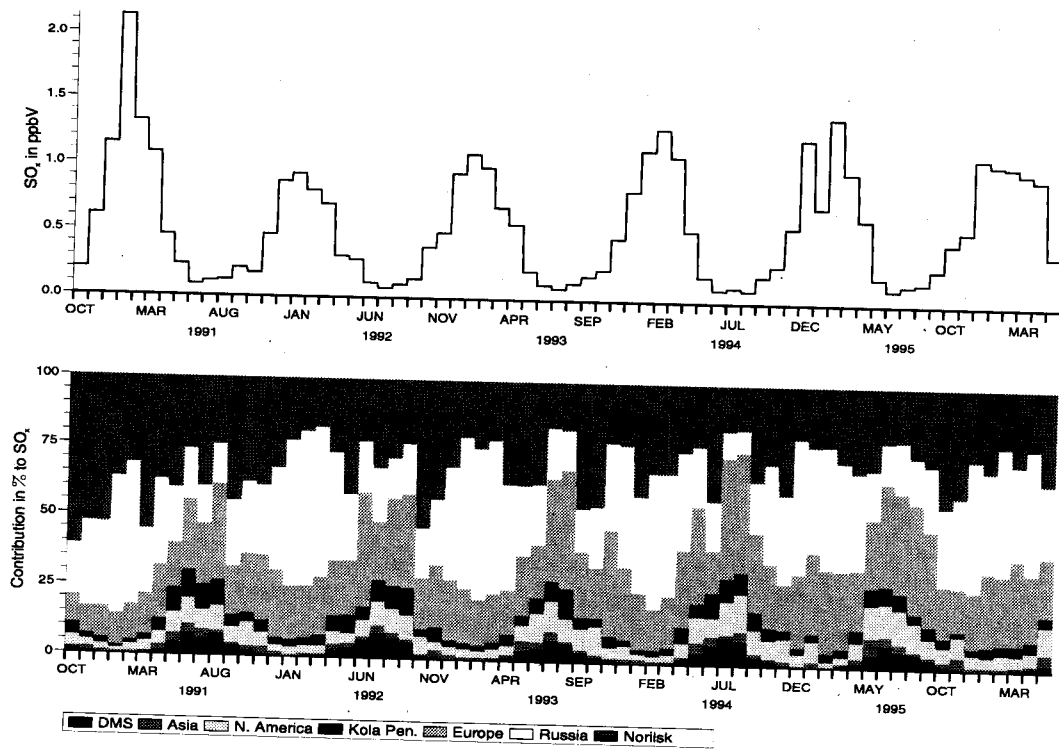Fig. 5.11. The calculated concentrations of SO_x in ppbV for the arctic boundary layer (upper), averaged over the area north of 75°N, and the contributions from the different sources to the concentrations (lower).
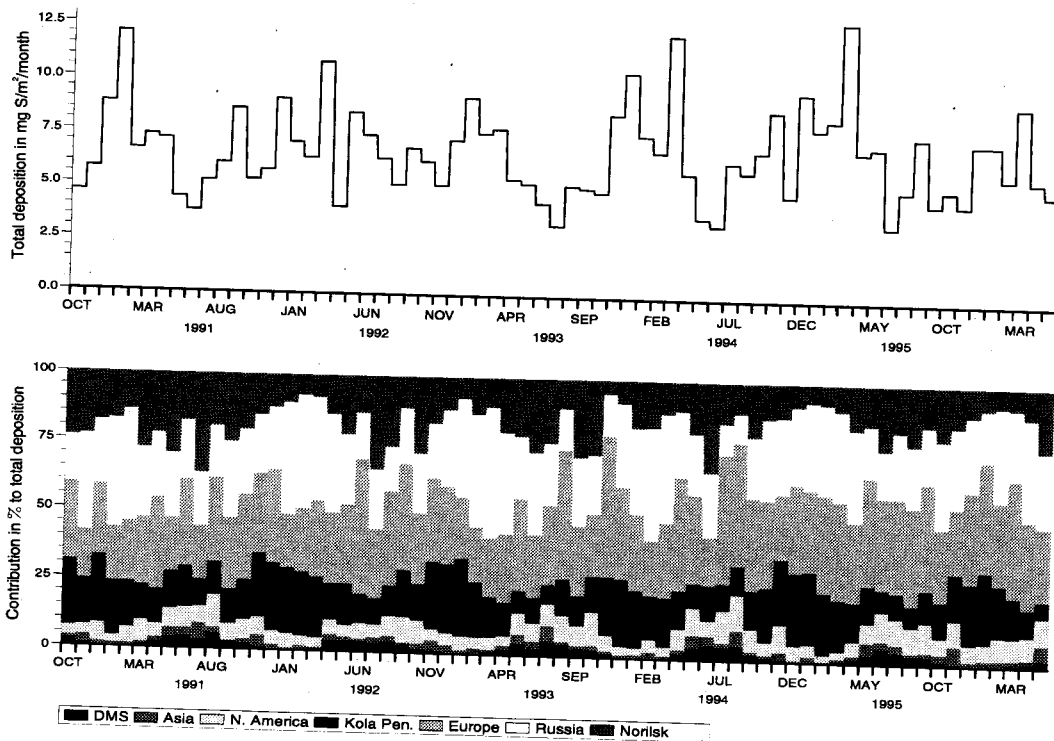

