

Multi-elemental composition and sources of the high Arctic atmospheric aerosol during summer and autumn

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(Manuscript received 5 September 1994; in final form 17 July 1995)

ABSTRACT

During the International Arctic Ocean Expedition 1991 (IAOE-91), total (i.e., $< 10 \mu\text{m}$ equivalent aerodynamic diameter (EAD)) and size-fractionated aerosol samples were collected using single filters, stacked filters and cascade impactors. The samples were analyzed for the particulate mass (PM) and up to about 50 particulate species and elements by gravimetry, instrumental multi-elemental analysis techniques and ion chromatography. The results from parallel samples, taken with the different devices and analyzed by independent techniques, were intercompared. In the samples collected over open waters (ocean subset), the median total ($< 10 \mu\text{m}$ EAD) concentrations of non-sea-salt S (nss-S) and Na were 124 and 490 ng/m^3 , respectively, but these medians were reduced to 25 and 20 ng/m^3 in the samples collected in the pack ice covered high Arctic (pack ice subset). For the mineral dust elements and anthropogenic metals, however, the levels tended to be higher in the pack ice subset than in the ocean subset. Overall, very low concentrations were observed for PM and the various particulate species in the pack ice subset, but the levels were quite similar to those obtained for background samples from the *Ymer-80* expedition. With the exception of elemental carbon, S and I, all species and elements measured, including the typical anthropogenic metals (e.g., Zn, As, and Sb), were predominantly associated with the coarse ($> 2 \mu\text{m}$ EAD) size fraction. The highest levels of the anthropogenic metals and of the mineral dust elements were found in air which in general had not been in contact with large continental or anthropogenic source regions during the last 5 or even 10 days prior to its arrival, and in an area of the pack ice which was influenced by continental river run-off from the Siberian coast. It is tentatively suggested that the elevated concentrations of both those metals and the crustal elements were the result of local mechanical windblown generation of coarse aerosols from the river effluent materials which were present on or at the surface of the ice. By relating the observed atmospheric nss-S levels to 3-dimensional air back trajectories, and from intercomparing the nss-S time trend with the trends of various other particulate species, it was concluded that the nss-S was mainly from anthropogenic origin (transported through the free troposphere) near the end of the IAOE-91, but that the marine biogenic sulfur source must have dominated during the first month and a half of the expedition.

1. Introduction

The primary objective of the atmospheric chemistry program of the International Arctic Ocean Expedition 1991 (IAOE-91) was to perform

a detailed study of the sulfur cycle in and over the Arctic Ocean and to investigate the possibility of biological control on climate through particle production and the associated impact on cloud reflectivity (Leck et al., 1991; Leck et al., 1996). The IAOE-91 took place during summer and early fall, when the input of anthropogenic sulfur into the marine boundary layer is thought to be of minimum significance relative to the contribution

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from marine biogenic dimethylsulfide (DMS) and its conversion products. Valuable information about the disturbance of the marine boundary layer by air masses from continental and/or anthropogenic origin can be obtained from the atmospheric concentrations of various particulate elements and species, including black (elemental) carbon, crustal elements and a variety of anthropogenic metals and metalloids (e.g., Sb, As, Zn). To date, however, there is only limited information available on the multielemental composition of the summer aerosol in the high Arctic (defined here as that part of the Arctic north of 80°N), and the spatial coverage of that region by the current data sets is very poor. Detailed data sets have been presented and discussed for two stations at the edge of the region, i.e., for Alert in the Canadian Arctic (e.g., Barrie and Barrie, 1990) and for Ny Ålesund on Spitsbergen (Maenhaut et al., 1989), but the multielemental aerosol composition over the high central Arctic Ocean has so far only been studied during the Swedish expedition with the *Ymer* icebreaker in 1980 (Lannefors et al., 1983). The atmospheric particulate levels of several anthropogenic elements can also advantageously be used in combination with data on non-sea-salt (nss) sulfate and on the DMS conversion product methane sulfonic acid (MSA) in order to apportion the nss sulfate in the Arctic to its anthropogenic source regions (Lowenthal and Rahn, 1985; Maenhaut et al., 1989) and to resolve the anthropogenic and marine biogenic contributions (Li and Barrie, 1993; Maenhaut et al., 1994).

In this paper, we present our results on the multielemental composition and on the black (elemental) carbon content of the summer aerosol in the high Arctic during the IAOE-91. The results were obtained by using a variety of aerosol samplers and by applying different analytical techniques. The data from the various samplers are intercompared and a comparison is also made with similar data sets from previous Arctic studies. Mass size distributions are presented and discussed for various elements. Furthermore, the atmospheric levels of the aerosol constituents are related to meteorological phenomena and in particular to the history of the air mass, as deduced from 3-dimensional back trajectories. These relationships, together with the variability of the atmospheric particulate levels as a function of sampling location and the information from the mass size

distributions, are used to infer the source regions and/or source processes for the various elements and the nss sulfate.

2. Experimental approach

The aerosol collections were performed onboard the Swedish icebreaker *Oden* during the about 70-days cruise from 1 August to 6 October, between 70°N and 90°N. Approximately 15 days were spent in the open waters and along the ice edge zone in the Greenland Sea-Fram Strait area, and the rest of the time was spent in the permanent pack ice of the Nansen and Amundsen basins, with a short visit to the Makarov basin (see Fig. 1).

2.1. The sampling system

A size-segregating inlet for simultaneous sampling of atmospheric aerosol particles and trace gases was used: The air was drawn in via ducts on a three-masted inlet system, which extended at an angle of 45° to about 3 m above the roof of the laboratory container. The top of the inlet system was situated at about 25 m above the sea surface. This set-up enabled sampling of air that was uncontaminated by the ship borne emissions, provided that the wind was within a sector of $\pm 70^\circ$ from the bow. Direct contamination from the ship was excluded by a condensation nuclei control with a wind sector controller. For sampling of aerosol particles and measurements of particle size distributions, 2 out of the 3 mast inlets were equipped with cyclones removing particles larger than $\sim 1 \mu\text{m}$ aerodynamic diameter (EAD), while the third inlet (from Anderson Samplers, Inc., Atlanta, GA) excluded particles larger than $\sim 10 \mu\text{m}$ EAD. The sampling system for both particles and gases is described in detail by Leck et al. (1996).

