Tellus (1994), 46B, 52–67
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TELLUS
ISSN 0280–6509

Seasonal variation of the atmospheric aerosol near the top of the marine boundary layer over Spitsbergen related to the Arctic sulphur cycle*

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(Manuscript received 14 April 1993; in final form 21 June 1993)

ABSTRACT

With an emphasis on marine biogenic sulphur the first 26 months of fine particle, (<1 μm radius), aerosol data from the new air chemistry station on Zeppelinfjellet, Spitsbergen, (79° N, 12° E, 474 m asl), were evaluated to elucidate source- and transformation processes of the Arctic aerosol. Results from 2 particle counters, an integrating nephelometer, and filter samples were available for our interpretation. On the filters we had analysed soot, (EC), sodium, (Na^+), methansulphonate, MSA^-, and sulphate, (SO_4^{2-}). Fine particle composition revealed a strong regional marine biological source of MSA^- and SO_4^{2-} which we estimated to contribute 26% to the non-sea salt sulphur in summer. In winter, no more than 2% of the non-sea-salt sulphur could be attributed to the marine biological source. Rigorous air mass analyses combined with the EC data as a tracer for regional anthropogenic combustion sources showed that this regional biological source became active already in March over the Barents Sea and over the North Atlantic. In summer, the levels of the biogenic sulphur components were very similar to those measured at the southern hemispheric marine site of Cape Grim, (1.5 and 0.92 nmol m^{-3} for MSA^- and nss-SO_4^{2-}, respectively). For samples with minimum anthropogenic influence we found a constant MSA^-/nss-SO_4^{2-} ratio in the fine particle size range. This ratio had a value of 28% and was temperature-independent. Our results comprise the first long-term record of Arctic aerosol data taken in the upper part of the planetary boundary layer which often is influenced by persistent Arctic stratus. With a cloud-segregation scheme we segregated the aerosol data into a group measured interstitially, i.e., inside boundary layer clouds, (INT), and an out-of cloud group, (OOC). Average INT/OOC-ratios of fine particle mass, nss-SO_4^{2-}, and soot were 0.19, 0.21, and 0.21, respectively. While exhibiting similar INT/OOC-ratios in winter, MSA^- had an average INT/OOC-ratio of 0.63 in summer implying that it was less scavenged than the other components. Complementary physical aerosol data corroborated our interpretation of MSA^- on average residing on smaller particles than nss-SO_4^{2-}. Together with the scavenging results our data support the concept that MSA^- most likely is formed by condensation onto existing particles while SO_4^{2-} predominantly is formed by in-cloud oxidation of SO_2.

1. Introduction

Since 1978 atmospheric trace substances have been measured near Ny-Ålesund, Spitsbergen. Two approaches have been followed during the first ten years of investigations. During shorter periods, sophisticated field experiments were conducted to elucidate specific properties while long-term trends were monitored with simple gas- and particle sampling programs with high reliability. Both approaches were severely affected by local emissions because the activities had to be located in the vicinity of the power generating facilities. In particular, during the summer months the annual maximum of activities around Ny-Ålesund coincides with the annual minimum in wind speed yielding least favourable conditions for sea-level

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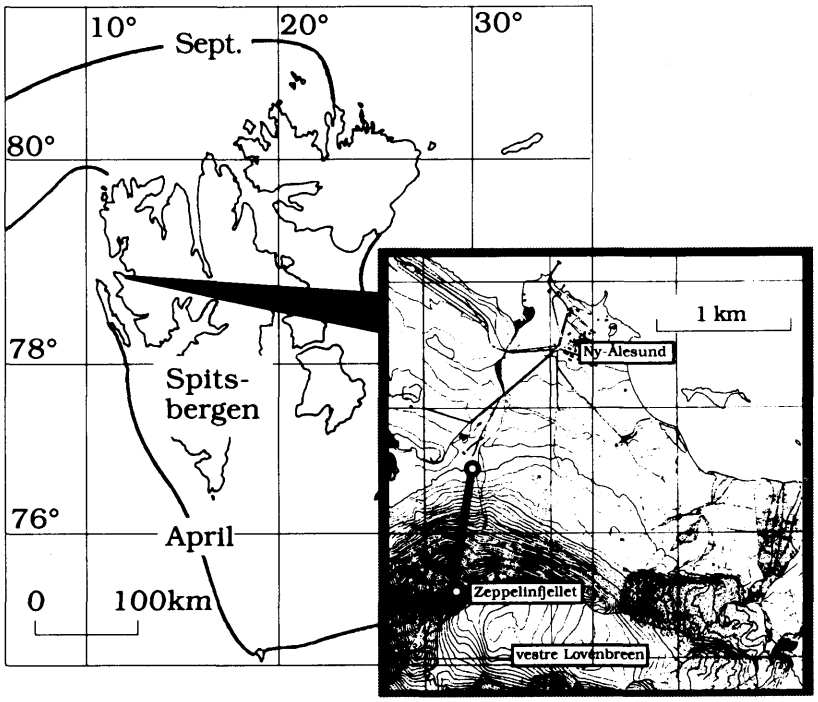

Fig. 1. The Svalbard area with an insert showing Ny-Ålesund and Zeppelinfjellet. The aerial tramway leading to the mountain station is indicated as thick line in the insert. Average pack ice limits in September and April are drawn on the main map.

study of atmospheric trace substances in the Kongsfjord area around the settlement (cf. Fig. 1).

Thanks to the initiative of the former director of the Norwegian Institute of Air Research (NILU), Dr. B. Ottar, an air chemistry station has been set up in 1988/89 on Zeppelinfjellet near Ny-Ålesund, (cf. Fig. 1). Location and protocol for its use allow for unique studies of the composition and processes in the Arctic atmosphere. The new location strongly reduces the risk of local contamination. Often, the station is in, or even above the cloudy region of the PBL. In this air chemistry station the Department of Meteorology, Stockholm University, (MISU), are operating an instrument set-up for baseline aerosol- and carbon dioxide, (CO_2), measurements.

We shall discuss below the results from the first 26 months of aerosol measurements at the new site on Zeppelinfjellet, (March 1990–April 1992). After comparing the levels of aerosol parameters to previous studies at sea surface level, we shall discuss the seasonal variation of fine particle composition, including elemental carbon, biogenic and anthropogenic sulphate and methane sulphonate, with an emphasis on segregating the influence of marine biological and anthropogenic sources. In addition, we shall explore the effect of cloud-scavenging processes on our results in order to derive information on the pathways of different particulate sulphur components in the marine boundary layer.