Fig. 5.12. The calculated total depositions of SO_x in mg S m^{-2} ·month^{-1} (upper), averaged over the area north of 75°N, and the contributions from the different sources to the depositions (lower).

Conclusions

Considerable air pollution

Measurements in Northeast Greenland in the period 1990 -1996 of air pollutants have shown that on a seasonal basis the region is burdened with a considerable load of atmospheric pollution. It has been found that the annual mean concentrations of many of these pollutants are only a factor 5-10 lower than annual means observed in rural areas in Denmark. In the winter period the maximum concentrations of total sulphur may even reach 25 - 50 % of the values in Denmark.

Natural and anthropogenic sources

The composition of this pollution reveals that it originates from a small number of both natural and anthropogenic source types. The natural sources are windblown soil dust that has been observed to be most influential in the autumn and spring and sea spray which reaches its maximum in the late winter and early spring.

Remote industrial sources

The anthropogenic components of the Arctic air pollution derive from a number of industrial activities, that by their very nature are located very far away. This type of pollution, the Arctic Haze, reaches its maximum in the late winter with high concentrations of a large number of anthropogenic pollutants.

Sulphuric Acid

The dominant pollutant type consists of products from a variety of combustion processes typical of power production and other industrial activities. The most abundant pollutant of this type is sulphur not only in particulate form which is highly acidic (sulphuric acid), but surprisingly also in the gas phase. Since 1993 the average mid-winter concentration of sulphur have decreased by a factor of 2, possibly reflecting a decrease in sulphur emission within the Arctic.

Heavy Metals

The Arctic aerosol has also been found to contain the heavy metals V, Cr, Zn, As, and Pb with origins in remote source areas. In addition a metallic component containing primarily Ni and Cu has been identified by receptor modelling. It has been observed episodically in mid-winter and presumably it originates in large metal smelters in northern Russia.

Tropospheric ozone depletion

Tropospheric ozone has been measured since March 1995. In the Spring the ozone concentration is highly perturbed. Within a few hours ozone may drop from about 45 ppbv to essentially 0 ppbv and is subsequently restored to the original level within a few days. This phenomenon is repeated several times. After this perturbed period ozone is stabilised at about 25 ppbv followed by a slow increase during autumn and winter to a level of about 45 ppbv just before the next perturbed period. The cause of this phenomenon remains somewhat unclear, but most probably Br atoms are responsible for the ozone depletion during the spring. However the origin of atomic bromine is not fully understood at the moment.

Transport model

A hemispheric model describing the transport of sulphur compounds has been developed. It is used as a tool for interpretation of the observations in terms of emissions and source areas, transport, transformation, and deposition processes. The agreement between model calculations and field measurements must be described as quite good.