The data discussed in the present paper were obtained from two kinds of samplers provided by the Institute for Nuclear Sciences of the University of Gent (referred to below as INWG) and from 4 types of samplers supplied by the Department of Meteorology, Stockholm University (referred to below as MISU). The 2 INWG samplers were a stacked filter unit (SFU) and a PIXE cascade impactor (PCI), whereas the MISU devices were a sampler for total suspended particulate matter (TSP), Berner cascade impactors (BCI), Millipore

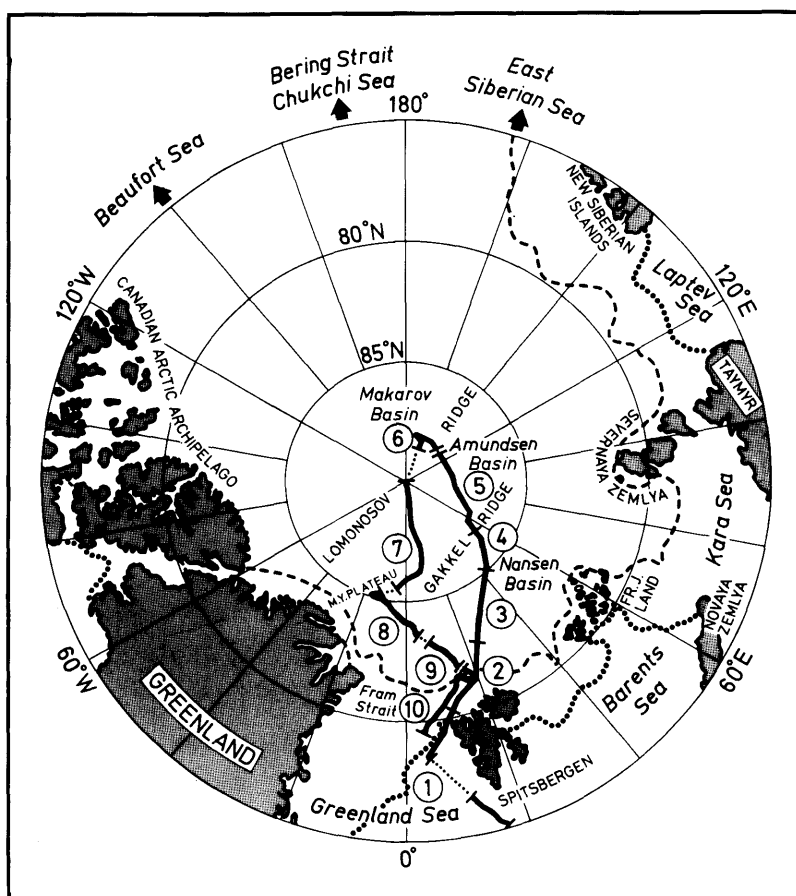


Fig. 1. Track of the *Oden* icebreaker during the International Arctic Ocean Expedition 1991 (IAOE-91). The 10 INWG sampling periods are indicated by full lines, and the start (and end) of each period is indicated by a dash. Dotted lines indicate parts of the track when no sampling took place or when the collection was interrupted (in the case of period no. 1).

Teflon filter holders (MTF) and a filter sampler for elemental carbon, soot (ST). Table 1 gives an overview of these various sampling devices and of the analyses performed on the samples from each device.

2.2. The INWG sampling devices and analyses

Both the SFU and PCI samplers were mounted on the $\sim 10 \mu\text{m}$ line. The SFU (Cahill et al., 1977; Heidam, 1981) consisted of 2 sequential 47-mm diameter polycarbonate filter holders, which contained a coarse ($8 \mu\text{m}$ pore size) Apiezon-coated and a fine ($0.4 \mu\text{m}$ pore size) Nuclepore polycarbonate filter, respectively. The coarse filter had a

50% collection efficiency at $2 \mu\text{m}$ EAD (John et al., 1983), and thus collected particles in the size range of 2 to $10 \mu\text{m}$, whereas the fine filter collected all particles $< 2 \mu\text{m}$. The SFU unit operated at a flow rate of 17 standard liters per min (slpm).

The 8-stage Battelle type PCI (Mitchell and Pilcher, 1959; Bauman et al., 1981) was operated at a nominal air flow rate of 1 slpm. The nominal cut-points (for 50% collection efficiency) of the 7 impaction stages (numbered 7 through 1) are 16, 8, 4, 2, 1, 0.50 and $0.25 \mu\text{m}$ EAD. As impaction foils we used $1.5 \mu\text{m}$ thick KIMFOL polycarbonate film which was coated with a thin layer of vaseline (for stages 7 through 2) or paraffin (stage 1) in

Table 1. Summary overview of the various INWG and MISU sampling devices, with indication of the analyses done on the samples^{a)}

	Device	Inlet line	No. of size fractions	Species measured	Analytical technique
INWG	SFU	10 μm	2	mass elements	gravimetry INAA + PIXE
	PCI	10 μm	8	elements	PIXE
MISU	TSP	10 μm	1	mass ions	gravimetry IC
	BCI ^{b)}	10 μm	3	ions	IC
	MTF ^{c)}	1 μm	1	ions	IC
	ST	1 μm	1	elem. carb. (EC)	light transmission

^{a)} Explanation of the various abbreviations used in this table:

INWG: Instituut voor Nucleaire Wetenschappen, Gent

MISU: Department of Meteorology, Stockholm University

SFU: stacked filter unit

PCI: PIXE cascade impactor

TSP: total suspended particulate sampler

BCI: Berner cascade impactor

MTF: Millipore Teflon filter sampler

ST: soot filter sampler

INAA: instrumental neutron activation analysis

PIXE: particle-induced X-ray emission analysis

IC: ion chromatography

^{b)} 2 BCI samplers were operated in parallel.

^{c)} 4 MTF samplers were operated in parallel (two at each of the two 1 μm inlets).

order to reduce bouncing off of large particles onto the walls and downstream stages. A 0.4- μm pore size Nuclepore polycarbonate filter served as a back-up filter.

The collection substrates in both INWG samplers were changed simultaneously when an effective sampling time of about 60–70 h was reached. This resulted in a total of 10 sampling periods, each extending over 3 to 7 days (see Table 2).

The coarse and fine Nuclepore filters of the SFU sampler were weighed in Gent before and after the sampling in order to determine the airborne particulate mass (PM) concentration. This weighing was done with a microbalance (with 1 μg sensitivity) in a room with rather well stabilized temperature and relative humidity (20°C and 50% relative humidity), and the filters were pre-equilibrated in this room for at least 24 h prior to weighing. Furthermore, during the actual weighing the static electricity was eliminated from the filters by means of a ²¹⁰Po radioactive source.