2. Methods

2.1. The monitoring station

The co-ordinates of the station are 79° N, 12° E, 474 m asl. The building has been erected on the eastern ridge of Zeppelinfjellet about 70 meters below the mountain top. It can only be reached by a dedicated aerial tramway from the valley station which is located at 52 m asl at a horizontal

distance of 930 m. The topography strongly affects the air flow around the station. Local wind directions between 100° and 270° are practically impossible because of the shadowing effect of the mountain. The most frequent wind sector is from ESE which indicates that the flow to the station predominantly comes up through the glacier valley of the Vestre Lovénbreen. If later micrometeorological studies would bear out these preliminary flow data they would explain the very rare occurrence of locally contaminated air at station level because flow in or out of the contaminated Kongsfjord would not be entering the side valley of the fjord leading up to the mountain station.

2.2. *Experimental and analytical procedures*

This report focuses on the fine particle measurements, (<1 μm radius), in terms of number, mass and chemical composition. In Fig. 2 we show a schematic picture of the instrumental set-up for the aerosol measurements of the station. All instruments including the filter sampler but excluding the high-flow counter 3760, (cf. Table 1), were operated downstream of a cyclone inlet at ambient conditions. These cyclones removed all particles (and cloud elements) above 1 μm aerodynamic radius. Thus, during cloud passages the instruments were monitoring the interstitial aerosol. The 3760 operated on a separate fast fine particle inlet which has a lead time of more than ten seconds as compared to the rest of the

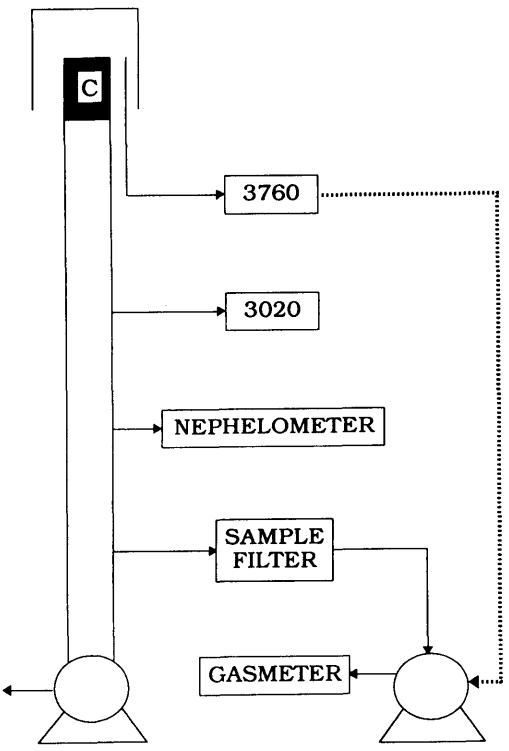

Fig. 2. Schematic picture of the set-up for aerosol measurements at the baseline station. C = cyclone inlet for particles <1 μm radius (cf. Table 1 for instrumental details).

Table 1. *Aerosol instrumentation and sample analyses on Zeppelinfjellet, Ny-Ålesund. EC = elemental carbon, SO_4^{2-} = sulphate, MSA^- = methansulphonate; W = weight of the sensor signal in the cloud segregation scheme*

ID	Method	Manufacturer	Detection limit	Precision %	*W*	Ref.
NEPH	integrating nephelometer $\lambda = 0.55$ μm	MISU	0.01	5	1.5	Heintzenberg and Bäcklin (1983)
3020	condensation nuclei counter	TSI Inc.	0.005 μm radius	15		Agarwal and Sem (1980)
3760	condensation nuclei counter	TSI Inc.	0.01 μm radius	15	1	Keady et al. (1986)
EC	integrating plate photometer	MISU	0.5 nmol/sample	20	0	Heintzenberg (1988)
Na^+	ion chromatography	Dionex	3 μmol/dm^3	15	0	
SO_4^{2-}	ion chromatography	Dionex	0.2 μmol/dm^3	15	0	
MSA^-	ion chromatography	Dionex	0.005 μmol/dm^3	15	0	

instrumentation. The signal of the 3760 was used in a parametric controller (Ogren and Heintzenberg, 1990) to turn off the sampler during time periods with rapidly increasing number concentrations. The controller turned off sampling when the on-hour running average of the 3760 reading was exceeded by 50% for one second and returned to sampling when that condition was not met any more for at least 1 min. This sample control minimised contamination from local combustion sources.

Because of the low mass concentrations of the Arctic aerosol, fine particle mass, (FPM), concentrations could not be determined gravimetrically on a routine basis. Instead, the results of the nephelometer can be interpreted as a measure of FPM (Waggoner and Weiss, 1980). Table 1 lists the essential information on the particle instrumentation and on the sample analyses. The complete instrumental arrangement of the baseline station has been described in detail in (Heintzenberg et al., 1991b).

The particulate filter samples were changed every two days except when severe weather conditions or other logistic difficulties made this impossible. The average collection time for the 326 integrated filter samples of the present study was 2.2 days (range 1–16). Sample periods shorter than ore or longer than three days were not considered in the discussion of cloud effects below.

For comparison with the integrated filter results, the data of the recording instruments were averaged over the individual sampling periods. These averages were only then accepted in the correlations of the different parameters when more than 50% of the filter sampling period was covered by the continuous measurements.

The particulate matter was collected on Nuclepore membrane filters with 0.4 μm pore diameter (flow rate 3–5 L/min). On the filters (sample and blank), we first determined elemental carbon, (EC), with a non-destructive optical technique. Then the filters were extracted with 5 ml of de-ionised water. The filter solutions were sonicated for 60 min. The extracts from the filter samples were then analysed by Ion Chromatography (IC). Strong anions were analysed with a Dionex AG4A/AS4A column. Methane sulphonate, (MSA^-), and sodium, (Na^+), ions were analysed with a Dionex AG4/AS4 and a CG3/CS3 column respectively. Thus, all sample analyses were done with the same particulate matter. All calculated concentrations were corrected for sampling and analytical blanks. By this procedure we correct for possible contamination during the EC analysis prior to the extraction for IC. With the help of the sodium concentrations and average sea water composition taken from Stumm and Morgan (1981), non-sea salt sulphate, (nss-SO_4^{2-}), concentrations were calculated.

The results of the continuous measurements and from the integrated filter samples had to be harmonised before attempting any kind of synopsis. From 1991 on, 1-min averages of 10-s readings were recorded on a digital data logger from the continuous instruments. For 1990, momentary results were read off a multipoint recorder every three hours. In order to create an internally consistent data set, the continuous data for the subsequent 16 months of 1991–92 were averaged over three-hour periods before further evaluations.