Sulphur from Euro-Asia

The calculations show that the sulphur which is the main pollutant in the combustion component of the Arctic atmospheric pollution reaches maximum concentrations in winter and that it originates in Russia (formerly the USSR), particularly the northern part, and central Europe. Since 1994 the measured concentrations have decreased to about half the calculated concentrations. This overestimation by the model may be caused by diminished emission in the Russian Arctic in the 1990's, whereas the emission data for this area refer to the mid 1980's. The deposition of sulphur in the Arctic may be similarly overestimated, the deposition is relatively low however amounting to 4-20% of typical European values.

Injections of polluted air

The cause for the phenomenon of Arctic Haze is a specific atmospheric circulation pattern which dominates the Northern Hemisphere in winter and early spring. Quite often the distribution of low and high pressure systems develop in a way that favours injections of polluted air from these source areas into the Arctic region. Therefore the observations in Northeast Greenland are believed to be representative for surface conditions in a major part of the Arctic. In addition the model shows that at higher altitudes pollution from other European source areas and from North America are of importance although the levels here are considerably lower than at the surface.

No pollution in summer

In summer the atmospheric circulation is confined within the Arctic region and consequently the High Arctic Troposphere contains virtually no anthropogenic pollutants.

Acknowledgements

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Danish summary - Dansk resumé

Forurening af den arktiske troposfære:
Nordøstgrønland 1990 - 1996

Faglig rapport fra DMU, Nr. 221

Niels Zeuthen Heidam, Jesper Christensen, Peter Wåhlin, Henrik Skov
Danmarks Miljøundersøgelser

Rapporten indeholder en beskrivelse af de målinger af luftforureningen ved Station Nord i Nordøstgrønland, som er gennemført siden 1990. Der er foretaget ugentlig prøvetagning af svovldioxid, partikulært svovl, gasformigt og partikulært kvælstof i både reducerede og oxiderede forbindelser. Derudover er koncentrationen af et stort antal grundstoffer i de arktiske aerosoler bestemt med PIXE-metoden.

Resultaterne viser, at selvom koncentrationerne er meget lave det meste af tiden forekommer der store årstidsvariationer, så koncentrationerne i et tilbagevendende mønster stiger til betragtelige værdier. Tilsvarende variationer er observeret ved andre stationer i Højarktis (nord for 75° N). Perioderne med høje koncentrationer forekommer på forskellige tider af året, dog hovedsageligt om vinteren, afhængigt af typen af forurening og dens kilder. De store vinterkoncentrationer af svovlforbindelser har i de senere år haft en nedadgående tendens, muligvis på grund af reducerede emissioner i det nordlige Rusland.

Der er udviklet en receptor model til identifikation og kvantisering af de vigtigste naturlige og antropogene (menneskeskabte) kilder, som har indflydelse på koncentrationerne ved Station Nord. De målte koncentrationer kan dermed opdeles i bidrag fra disse få kilder, hvis årstidsvariation derpå kan fastlægges. Den tilbagevendende indflydelse fra fjerntliggende kilder på luftkvaliteten i Højarktis viser, at der er tale om et meteorologisk fænomen, som gentages på stor skala år efter år.

For svovlforbindelsernes vedkommende bekræftes denne hypotese af modelberegninger. Resultater, som er opnået med en hemisfærisk model af euler-type viser, at der i vinterperioden foregår en omfattende atmosfærisk transport af forurening fra fjerntliggende kilder i industriområderne i Europa og Rusland. Denne transport er ofte af episodisk karakter. Derimod er depositionen af svovl i Arktis ikke særlig stor.

Der er foretaget målinger af ozon siden marts 1995. Resultaterne udviser et særpræget mønster, hvor ozonkoncentrationen i forårstiden pludseligt kan falde til næsten nul i perioder fra et par timer til et par dage. Det antages at fænomenet skyldes dagslysets tilbagevenden, som ved den polare solopgang sætter gang i en række fotokemiske processer, der formentlig involverer det ozonnedbrydende brom, hvis oprindelse dog ikke er klarlagt.

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