All INWG samples and a number of field blanks

were subjected to multielement analysis by particle-induced X-ray emission (PIXE) and instrumental neutron activation analysis (INAA). These analyses were performed in Gent after the end of the expedition. The PCI samples were analyzed by PIXE only, while the SFU filter substrates were analyzed by both techniques. Up to 22 and 39 elements with atomic number greater than 10 were measured in the PIXE and INAA analyses, respectively.

The PIXE bombardments were done with a proton beam of 2.4 MeV; the beam size at the target (specimen) was 0.54 cm² for the SFU filters and for stages 7, 6 and the back-up filter of the PCI, for the other PCI stages a beam size of 0.177 cm² was used; the beam current with the larger beam was typically 150 nA, and with the smaller beam 50 nA; the PIXE spectra were accumulated with a Si(Li) detector, and a so-called "funny filter" was interposed between specimen and detector; the spectra were collected for a proton beam preset charge of up to 50 μC . Details of the experimental set-up and of the PIXE spec-

Table 2. Overview of the INWG sampling periods, and % coverage of the effective INWG sampling times by the averaged MISU sampler data

no.	INWG sampling period			% time coverage of INWG period by MISU samples			
	Start-end (Julian day)		Effect. sampl. time (h)	TSP	BCI	MTF	ST
1	213–218	[Aug. 1–Aug. 6]	76.2	70	32	31	87
2	218–219	[Aug. 6–Aug. 7]	62.8	90	84	34	89
	& 229–231	[Aug. 17–Aug. 19]					
3	231–236	[Aug. 19–Aug. 24]	67.8	96	39	66	148
4	236–239	[Aug. 24–Aug. 27]	66.9	99		81	67
5	239–244	[Aug. 27–Sept. 1]	66.7	96	38	59	87
6	244–250	[Sept. 1–Sept. 6]	60.4	86	102	101	81
7	250–258	[Sept. 7–Sept. 15]	65.5	100	55	77	89
8	258–268	[Sept. 15–Sept. 24]	67.6	69	81	99	100
9	268–275	[Sept. 25–Oct. 2]	68.2	44	54	54	100
10	275–279	[Oct. 2–Oct. 6]	50.3	100	109	109	100

trum analysis and quantification procedures can be found elsewhere (Maenhaut et al., 1981; Maenhaut and Raemdonck, 1984; Maenhaut and Vandenhoute, 1986).

The INAA procedures were similar to those described by Maenhaut and Zoller (1977) and Schutyser et al. (1978). The analysis involved two separate irradiations of each sample at a flux of $1\text{--}3 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ in the Thetis reactor of the University of Gent. After each irradiation two or three subsequent gamma spectrometric measurements with a high-resolution Ge detector were carried out.

2.3. The MISU sampling devices and analyses

The TSP device was mounted on the $\sim 10 \mu\text{m}$ inlet, the aerosol particles were collected on a 47-mm diameter Gelman Teflo filter ($2.0 \mu\text{m}$ pore size), and the air flow rate through the filter was about 300 slpm. The samples were first analyzed for total particulate mass (as will be described below), and filter extracts from the samples were then analyzed for major cations and anions by ion chromatography (IC).

The sampler for soot analysis (ST sampler) used a Nuclepore membrane filter with $0.4 \mu\text{m}$ pore size, and the effective sampling diameter was confined to 8 mm by a mask. The ST was installed on the $\sim 1 \mu\text{m}$ inlet line and was operated at a flow rate of 3–5 slpm. The elemental carbon (EC) content of the samples was derived from a

measurement of the 550 nm light intensity transmitted through samples and blank filters. Full details on this optical technique can be found in Heintzenberg (1988).

The MTF samplers were installed on the $\sim 1 \mu\text{m}$ inlet. These devices were intended for simultaneous measurements of particulate phase methane sulfonate (MSA), sulfate (SO_4^{2-}), and sodium (Na^+). The collection substrate was a 47-mm diameter Millipore Teflon aerosol particle filter ($1.0 \mu\text{m}$ pore size). Each sample set consisted of four parallel samples and one blank (average sample flow rate: 90 slpm, and blank flow rate: 0 slpm). Duplicate 3-stage BCI samplers (Berner and Lürzer, 1980; Berner, 1984) installed on the $\sim 10 \mu\text{m}$ inlet were used to collect samples for the determination of the mass size distributions of MSA, SO_4^{2-} , Na^+ , and chlorine (Cl^-). The size ranges collected by the three stages were 5.3–1.6, 1.6–0.53 and 0.53–0.16 μm EAD, respectively. The samplers were operated at 80 slpm. Tedlar films were used as collection substrate. Blank samples were obtained by loading the impactor with the substrates at the sampling site for the length of the sampling period, but with no air drawn through the device.

The sampling times for the MISU devices ranged from 4 to 24 h, depending on real time concentration levels. After each sampling, the collection substrates for the TSP, MTF and BCI samplers were changed in an SO_2 and particle-free

glove box to minimize contamination. For PM determination, the TSP filters (actual samples and blanks) were weighed with a CAHN micro balance both before and after sampling. For the blanks no significant weight change was noticed between these two weighings. The precision (one standard deviation) of the PM determination, expressed as percentage of the mean, was $\pm 0.4\%$. The TSP and MTF filters and BCI collection substrates were ultrasonically extracted inside the glove box for 60 min, using a total volume of 5 ml 10% methanol solution. The extracts were analyzed by IC, and corrections were applied for sampling and analytical blanks. The results from duplicate samples differed less than 15% for all ions. A more detailed description of these IC analyses is given by Leck and Persson (1996a).

All atmospheric concentrations of aerosol species were expressed in mass/m³ at standard temperature and pressure (STP; 273.15 K and 1013.2 hPa). Non-sea-salt sulfur (nss-S) and non-sea-salt sulfate (nss-SO₄²⁻) levels were obtained by correcting the S and SO₄²⁻ concentrations for the contribution from sea-salt, using Na as a sea-salt indicator and the sea water composition of Riley and Chester (1971). In order to create an internally consistent aerosol data set, the higher time resolved MISU results were averaged for each of the 10 INWG sampling periods. As the INWG samplers were operated more continuously than the MISU devices, the averaged MISU data sometimes cover a 30–60% time fraction of the INWG effective sampling time only. The specific coverage by the various MISU samplers in each INWG sampling period is indicated in Table 2.