For the interpretation of the aerosol data, both 5- and 10-day 3-D back-trajectories were used to estimate the origin of the sampled air masses. 10-day trajectories were used during the winter and spring period when the residence time of the aerosol is expected to be longer than in summer. The trajectories were calculated according to an algorithm developed by McGrath (1989) from analysed pressure and wind fields from the European Centre for Medium-Range Weather Forecasts with our mountain site as the arrival point. The trajectory analysis will be discussed in detail in the section on biogenic sulphur in different seasons.

3. Results

In order to allow an assessment of the scope of our results we display the complete analytical results of the sample data in Fig. 4. Corresponding sample averages of the continuously operating instruments are given in Fig. 3. There is a considerable inter-sample variability in the results which we discuss in detail below. Near the top of the PBL an additional variability is common due to local cloud-scavenging processes as compare to surface aerosol measurements.

Nephelometer, (FPM), non-sea salt sulphate and soot data show the typical Arctic haze seasonality established by Rahn et al. (1980). This

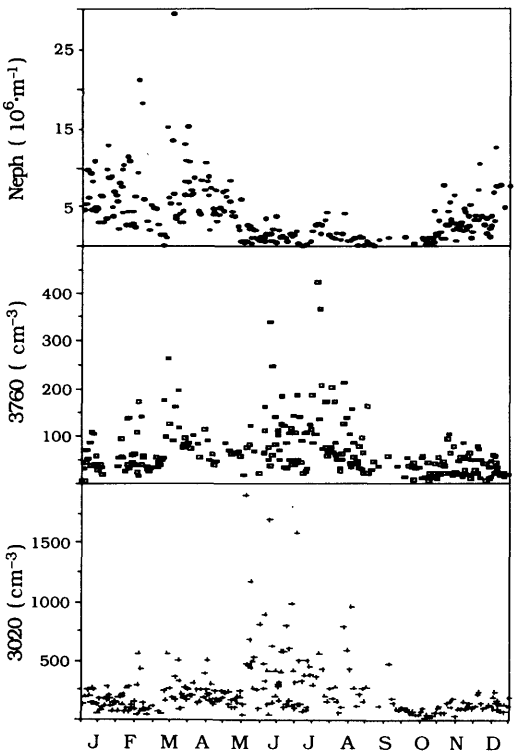

Fig. 3. Seasonal variation of fine particle composition from 2-day samples taken March 1990–April 1992 on Zeppelinfjellet, Spitsbergen (cf. Table 1 for acronyms).

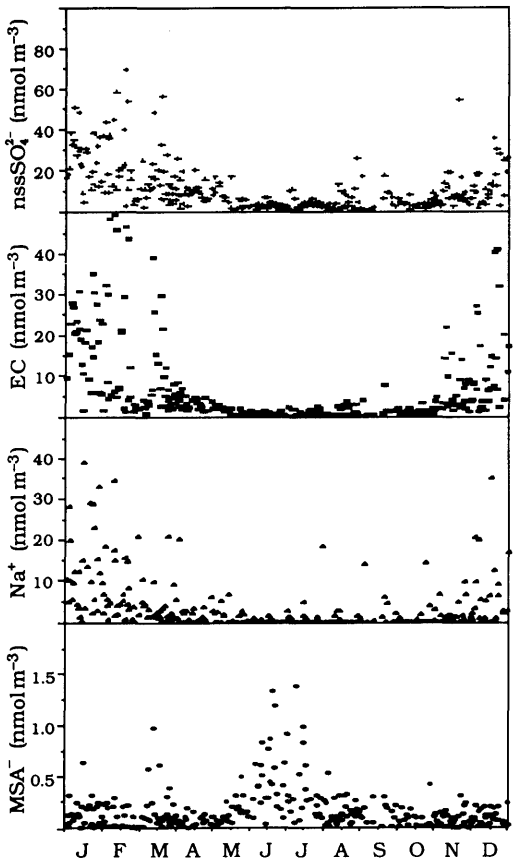

Fig. 4. Seasonal variation of fine particle properties on Zeppelinfjellet, Spitsbergen, averaged over the sample periods in Fig. 3 (cf. Table 1 for acronyms).

seasonality is based on a strong import of polluted mid-latitude air during the period November–April into a source-free Arctic. According to this concept, the annual minimum pollution import is reached during June–August. Sodium shows a winter maximum, reflecting the annual maximum of local wind speed in winter and therefore of the sea salt source (Heintzenberg et al., 1991a). Particle number concentrations showed summer maxima with secondary maxima in late winter during Arctic haze. Earlier observations of summer maxima in aerosol properties were seen as rare events with intrusions of southern air (Heintzenberg and Larssen, 1983). Most frequent during summer there are long times of air mass residence in the Arctic basin, (Heintzenberg et al., 1991c). Nephelometer and sulphate signals have secondary maxima in summer indicating processes that do not fit into the traditional Arctic picture. In the new data set shown in Figs. 3, 4, the number maxima coincide with the strong absolute maxima in MSA^- concentrations during the summer period. Superimposed on this distinct annual cycle of MSA^-, we see cases of elevated concentrations during the period of maximum Arctic haze (January–April).

Oceanic emissions of dimethyl sulphide, (DMS), are the only known source of particulate MSA. The existence of a seasonal cycle in oceanic DMS has been reported in the literature (Bates et al., 1992a; Leck et al., 1990; Turner et al., 1989), who found it to be most pronounced in temperate latitudes with a summer maximum and winter minimum in concentrations. This seasonal variation in DMS concentration is related to the biological activity of phytoplankton and zooplankton (Leck et al., 1990). The Arctic seas,

including the Norwegian, Bering and the Greenland Seas, are characterised by special conditions for marine life such as the low sun elevation (<40–50°), extreme seasonal variations in solar irradiance and day length, and low sea temperatures (−1.8 to 6°C). In general, the melting ice edge gives rise to a "spring" bloom of phytoplankton. In the wake of the receding ice, episodic blooms occur throughout the summer season (Sakshaug and Slagstad, 1991). In the Svalbard region, minimum ice cover is reached in late August, (cf. Fig. 1). This existence of a strong seasonality of the biological activity in the Arctic seas is likely to give a production of oceanic DMS and consequently particulate MSA between March (75°N) and August (85°N) with a maximum in June.

Except for the cases of elevated MSA^- concentrations during Arctic haze episodes, we did not see any evidence for the production of oceanic DMS between March to the middle of May suggested by the marine investigations in the Barents Sea, (cf. Fig. 3). We explain this period of low biogenic *and* low anthropogenic aerosol concentrations by a shift in the Arctic circulation pattern. According to Liljequist (1970), the changing weather regime forces the air to reach Spitsbergen via much longer pathways over the non-productive Central Arctic as compared to the Arctic haze period in the beginning of the year. This change of regime is borne out by our trajectory data.

The MSA^- concentrations reported in this study ranged from 1.5 nmol m^{-3} in summer to 0.05 nmol m^{-3} in winter, similar to the values observed by Ayers and Gras (1991) at Cape Grim (41°S, 144°E). We note the non-zero winter levels of MSA^- which occurred while the Arctic proper was dark and mostly ice-covered at the same time as biological activity in the surrounding marine areas were at their annual minima.

3.1. The cloud segregation scheme

Throughout the year, cloud passages occur at the sampling altitude on Zeppelinfjellet. There is a distinct seasonal cycle of low-level cloudiness with a maximum of persistent Arctic stratus in July, (Huschke, 1969; Schweiger and Kley, 1992; Steffensen, 1969). During cloudy periods, all instruments and filters sample only the interstitial aerosol. As the cloud sensor utilized at the station on Zeppelinfjellet did not work during this study, we had to use a data reduction scheme which attempts to segregate results of the filter samples which were taken interstitially. During cloud passages, (INT), measurements by the two particle counters and the nephelometer were expected to be significantly reduced compared to out-of-cloud, (OOC), situations. In order to quantify the signal reduction due to suspected cloud scavenging, we compared the momentary values to average values taken over all data from longer periods. Because of the strong seasonal variations in the Arctic aerosol, we chose monthly averages for comparison whith the momentary readings. The monthly averages contained cloudy as well as non-cloudy periods. Thus, we added a safety margin to our segregation by asking for a certain maximum threshold in the ratio of the suspected interstitial data to the monthly averages before estimating individual results to be due to interstitial conditions. For all three cloud-sensitive aerosol instruments we chose a threshold of one half of the monthly average signal as indicative of cloud presence. In general, the atmospheric aerosol exhibits larger mass median radii than the corresponding number medians. Thus, we expect the mass-sensitive nephelometer to be more sensitive to nucleation scavenging in clouds than the particle counters. Accordingly, we assigned a higher weight to the nephelometer signal in the cloud-segregation scheme (cf. Table 1). A sample was classified as interstitial when at least one of the counters *and* the nephelometer indicated signals below the maximum threshold at least 70% of the sampling time. On average, the samples classified as INT met this condition during 95% of the sampling time. A filter sample was classified as out-of cloud if none of the three sensor signals were below the corresponding thresholds. Again, at least 70% of the sampling time that condition had to be true. With this scheme 65% of the 326 filter samples were classified as OOC while 12% were in the INT-group leaving 33% of the samples unclassified because of ambiguous or incomplete data.

Our cloud segregation scheme does not prove any sample to be cloud-interstitial or out-of-cloud because it does not rely on a cloud sensor. Instead, it yields two sub-populations of data that are classified according to the segregation scheme. Basically, the INT-group contains low concentra-

tion data that may not only have been caused by cloud passages. However, there are several arguments for the INT-group representing mostly cloud-interstitial data.

(1) In agreement with the classification scheme, periods of cloud passages during INT-periods could be identified in the analog recordings of nephelometer and CPCs by rapid decreases in signals over periods on the order of minutes.

(2) The logic of the sample controller described above minimised the collection of out-of cloud particles during periods of intermittent cloudiness and after the passage of a cloud.

(3) We did not find a single sampling period which had been classified as INT having any of the aerosol data on levels above the corresponding seasonal average out-of-cloud.

(4) During a short control experiment in June 1992, we took interstitial- and out-of cloud samples with operator-supervised sampling conditions which confirmed the average summer results reported below within the reported uncertainties.

Despite these arguments for the INT-group representing cloud-interstitial data, the remaining uncertainties will limit the conclusions which can be drawn from INT/OOC comparisons.

4. Discussion

4.1. Previous sea-level results and seasonal differences

Our results comprise the first long-term record of Arctic aerosol data taken in the upper part of the planetary boundary layer. Thus, as a first step in the discussion we compare the new figures with previous measurements at sea level on Spitsbergen in Table 2. Note that the new data in Table 2 only contain out-of cloud results according to the classification scheme introduced above. Because of the well-established Arctic haze phenomenon (Rahn et al., 1980), a discussion of annual averages is meaningless. Thus, for a first synopsis we divided the out-of cloud data into a winter period

Table 2. *Average levels of aerosol properties out-of cloud and interstitially for the periods 16 May–15 October, (winter), and 16 October–15 May, (summer)*

Season	EC (nmol m^{-3})	Na^+ (nmol m^{-3})	SO_4^{2-} (nmol m^{-3})	MSA^- (nmol m^{-3})	3760 (cm^{-3})	NEPH (10^{-6} m^{-1})	3020 (cm^{-3})	3020–3760 (% of 3020)
winter								
<1990	5.5	n.a.	24	n.a.	n.a.	16	370	
90–92	7.78	3.65	15	0.06	59	5.7	172	99 (59%)
M/V	1.42	n.a.	0.6	n.a.	n.a.	0.36	0.47	
INT/OOC	0.23	n.a.	0.21	0.22	0.30	0.19	0.33	
σ [%]	14	n.a.	10	35	18	14	17	
summer								
<1990	0.38	n.a.	2.3	n.a.	n.a.	1.5	145	
90–91	0.89	1.34	4.1	0.19	91	1.7	320	223 (67%)
M/V	2.35	n.a.	1.8	n.a.	n.a.	1.13	2.21	
INT/OOC	0.19	n.a.	0.22	0.63	0.36	0.19	0.51	
σ [%]	14	n.a.	11	51	16	12	35	
winter/summer								
<1990	14	n.a.	10	n.a.	n.a.	10.7	3	
90–92	9	3	4	0.3	0.7	3	0.5	

<1990 = average sea level results from the period 1979–1989. 90–92 = average results from March 1990–April 1992 on Zeppelinfjellet (out-of cloud data only). $M/V = (90\text{–}92)/(<90)$. INT/OOC = average interstitial to out-of cloud ratios for the two seasons, σ = relative standard deviation of the average interstitial ratios (before 1990 the sea salt fraction of SO_4^{2-} was often not determined), n.a. = not available (cf. Table 1 for acronyms).

(16 October to 15 May), and a complementary summer period.

In winter, the data related to total number and mass are lower by roughly a factor of two at the mountain station while in summer the opposite was the case. EC, on the other hand, showed a different behaviour. In winter and summer the mountain data are higher by factors between 1.5 and 2.5. One explanation for these findings is that the new site and/or sampling protocol is more subject to local contamination than the old site. We consider this unlikely because the sample controller indicated sample contamination less than one per cent of the time during the first years on the mountain station. Only during very strong northerly winds, contaminated air was pushed up to the top of Zeppelinfjellet. With the limited material available to date we can only offer two alternative explanations. (1) The increases on the mountain could be caused by the strong interannual variations which have been observed previously (Heintzenberg, 1989), in particular during the Arctic haze period. (2) Because the new mountain site is more open to regional air mass transport, it may be more exposed to emissions from other settlements and activities on Spitsbergen. The higher EC concentrations on the mountain might reflect this regional pollution.