3. Results

3.1. Intercomparison of the results from the various samplers; data quality

As explained above, the results for the 10 INWG sampling periods were derived from a variety of samplers with different designs and by analyzing the samples with independent analytical techniques. In order to validate the results, an intercomparison seemed worthwhile. The concentration levels for the 10 INWG sampling periods, as derived from the various samplers, are presented in Fig. 2 for total (i.e., $<10\ \mu\text{m}$ EAD) and fine frac-

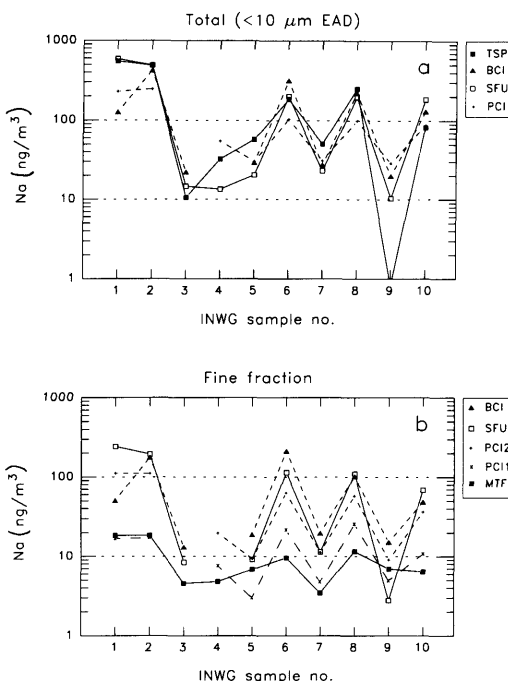


Fig. 2. Atmospheric Na concentrations for the 10 INWG sampling periods, as derived from the various INWG and MISU aerosol collection devices (SFU: stacked filter unit, PCI: PIXE cascade impactor, TSP: total suspended particulate sampler, BCI: Berner cascade impactor, MTF: Millipore Teflon filter sampler); (a) presents the data for the total aerosol ($<10\ \mu\text{m}$ EAD), (b) those for the fine fraction ($<2\ \mu\text{m}$ EAD for SFU and PCI2, $<1.6\ \mu\text{m}$ EAD for BCI, and $<1\ \mu\text{m}$ EAD for PCI1 and MTF).

tion Na, and in Fig. 3 for total ($<10\ \mu\text{m}$ EAD) and fine fraction S (sum of SO₄²⁻-S and MSA-S). For the SFU and BCI samplers, the fine fraction represents particles <2 and $<1.6\ \mu\text{m}$ EAD, respectively. From the PCI sampler two different sets of fine fraction data were derived, of <2 (PCI2) and $<1\ \mu\text{m}$ EAD (PCI1), respectively. The MTF devices collected particles $<1\ \mu\text{m}$ EAD. The total and fine data for the BCI and PCI were obtained by summing over all stages or over the fine particle stages only.

Total Na (Fig. 2a) exhibits a similar pattern for the various devices, with high values in periods 1, 2, 6, 8 and 10. However, for the peak Na periods, the PCI sampler clearly tends to provide lower values than the other three devices. A similar

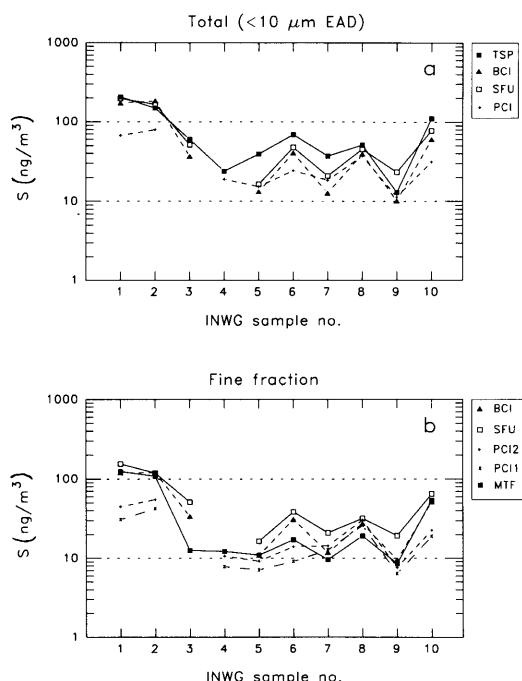


Fig. 3. Atmospheric S concentrations for the 10 INWG sampling periods, as derived from the various INWG and MISU aerosol collection devices; (a) presents the data for the total aerosol ($<10 \mu\text{m}$ EAD), (b) those for the fine fraction. See caption to Fig. 2 for further explanation.

phenomenon was observed for both total Cl and total K, and is also seen for total S (Fig. 3a). This suggests that the differences do not primarily result from analytical artifacts, but rather from sampling artifacts. The low PCI data probably have to be attributed to bounce off effects and wall losses, which are expected to become more severe as the loading on the impaction stages increases (thus for the samples with the higher concentrations). In an intercomparison exercise which was conducted at the Atlantic Ocean site of Mace Head, Ireland, François et al. (1995) also obtained lower sea-salt element concentrations with a PCI than with a SFU, especially when maritime air was sampled.

For S in the fine fraction (Fig. 3b), the PCI sampler has again a tendency to give lower values than the other devices, in particular for the samples collected over open waters (INWG periods no. 1, 2 and 10). For fine Na (Fig. 2b) there is a large spread in the data from the different samplers, with

the PCI1 and MTF results being much lower than the other data. A similar phenomenon was seen for the other sea-salt elements Cl and K. As will be discussed below, Na, Cl and K are mainly associated with the coarse size fraction, whereas S is essentially in the fine size fraction. The spread in Fig. 2b (and for Cl and K) can therefore to a large extent be explained by the differences in the upper cut-sizes for the various fine fractions ($1 \mu\text{m}$ EAD for MTF and PCI1 versus $2 \mu\text{m}$ EAD for SFU and PCI2 and $1.6 \mu\text{m}$ for BCI).