Previously, aerosol parameters related to fine particle mass or anthropogenic combustion sources exhibited winter/summer ratios of ten or higher (cf. Table 2 or (Heintzenberg, 1989)). On the mountain, only EC maintained this behaviour. For sulphate and nephelometer, (related to fine particle mass), the winter summer ratios sank to about four while number-related results even showed a reversal in winter/summer ratios on the mountain. Including the additional biogenic component MSA^- to this last group we found quite similar winter/summer ratios between 0.3 and 0.7. It should be noted that in previous studies, no well-defined upper size limit was applied to the particle measurements. Heintzenberg et al. (1981) have shown that the coarse particle fraction ($>1\ \mu$m radius) contributes less than 25% to mass-related measurements of the Arctic aerosol. For area- or number-related measurements the corresponding contributions must be less.

The summer Arctic usually is seen as a sink area (with the exception of a small source of sea salt) for atmospheric trace substances. Infrequently, polluted air masses from southern latitudes would invade this region in summer, in particulate during August (Heintzenberg and Larssen, 1983). These intrusions were expected to be scavenged rapidly in the Arctic stratus resulting in rather even surface concentrations at levels which were the lowest reported in the northern hemisphere (Lannefors et al., 1983). The absolute levels and the winter/summer ratios with values below one on Zeppelinfjellet indicate a new picture of the Arctic aerosol. While being significantly lower than in winter, fine particle mass and nss-SO_4^{2-} are more than two times higher in summer on Zeppelinfjellet than at sea level. Average number concentrations and MSA^- concentrations are more than two times higher during the summer period than in winter. The conspicuously similar seasonal variations of particle number and MSA^- indicate the possibility of a regional biological source of particles in the Arctic which we will explore by a detailed discussion of the summer period below.

The aerosol size distribution contains valuable information about particle sources and about the age of the aerosol. In our long-term monitoring program there was no possibility of routine measurements of particle size distributions. However, we can combine the data of the two particle counters to derive some information about the shape of the particle size distribution in way similar to the approach taken by Covert et al. (1992) with a different combination of sensors. In Table 2, we listed the difference (3020–3760) as a measure of the number-fraction of particles between 0.005 and 0.01 μm radius. Because of the rather broad lower size cut of the 3020 the ratio is biased towards 0.01 μm, (Agarwal and Sem, 1980). In winter, half as many particles, ($\approx 100\ cm^{-3}$), were found in that range as compared to the summer period, (cf. Table 2). On average, about 60–70% of the signal of the 3020 was due to particles below 0.01 μm. Clearly, the sampled aerosol was less aged in summer than in winter, most likely because of a regional particle source.

4.2. The Arctic haze period in 1991

During the Arctic haze period of February through April, we found frequent events of elevated MSA^- concentrations. For our understanding of the Arctic sulphur cycle we needed to find out if that particulate MSA was important from biologically productive mid-latitude marine

areas or if it resulted from early spring blooms of the Arctic or north Atlantic region. For that purpose, our limited set of chemical tracers had to be complemented with three-dimensional back-trajectories. We exemplify this type of source investigation with the case study of March–April 1991. The time series of our aerosol tracers are collected in Fig. 5. The first rise in concentrations in all channels occurred during sample period #2. Back-trajectories clearly indicated that the air had passed over Eastern and Central Europe before moving on the path North Sea- North Atlantic to the sampling site. Over the North Sea heavy precipitation scavenged much of the European air pollution. At first glance, it was surprising to see that the long pathway over the Atlantic marine source region only lead to a very minor increase in MSA^-. We explain this finding with a strong sea salt mode in the aerosol (cf. the high fine particle sodium concentrations during #2 which indicated large amounts of coarse particle sea salt). Note that MSA scavenged by coarse-mode sea salt did not show up in our fine particle samples because of the cyclone inlet.

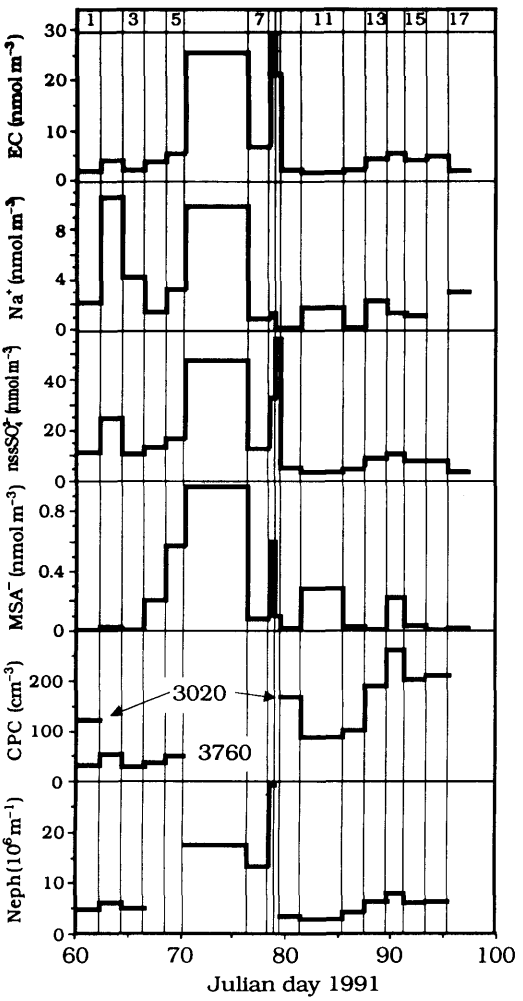

Fig. 5. Time series of aerosol tracers during the Arctic haze period of March–April 1991. CPC = condensation particle counter (cf. Table 1 for other acronyms). The lower abscissa is divided in Julian days 1991. Sequential sample numbers are given on the upper abscissa.

The main intrusion of polluted air masses built up during samples #4 through #6, the last one covering 6 days for logistic reasons. MSA^- concentrations close to 1 nmol m^{-3} were measured at the same time as all anthrogpogenic tracers reached high values. During the first 2 sampling days of #6, the trajectories did not touch open water for the previous ten days of travel. For the rest of sample #6, the trajectories passed over Kara Sea and Barents Sea, thus being able to collect biogenic sulphur from early spring blooms near the ice edges. The air flow during sample #7 came from the Russian anthropogenic source region and passed over the central parts of the Barents Sea. Nevertheless, all parameters except the FPM sank to relatively low values. The explanation lies in the vertical co-ordinate: only air arriving during the first day of sample #7 had dipped into the marine boundary layer over the Kara Sea. The rest of the air in sample #7 had spent the last ten days before arrival in the free troposphere. The air in the short sample #8, on the other hand, had been forced to spend about two days in a subsiding air mass with little horizontal displacement over the partly ice-free Barents Sea. 6 days before that stop-over, it had passed over the highly industrialised region of Kuibychev. Consequently, we measured very high concentrations of both anthropogenic and biogenic pollutants in sample #8. The next short sample, (#9), was determined by air that had travelled over the industrial centres of the southern Ural before passing over Kara Sea and northern Barents Sea to Spitsbergen. Nowhere north of the Siberian coast the trajectory touched pressure levels above 900 hPa. Thus, little marine aerosol could be picked up before arrival at the site.