While the data sets from the MISU samplers had only a limited number of elements in common with those of the INWG devices, many more elements were in common for the SFU and PCI samplers. The data from these two samplers were compared with each other in terms of ratios PCI/SFU. The median values of the PCI/SFU elemental ratios for the total aerosol and the interquartile ranges of these ratios over the 10 INWG periods are presented in Table 3. For the sea-salt elements, including sulfur and the halogens, the median PCI/SFU ratio is about 0.5–0.6 and virtually independent upon the element. Furthermore, the PCI/SFU ratios for those same elements, and particularly for Na and Cl, were also

Table 3. Medians and interquartile ranges for the total aerosol PCI/SFU elemental concentration ratios over the 10 INWG sampling periods

Element	Median ratio	Interquartile range
<i>Sea-salt elements</i>		
Na	0.52	0.50–1.50
Mg	0.31	
S	0.51	0.48–0.88
Cl	0.58	0.45–2.2
Br	0.57	
Sr	0.93	
<i>Crustal elements</i>		
Al	0.33	0.28–0.70
Si	0.53	0.27–1.23
K	1.02	0.56–1.66
Ca	1.42	0.68–2.8
Ti	1.09	0.43–1.85
Mn	0.66	0.35–0.83
Fe	0.97	0.90–2.0
<i>Heavy metals</i>		
Cu	2.7	1.60–3.3
Zn	10	6.3–18

fairly similar within each individual INWG period, but the ratios varied substantially from period to period, as indicated by the interquartile ranges for Na and Cl in Table 3. This concurrent behavior of the elements from the same aerosol component is consistent with our above suggestion that the difference between the data from the various samplers is essentially due to sampling artifacts. For the crustal elements, the median PCI/SFU ratio is closer to one, with Al forming an exception. Interestingly, in their Mace Head study, François et al. (1995) also found better agreement between the PCI and the SFU for the crustal elements than for the sea-salt elements. Finally, for the heavy metals Cu and particularly Zn, the PCI/SFU ratio is much larger than one, and this was systematically so over all INWG periods (see the interquartile range for Zn in Table 3). The reason for this large discrepancy is not clear, but it cannot be excluded that it resulted from contamination of the PCI collection substrates, whose exchange between subsequent samplings required much more complex manipulations than was the case for the SFU. For this reason, together with the fact that the SFU data were lower than the PCI results for contamination-prone elements, the SFU data set is considered to be the more reliable of the two. Also from a pure analytical point of view, the SFU data set should be the better one, as the SFU samples were analyzed by both PIXE and INAA, so that an internal quality control could be done for the elements measured by both techniques.

When comparing the SFU total ($<10\text{ }\mu\text{m}$ EAD) airborne particulate mass (PM) concentrations with the results from the TSP sampler, it turned out that the SFU data were typically a factor of two larger. As the air flow rate through the TSP was 20 times higher than through the SFU, and, moreover, the mass was contained in one size fraction instead of two, the net filter weights were much larger for the TSP samples. Therefore, the TSP PM data were considered more reliable, and in any further discussion on total PM concentrations we will make use of the TSP PM data set only.

3.2. Concentrations of atmospheric particulate elements during IAOE-91, and comparison with other Arctic summer data sets

The atmospheric concentrations of PM, EC and selected sea-salt, mineral and anthropogenic

elements during the 10 INWG sampling periods are presented in Fig. 4. All data are total ($<10\text{ }\mu\text{m}$ EAD) atmospheric particulate phase concentrations, with the exception of those for EC ($<1\text{ }\mu\text{m}$ EAD). Furthermore, all data shown were derived from the SFU sampler, except those for PM and EC, which were obtained from the TSP and ST devices, respectively.

As will be discussed in the next Subsection (3.3), most of the mass of the various species of Fig. 4 was associated with the coarse ($2\text{ }\mu\text{m} < \text{EAD} < 10\text{ }\mu\text{m}$) size fraction, except for nss-S, I and EC. The latter three species were predominantly present in the fine ($<2\text{ }\mu\text{m}$ EAD) fraction, and from a comparison of the PCI2 and PCI1 data (Fig. 3b) it appears that the fine nss-S was essentially associated with particles of $<1\text{ }\mu\text{m}$ EAD. As already indicated in Subsection 3.1, both total and

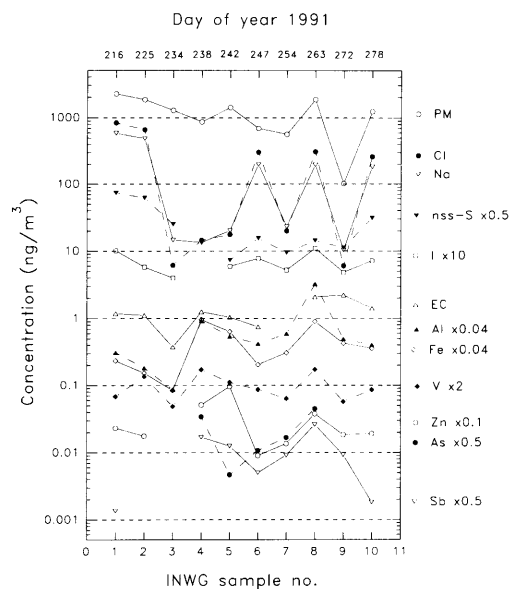


Fig. 4. Total ($<10\text{ }\mu\text{m}$ EAD) atmospheric concentrations for particulate matter (PM) and several elements, and fine ($<1\text{ }\mu\text{m}$ EAD) elemental carbon (EC) concentrations during the 10 INWG sampling periods. All data were derived from the INWG SFU samples, except those for PM and EC, which were obtained from the MISU TSP and ST samples, respectively. Missing data for Zn, As and Sb indicate that the concentration was below the detection limit. The day of year 1991 (Julian day) refers to the middle of each INWG period. This day is not very relevant for period no. 2, as there was a long interruption in sampling (see Table 1).

Table 4. Median atmospheric concentrations (ng/m^3 STP) during IAOE-91; comparison with other Arctic summer data

Species	IAOE-91 ^{a)} Ocean subset		IAOE-91 ^{a)} Pack ice		Ymer-80 ^{b)}		Ny Ålesund ^{c)}	
	<2 μm	<10 μm	<2 μm	<10 μm	Bkgd	Gr. av.	Sea level	Zeppelin
PM ^{d)}		1840 ⁺		870 ⁺	170 ^{&}	1900 ^{&}		
EC	1.18 ⁺		1.14 ⁺		1.3 ^{&}	4.5 ^{&}		11 ^s
Na	194	490	10	20			62	38
Mg	19*	49	3.0*	8.5*			13.2	9.4
Al	1.50	7.8	0.48	13.5			14.2	12.9
Si	5.4*	28*	4.6*	22*			<60	31
P	0.28*	1.69*	0.27*	1.26*			<12	
S	119	165	26	32	13	99	142	92
nss-S	102	124	21	25				
Cl	196	670	4.0	17.6	53 ^{&}	910 ^{&}	<30	26
K	8.9	22	1.12	2.1	0.59	2.6	7.4	5.9
Ca	9.0	23	0.76	3.0	2.2	2.7	<20	13.8
Sc	<0.002	<0.004	<0.0017	<0.003			0.00166	0.00165
Ti	<0.25	0.27	<0.2	0.44	0.045	0.16	<0.7	0.45
V	0.029	0.043	<0.01	0.043			0.041	0.039
Cr	<0.7	<1.1	<0.6	<1.0			<0.3	<0.06
Mn	0.062	0.085	<0.02	0.26			0.155	0.132
Fe	1.06	5.9	0.57	10.6	0.41	1.1	4.8	5.1
Co	<0.02	0.0142	<0.02	0.019			0.0041	0.0043
Ni	<0.08	<0.2	<0.08	<0.18	<0.032	<0.058	<0.14	0.047
Cu	<0.07	<0.15	<0.07	0.16	0.007	0.041	<0.5	<0.2
Zn	0.077	0.191	<0.07	0.18	0.036	0.14	0.59	0.24
Ga	<0.12	<0.16	<0.019	<0.04			<0.02	<0.03
Ge	0.0035*	0.024*	0.0025*	0.023*				
As	<0.03	<0.06	<0.010	0.022			0.0168	0.0118
Se	0.088	0.088	<0.12	<0.2			0.034	0.033
Br	0.52	1.26	0.106*	0.25*			0.98	0.96
Rb	0.027*	0.052*	0.0084*	0.042*			<0.05	<0.04
Sr	0.061*	0.22*	0.041*	0.100*			<0.7	<0.4
Zr	0.0165*	0.066*	0.034*	0.056*				<0.5
Mo	<0.14	<0.3	<0.09	<0.16			<0.017	0.0140
Ag	<0.07	<0.14	<0.06	<0.13			<0.008	<0.003
Cd	<0.3	<0.55	<0.18	<0.3			<0.06	<0.03
In	<0.002	<0.0055	<0.0012	<0.002			<0.0008	<0.0005
Sn	<3	<7	<2	<5				<0.8
Sb	0.0027	<0.005	<0.004	0.019			0.0071	0.0026
I	0.56	0.72	0.46	0.55			0.37	0.29
Cs	<0.019	<0.04	<0.019	<0.04			0.00146	0.00130
Ba	<2	<5	<1.7	<4			<0.3	<0.3
La	<0.015	<0.03	<0.007	<0.013			0.0065	0.0053
Ce	<0.14	<0.3	<0.13	<0.3			<0.03	<0.03
Sm	<0.0013	<0.003	<0.0007	0.00049			<0.0010	0.00102
Eu	<0.011	<0.016	<0.006	<0.010			<0.0006	<0.0003
Lu	<0.003	<0.007	<0.003	<0.006			<0.0004	<0.0004
W	<0.04	<0.09	<0.014	<0.03			<0.005	<0.004
Au	0.00048	0.00082	0.00019	0.00046			<0.0005	<0.00007
Pb	0.059*	0.30*	0.039*	0.20*	<0.031	0.14	<1.0	<0.3
Th	<0.017	<0.035	<0.016	<0.03			0.0020	0.00162

^{a)} This work; the data for the ocean subset are the medians for the INWG periods 1, 2 and 10, and those for the pack ice subset are the medians for the periods 3–9; the data were derived from the SFU samples, unless they are

fine sea-salt Na exhibited quite some variability over the 10 INWG periods (see Fig. 2). Total sea-salt Cl (Fig. 4) shows a similar variability, with highest concentrations in the Greenland Sea-Fram Strait area, during periods no. 1, 2 and 10. Similarly high sea-salt levels are also noted for periods no. 6 and 8. The temporal variability for total nss-S and I resembles those of the sea-salt elements in the sense that all four elements show maxima and minima for the same sampling periods, but the concentration range for nss-S and I is clearly much smaller than for the two sea-salt elements. The other species in Fig. 4 are either mineral dust elements (Al, Fe), typical anthropogenic aerosol constituents (EC, Zn, As and Sb) or a mixture of both (V). All these species show a rather similar pattern, which is quite different from that for nss-S, I and the two sea-salt elements. Indeed, the crustal elements and most anthropogenic species have their lowest concentrations in periods no. 3, 6, 7, 9 and 10 and above average levels in periods no. 4, 5 and 8; EC also shows low values for periods 3 and 6, but has its highest concentrations for periods 8, 9 and 10. Incidentally, during sampling period no. 8 high values are noted for all species, including sea-salt. The particulate mass has its highest levels in the samples with largest sea-salt content, but it exhibits notably less variability, except for the low value measured in period no. 9. This lower variability for PM is most likely due to the contributions from the mineral dust and pollution components, as these two components exhibit a time trend which is roughly complementary to that of sea-salt and nss-S.

For a comparison of the IAOE-91 results with other Arctic summer data, we divided the 10 INWG periods in 2 subsets, with, on the one hand, periods no. 1, 2 and 10 (referred to as the ocean subset) and, on the other hand, periods no. 3 through 9 (pack ice (high Arctic) subset). The median atmospheric concentrations in both the fine ($<2\text{ }\mu\text{m EAD}$) and total ($<10\text{ }\mu\text{m EAD}$) size fractions for each of these two subsets are presented in Table 4, together with other Arctic summer data sets. The IAOE-91 data in this table are generally those obtained from the SFU samples. PCI data were only used when the SFU data were below the detection limit and when both data sets were internally consistent (that is that the "real" PCI concentrations were lower than the upper limits from the SFU). The IAOE-91 medians for PM and EC were derived from the TSP and ST samplers, respectively.

The Ymer-80 data in Table 4 were taken from Lannefors et al. (1983); they were obtained in an area that extended from 20°W to 40°E between 78°N and 82°N , thus corresponding to the IAOE-91 open ocean subset sampling area. In addition to grand average mass concentrations, Lannefors et al. (1983) reported averages for samples that were considered to be representative for the Arctic background; these latter averages are expected to be comparable with the IAOE-91 high Arctic (pack ice) values. Except indicated otherwise, the Ymer-80 data of Table 4 are for the fine size fraction, with upper cut-point at 2 to $3\text{ }\mu\text{m EAD}$.