During sample #10 no air was collected that had spent significant time south of 60° N. Any passage over continental areas north of that latitude happened above the boundary layer and only short residence times in the marine boundary layer of the Barents Sea occurred. For sample #11, the air mass origin changed to the Canadian Arctic. Most of the sample air had spent several days over the Greenland Sea before arrival at Zeppelinfjellet, thus explaining the low levels of anthropogenic pollutants concurrent with high levels of biogenic components. During most of the remaining samples of this episode, a steady circumpolar flow carried the air for 10 days over the central Arctic and the Canadian North-western Territories before arriving at the sampling site. During sample #14, the trajectories indicate a short residence time in the boundary layer over ice-free part of the Fram Strait which can explain the elevated levels of MSA^-. We can summarise the results of the Arctic haze period as evidence for early spring blooms in the open seas in the vicinity of the Svalbard region.

4.3. Cloud processes

Above we developed a cloud segregation scheme with which we formed 2 subgroups of the total data set, termed out-of-cloud (OOC) and interstitial (INT). By comparing these 2 groups, we estimated the effect of cloud processes on the properties of the Arctic aerosol. Because of our single point air sampling program no individual INT/OOC data pairs could be formed. Instead, we calculated average INT/OOC ratios for the different aerosol properties during the winter and summer periods defined above and included them in Table 2. Because of the large span of the data, geometric means were determined. Following the rules of error propagation, geometric standard deviations of the mean ratios were calculated by combining the geometric variances of the means of the corresponding two subgroups. Thus, we derived a measure of uncertainty for the average scavenging parameters which we added to the information in Table 2.

There are systematic differences in the interstitial ratios of the different variables which can be explained by the fact that (a) cloud nucleation scavenges the particle size distribution from the largest to smaller sizes and (b) for all polydisperse size distributions number concentration maxima are to be found at smaller sizes than the corresponding mass concentration maxima. Consequently, the relatively highest interstitial ratios should be measured with the 3020 which senses the smallest particles ($\geqslant 0.005\ \mu$m radius). The 3760 has a lower size limit which is an octave higher in particle size. Consequently, its interstitial ratios should be lower than those of the 3020. Even lower interstitial ratios one would expect for hygroscopic, mass-related variables, (FPM, nss-SO_4^{2-}, and MSA^-). In winter, all measured aerosol parameters indeed had interstitial ratios which fit into this general picture of scavenging processes in relation to the aerosol size distribution (cf. Table 2). With one exception, this holds for the summer period as well.

In summer, MSA^- showed a scavenging behaviour which strongly deviated from the other mass-related components. Its interstitial ratios were similar or even higher than the values measured independently with the particle counter 3020. From this similarity one might hypothesise that MSA formed those small particles that controlled the counter signal. Most of the MSA we expect to be formed by gas phase oxidation processes with subsequent condensation on pre-existing particles or cloud droplets without the nucleation of new particles, (Hoppel, 1987; Hoppel et al., 1987; Kreidenweis and Seinfeld, 1988a, b). H_2SO_4 produced concurrently from DMS in the gas phase follows the same condensational pathway or nucleates new particles, depending on relative humidity and available particulate surface area (McMurry and Friedlander, 1979). In the Arctic region, the condensation of oxidation products takes place on imported or regionally formed submicrometer particles or on coarse particle sea salt in case of open water and high winds. No differences in interstitial ratios between MSA^- and sulphate can be expected as a result of this condensation process.

Hegg (1985), Langner and Rodhe (1991), and Lelieveld (1993) have shown that the dominating fraction of sulphate is formed in cloud water by liquid phase oxidation of SO_2. At present, there is no consensus about how much of the DMS is expected to be oxidised to SO_2. Values up to 70% have been given by Yin et al. (1990a, b) while other authors reported lower figures (Bandy et al., 1992; Lin and Chameides, 1993). Most of this SO_2 will form sulphate through cloudwater oxidation.

In the Arctic the marine biological sulphur source peaks at the same time of the year as the boundary layer cloudiness (Steffensen, 1969). Thus, most of the biogenic sulphur in summer can be expected to yield cloud-processed sulphate. This additional sulphate produced by non-precipitating clouds will shift the mass median diameter of sulphate in the aerosol to larger sizes (Lelieveld and Heintzenberg, 1992) thus making cloud-processed particles more susceptible to subsequent nucleation scavenging. This shift of the mass median of sulphate will be the same for that part of the MSA^- that has been activated. In order to arrive at our measured scavenging differences, the activated part of MSA^- must be small compared to the inactivated rest. Otherwise, the mass median of MSA^- would eventually follow that of SO_4^{2-} to larger sizes which is inconsistent with the measured scavenging behaviour of MSA^-.

No detailed particle size distributions and cloud activation data were available to support our findings on particle scavenging. We ascribe the agreement between the scavenging of MSA^- and 3020 to a fortuitous similarity of the mass-size distribution of MSA^- and the number-size distribution of the total aerosol folded with size sensitivity of the counter. Despite the remaining uncertainties in the interpretation of the interstitial ratios our results suggest that MSA^- during summer is connected with smaller particles than nss-SO_4^{2-}. Size distributions of MSA^- and nss-SO_4^{2-} by Pszenny et al. (1989) taken in corresponding settings of the southern hemisphere clearly showed smaller mass median for MSA^- than for nss-SO_4^{2-}. For sake of completeness, it should be mentioned that significant amounts of coarse particle sea salt acting as condensational receptor would have caused MSA^- to be scavenged more efficiently than sulphate. In our data set we found no MSA^- interstitial ratios which would point to this process.

Despite the statistical uncertainties of the INT/OOC-ratios, we can exploit consistent winter/summer differences to find cloud-physical indications for the origin of the sampled aerosol. MSA^- and both particle counters yielded lower interstitial ratios in winter than in summer. This can be interpreted with the corresponding property-averaged particle sizes being larger in winter than in summer which is consistent with a more aged aerosol in winter when the regional biological aerosol production has its annual minimum.