The Ny Ålesund summer aerosol data of Table 4 also apply to the fine size fraction ($<2\text{--}2.5\text{ }\mu\text{m}$

marked with a + or *; the latter data were obtained from the PCI samples (see text); the data for the particulate mass (PM) were derived from the MISU TSP sampler and those for elemental carbon (EC) from the MISU ST sampler on the $1\text{ }\mu\text{m}$ intake line.

^{b)} Data taken from Table 2 of Lannefors et al. (1983); the results are average concentrations instead of medians; Bkgd indicates Arctic background and Gr. Av. stands for Grand average; the data apply to the fine size fraction (less than $2\text{--}3\text{ }\mu\text{m EAD}$), except for those marked with a *, which are for the total aerosol; the data for K and Ca represent the non-sea-salt concentration in the fine fraction.

^{c)} All Ny Ålesund data, except those for EC, apply to the size fraction $<2.5\text{ }\mu\text{m EAD}$ and were obtained from samplings with a modified Sierra-Andersen Hi-Vol cascade impactor; the left column gives median values for the 1984, 1986 and 1987 summer samples (58 samples), when the sampler was located at sea level (Cornille, 1991), the right column gives median values for the 1991, 1992 and 1993 summer months (June, July, August; 120 samples in total), with the sampler located at the Zeppelin station at 474 m above sea level (Maenhaut et al., 1994); the S value for the Zeppelin site is the sum of $\text{SO}_4\text{-S}$ + MSA-S . The EC value for Zeppelin (marked with *) was taken from Heintzenberg and Leck (1994); it applies to the $<2\text{ }\mu\text{m EAD}$ size fraction and represents the average value for the 1990 and 1991 summers.

^{d)} PM stands for the particulate mass.

EAD). They were derived from measurements at sea level in the Kongsfjord area and at the air chemistry station on Zeppelinfjellet (474 m asl) (Cornille, 1991; Maenhaut et al., 1994; Heintzenberg and Leck, 1994). Because the 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 elevated EC levels at the mountain seem to suggest such regional air pollution.

Overall, the IAOE-91 pack ice fine fraction medians are quite similar to the *Ymer-80* Arctic background means. The higher sea-salt element levels in the IAOE-91 open ocean subset undoubtedly have to be attributed to the proximity of open water in the Greenland Sea area. This is also the case for the Ny Ålesund data and for the *Ymer-80* grand average concentrations. During summer, the marine boundary layer (MBL) of the central Arctic Ocean is only marginally influenced by polluted air masses from lower latitudes, but it is expected to contain high levels of non-sea-salt sulfate and methane sulfonate aerosol because of the strong marine biological sulfur sources in the open water areas and along the ice edge zones (Heintzenberg and Leck, 1994; Leck and Persson, 1996b). The fact that the S concentrations for the IAOE-91 open ocean subset and Ny Ålesund samples are substantially larger than those for the IAOE-91 pack ice subset and the *Ymer-80* background samples probably reflects that the former samples were taken within the marine source area itself (more than 80% of the S was nss-S in all these cases). The fine fraction concentrations of the crustal elements (Al, Si, Fe) are quite similar in the IAOE-91 and *Ymer-80* data sets, but they are about an order of magnitude lower than those observed at Ny Ålesund. The reason for this difference is not clear, but it is possible that there is a notable contribution from local soil dust at the latter site. On the other hand, there may also be a substantial difference in fine/coarse separation between the IAOE-91 and Ny Ålesund samplers. Interestingly, the Ny Ålesund fine fraction data are similar to the total ($<10 \mu\text{m}$ EAD) IAOE-91 data for the various mineral elements. As to the typical anthropogenic elements (e.g., Zn, As, Sb), a comparison between IAOE-91 and Ny Ålesund is difficult, since several fine fraction IAOE-91 medians are upper limit values, whereas "real" data were obtained for Ny Ålesund. Overall, though, the

data for these anthropogenic elements are not inconsistent with each other.

3.3. Elemental mass size distributions

From the data for the SFU and PCI samples, percentage concentration ratios fine/total ($<2 \mu\text{m}$ EAD/ $<10 \mu\text{m}$ EAD) were calculated for every element in each INWG sampling period, and average ratios and associated standard deviations were subsequently calculated for the ocean subset and pack ice subset, respectively (Table 5). For several elements fine/total ratios could be derived from both the PCI and the SFU, and, as can be seen in Table 5, the data from both sampler types are in general consistent. Furthermore, the fine/total ratios for the ocean subset are quite similar to

Table 5. Average % fine/total ($<2 \mu\text{m}$ EAD/ $<10 \mu\text{m}$ EAD) concentration ratios and associated standard deviations, as derived from the INWG PCI and SFU samplings, for the ocean and pack ice INWG subsets

Elem.	Ocean subset [$N=3$]		Pack ice subset [$N=7$]	
	PCI mean $\pm$ s	SFU mean $\pm$ s	PCI mean $\pm$ s	SFU mean $\pm$ s
PM ^{a)}		52 $\pm$ 4		51 $\pm$ 7
Na	45 $\pm$ 3	39 $\pm$ 2	42 $\pm$ 14	49 $\pm$ 12
Mg	41 $\pm$ 2		43 $\pm$ 12	
Al	17 $\pm$ 7	25 $\pm$ 14	18 $\pm$ 4	11 $\pm$ 9
Si	18 $\pm$ 2		25 $\pm$ 7	
P	18 $\pm$ 15		23 $\pm$ 18	
S	69 $\pm$ 2	78 $\pm$ 6	67 $\pm$ 11	78 $\pm$ 6
Cl	42 $\pm$ 2	28 $\pm$ 3	51 $\pm$ 14	36 $\pm$ 17
K	36 $\pm$ 4	37 $\pm$ 6	33 $\pm$ 13	47 $\pm$ 9
Ca	30 $\pm$ 5	35 $\pm$ 5	31 $\pm$ 4	37 $\pm$ 15
Ti	15 $\pm$ 4		22 $\pm$ 4	
V				38 $\pm$ 12
Cr	20 $\pm$ 4		34 $\pm$ 8	
Mn	16 $\pm$ 2		28 $\pm$ 11	
Fe	19 $\pm$ 9	20 $\pm$ 12	27 $\pm$ 6	14 $\pm$ 9
Ni	45 $\pm$ 16		39 $\pm$ 20	
Cu	37 $\pm$ 25		32 $\pm$ 9	
Zn	25 $\pm$ 7	39 $\pm$ 9	29 $\pm$ 8	
Ge	36 $\pm$ 31		27 $\pm$ 25	
Br	40 $\pm$ 5	42 $\pm$ 3	43 $\pm$ 11	
Rb	43 $\pm$ 12		32 $\pm$ 31	
Sr	26 $\pm$ 11		34 $\pm$ 13	
Zr	60 $\pm$ 57		34 $\pm$ 10	
I		80 $\pm$ 5		85 $\pm$ 3
Pb	16 $\pm$ 5		21 $\pm$ 13	

^{a)} PM stands for the particulate mass.