In our study, we made the first attempt to quantify the effect of cloud-processing on aerosols in the remote marine atmosphere. In order to strengthen our results, we compared them with similar data from clouds in air masses with varying particle concentrations. The references of a literature survey underlying this comparison are collected in Table 3. In Fig. 6 we plotted all data in three groups "highly polluted", "non-urban continental", and "remote marine". There were considerable differences between the experimental approaches which were used in the various scavenging experiments cited above. Furthermore, when discussing sulphate, in-cloud-production often could not be separated from nucleation scavenging. It should also be noted that the cited aircraft results were hampered by interstitial data being close to the detection limits and by out-of-cloud data which were not necessarily from the same air mass.

There is a systematic decrease in interstitial ratios of different aerosol properties from values in the upper quartile in highly polluted clouds to values in the lower quartile in the least polluted Arctic clouds. This trend in interstitial ratios from source-to-sink areas can be expected when considering the size-dependent atmospheric lifetimes of aerosol particles (Jaenicke, 1988). With increasing atmospheric residence time, thermal diffusion clears the size distribution from the smallest par-

Table 3. *Reference information concerning the literature review of scavenging data collected in Fig. 6*

Air mass	Reference
highly polluted	Hallberg et al. (1992); Noone et al. (1992)
non-urban continental	Daum et al. (1984); Daum et al. (1987); Hallberg, 1993, private communication; Hegg et al. (1984); Hegg and Hobbs (1988); Heintzenberg et al. (1989); Leaitch et al. (1986); Oberholzer et al. (1992); Sievering et al. (1984); Strapp et al. (1988); Ten Brink et al. (1987); Van Valin et al. (1987)
remote marine	this work

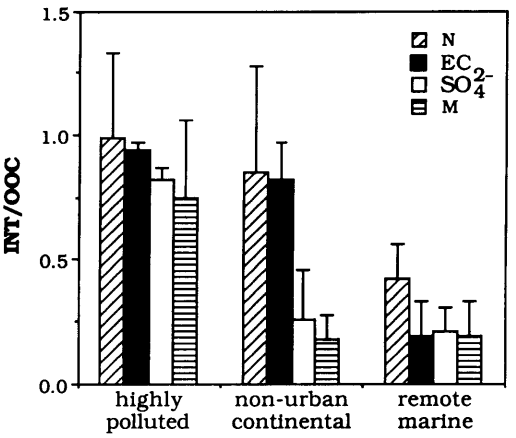

Fig. 6. Interstitial ratios of different aerosol components in different air masses, taken from a literature survey summarised in Table 3. EC = elementary carbon; M = particulate mass concentration; N = particle number concentration; SO_4^{2-} = sulphate.

ticles to about 0.2 μm radius while gravitational settling does the same coming from the largest sizes. The accumulation mode particles arriving at a remote marine site like Zeppelinfjellet will be removed most effectively through cloud scavenging processes. In principle, condensational competition between growing particles in clouds with varying levels of number concentrations is another factor leading to higher interstitial ratios in high air pollution settings. Here, different cloud types and sampling positions in the cloud will play important roles which are beyond the framework of the present study.

In more polluted atmospheres, interstitial ratios by number were higher than those by mass or by chemical mass fractions, analogous to our findings at a remote marine site. Most of the chemical scavenging data have been reported for sulphate whose behaviour is very similar to that of the total fine particle mass. EC, on the other hand, shows very high interstitial ratios in highly polluted clouds and a scavenging behaviour close to total mass- or sulphate-scavenging in the remote marine setting, (cf. Fig. 6). It has been shown for aerosols below 100% r · H in source regions and in a few Arctic haze cases that EC is much less hygroscopic than sulphate and fine particle mass (Covert and Heintzenberg, 1984; Covert and Heintzenberg, 1993; Heintzenberg and Covert, 1987). In the results of these studies, there was also some evidence for EC exhibiting hygroscopic behaviour in strongly aged air masses. We interpret this source-to-sink trend by an ageing process of an initially hydrophobic EC. During its lifetime in the atmosphere it acquires hygroscopic properties through coagulation with hygroscopic particles, through the condensation of material such as H_2SO_4 from the gas phase or by processing through non-precipitating clouds. Despite the uncertainties of our cloud-segregation scheme, our estimates of interstitial ratios fit into an internally consistent picture cloud-scavenging as a function of pollution level.

4.4. Biogenic sulphur during the different seasons

The quantification of biogenic aerosol components was a major objective of the present study. For that purpose, we focussed our attention on the data of the 2 summer seasons because there we expected biological sulphur sources to be at a maximum at the same time as the import of anthropogenic aerosols was at a minimum. Nevertheless, even in summer meteorological processes allow for influence of non-biological sulphur sources imported from lower latitudes, from the free troposphere or from sources on Spitsbergen. Thus, we went through a rigorous air mass analysis with the help of (a) soot concentrations above two standard deviations above the summer average as tracer for combustion sources of sulphur, (b) daily 3-dimensional trajectories reaching back five days, and (c) weekly ice maps produced by the National Climatic Data Centre, Asheville, NC, USA.

Besides anthropogenically influenced data, we excluded samples in air masses arriving with no exposure to ice-free waters after having spent at least five days over the central Arctic. After this classification 30 of the 124 OOC-samples remained for the summer seasons of 1990–91 (May 16 to October 15). They covered the period from the last week in May until the first week of September. Geometric mean concentrations out-of-cloud for that "biogenic" sub-population were 0.48 and 2.3 nmol m^{-3} for MSA^- and "biogenic" nss-SO_4^{2-}, respectively. Both means had a geometric standard deviation of 17%. Our corresponding average values for the whole summer period are 0.19 and 4.1 nmol m^{-3}, (cf. Table 2). The concentration differences between the total- and the "biogenic" sub-populations showed that

our air mass segregation narrowed the results to the most productive part of the summer season at the same as it reduced the influence of imported nss-SO_4^{2-}. Assuming that all of the nss-SO_4^{2-} in the sub-population was biogenic we scaled down our nss-SO_4^{2-} results according to the MSA^- ratio of the sub-population to the whole summer set and arrived at a seasonal average of 0.92 nmol m^{-3} for "biogenic" nss-SO_4^{2-} at Zeppelinfjellet. This value and the corresponding result for MSA^- are very close to summer averages at Cape Grim for the Austral summer period 16 October to 15 May of the years 1988–90. From Ayers et al. (1991), we derived for Cape Grim 0.19 and 1.1 nmol m^{-3} for MSA^- and nss-SO_4^{2-}, respectively. If we thus can accept the seasonal average value of 0.92 nmol m^{-3} for "biogenic" nss-SO_4^{2-} at Zeppelinfjellet we arrive at a 22% biogenic contribution to the 4.1 nmol m^{-3} nss-SO_4^{2-} during the summer in the Svalbard region. Using the MSA^-/nss-SO_4^{2-} ratio of our "biogenic" sub-population and our winter average for MSA^- we estimated a corresponding biogenic contribution for the winter season to be no more than two percent.

The MSA^-/nss-SO_4^{2-} ratio, called MSR in the following, is a widely used parameter describing the chemical branching of the oxidation of DMS between MSA on the one hand and SO_2 to subsequent sulphate formation on the other hand. A constant value of MSR in the remote marine boundary layer would yield a method to quantify the amount of biogenic nss-SO_4^{2-} in any air mass (Savoie and Prospero, 1989). However, in agreement with Hynes et al. (1986) laboratory studies, Bates et al. (1992b) observed an increase of MSR with decreasing temperature. On the other hand, Ayers et al. (1991) measured MSR values over the southern ocean that varied in the opposite sense with temperature. In part, these discrepancies in MSR could be explained by differences in sampling techniques. A seasonally varying contribution of non-marine sulphate has been suggested by Bates et al. (1992b) as an alternative explanation.

In different marine experiments, MSR values from 6.5% to almost 100% were measured. The unclassified summer data on Zeppelinfjellet cover most of this range. In the "biogenic" sub-population the MSA^- and nss-SO_4^{2-} data yielded MSR values mostly above 15%. They were highly correlated ($R^2 = 0.73$), with an arithmetic average value of 28%, (cf. Fig. 7). This value is close

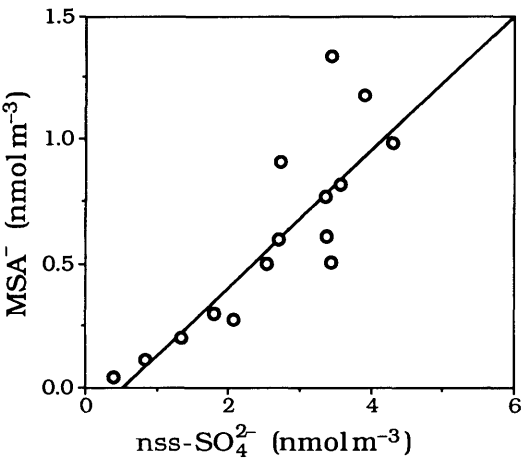

Fig. 7. Scatter plot of MSA^- and nss-SO_4^{2-} concentration in the "biogenic" sub-population during the summers 1990–91, (cf. Table 1 for acronyms). The regression line ($MSA^- = -0.15 + 0.28 \cdot$ nss-SO_4^{2-}, $R^2 = 0.73$) is included.

to range of corresponding MSR data which have been reported by Pszenny et al. (1989) and Bates et al. (1992b) in regions with minimum anthropogenic influence near Antarctica (41% and 32%, respectively). We emphasize that our observed MSR values in the "biogenic" sub-population did not correlate with observed temperatures (−10°C to 10°C), and explain this finding by the sum of the processes controlling the measured particle properties not exhibiting a net temperature dependence.

5. Conclusions

With an emphasis on the marine biogenic sulphur, the first 26 months of aerosol data from the new mountain station on Zeppelinfjellet, Spitsbergen were evaluated to elucidate source and transformation processes of the Arctic aerosol.

In the out-of-cloud data, we found several pieces of evidence pointing to a regional biological aerosol source (by number and mass), in summer.

- Average number concentrations and MSA^- concentrations were more than two times higher during the summer period than in winter.
- There were conspicuously similar summer variations of particle number and MSA^- with the

number maxima coinciding with the strong absolute maxima in MSA^- concentrations.

- In winter, half as many particles, ($\approx 100\,cm^{-3}$), were found in the radius range below 0.01 μm as compared to the summer period indicating that the aerosol was less aged in summer than in winter.
- Rigorous air mass analyses in conjunction with our chemical data showed that this regional biological source became active already in March over the Barents Sea and over the Northern North Atlantic in agreement with independent marine biological findings.

In summer, we estimated this regional marine biological source to contribute 26% to the non-sea salt sulphur as the sum of MSA^- and sulphate. In winter no more than 2% of the non-sea-salt sulphur could be attributed to the marine biological source.

By assuming that well-defined sub-set of our data was correctly classified as in-cloud data we can make estimates about physical and chemical processes controlling the aerosol in the Arctic marine boundary layer:

- There were systematic differences in the cloud-scavenging properties of MSA^- and nss-SO_4^{2-}. In summer, only 40% of the submicrometer MSA^- was scavenged while the corresponding figure for nss-SO_4^{2-} was 80%. In winter, on the other hand, we saw no significant differences in the mass scavenging of any component.
- In general, cloud scavenging by number was lower than that by mass or mass fractions with the exception of MSA^-. Its mass scavenging properties in summer were similar to those of the particle number measured above 0.05 μm radius.
- Our results suggest that MSA^- during summer is connected with smaller particles than nss-SO_4^{2-}.

We hypothesise that the measured differences between MSA^- and nss-SO_4^{2-} during summer are a consequence of the dominating chemical and physical pathways of the gaseous oxidation products of DMS to the measurable biogenic particulate components MSA^- and SO_4^{2-}. Our measured scavenging differences are consistent with the concept that MSA^- most likely is formed by condensation onto existing particles while SO_4^{2-} predominantly is formed by in-cloud oxidation of SO_2. Both cloud-related results and the out-of-cloud data yielded an internally consistent picture of a biological aerosol source in the summer Arctic.

Opposite to earlier marine sulphur studies, we found a constant MSA^-/nss-SO_4^{2-} ratio in the fine particle size range for samples with minimum anthropogenic contamination. This ratio had a value of 28% and was temperature-independent. The large variability in the MSA^-/nss-SO_4^{2-} ratio of earlier studies (6.5–100%) may have been caused by varying anthropogenic perturbations. Langner and Rodhe (1991) have shown with model calculations that the entire northern hemisphere is perturbed by an anthropogenic aerosol burden. They found the southern hemisphere hardly to be affected at all.

Since the central Arctic in summer is separated to a large extent from long-range-transported air masses from lower latitudes, it is an optimum location in the northern hemisphere where a MSA^-/nss-SO_4^{2-} ratio representative for the remote marine air can be established.

6. Acknowledgements

Maintaining high quality aerosol measurements at a remote Arctic site over years requires the collaboration of many dedicated persons. Instead of giving a long list of names we would like to thank the staff at the Zeppelin-station, our Norwegian colleagues at NILU, our project collaborators at MISU, and the staff at the European Centre for Medium Range Weather Forecast in Reading, UK for their essential contributions all the way from the point of sampling to the laboratory analyses and data reduction procedures.

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