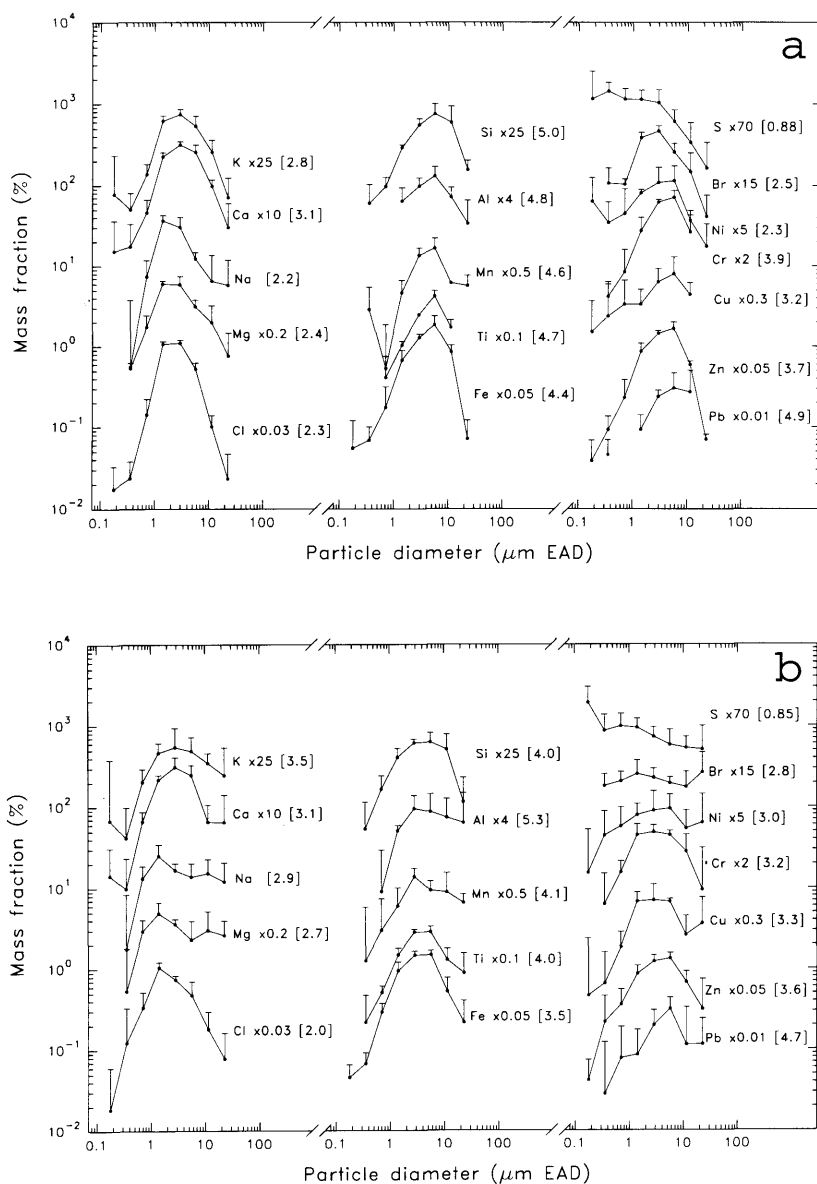


Fig. 5. Average elemental mass size distributions, as derived from the PCI samples, for the ocean sample subset (a) and for the pack ice (high Arctic) subset (b). The data represent the average mass fraction per stage and associated standard deviation. The numbers in square brackets are mass median aerodynamic diameters (MMADs) in μm , and were calculated from the average size distributions. The particle diameters in the abscissa indicate the geometric mean of the size range limits for each stage. For the open-ended upper stage (no. 7) and the back-up filter, the diameters were set at 23 and $0.18 \mu\text{m}$ EAD, respectively.

those for the pack ice subset. Most of the elements have less than 50% of their mass in the fine size fraction. For the sea-salt elements Na, Mg and Cl, and also for Br and the particulate mass (PM), about 40–50% is associated with the $<2\text{ }\mu\text{m}$ EAD fraction; for the typical mineral dust elements Al, Si, Ti, Mn and Fe (and Rb and Zr), the value is only 20–30%, and for elements that have important contributions from both sea-salt and mineral dust (i.e., K, Ca, Sr), intermediate values of 30–40% are observed. Interestingly, the metallic elements that are typically attributed to anthropogenic sources, such as V, Ni, Cu, Zn and Pb, also have average fine/total ratios of about 30–40% or even less. In fact, of all the elements measured, only two (i.e., S and I) appear to be predominantly associated with the $<2\text{ }\mu\text{m}$ EAD particles.

From the PCI data average elemental mass size distributions and average mass median aerodynamic diameters (MMADs) were calculated for the ocean and pack ice subsets, and the results are presented in Fig. 5. Similarly as for the fine/total ratios, the average size distributions and MMADs of the ocean subset (Fig. 5a) are quite similar to those for the pack ice subset (Fig. 5b). Fig. 5 shows that all size distributions are essentially unimodal. Furthermore, nearly all elements have an MMAD value of larger than $2\text{ }\mu\text{m}$, with S (MMAD: $0.8\text{--}0.9\text{ }\mu\text{m}$) being the only exception (Note, though, that I was not measured in the PCI samples). The size distributions and MMADs for the typical sea-salt and crustal elements agree in general with what could be expected on the basis of previous size distribution measurements in remote continental and oceanic regions and in the Arctic and subarctic (Milford and Davidson, 1985; Du Castel et al., 1991; Pacyna et al., 1984; Li and Winchester, 1990; Hillamo et al., 1993; Maenhaut et al., unpublished results). For the metallic pollution elements, such as Ni, Cu, Zn and Pb, on the other hand, one typically observes at remote locations either a unimodal distribution with maximum in the submicrometer size range or occasionally a bimodal size distribution with separate fine and coarse modes. This is clearly in contrast with the data in Fig. 5. Considering the discussion in Subsection 3.1 about the possible contamination for Cu and particularly for Zn in the PCI samples, the shape of the size distribution (and the coarse particle association) for elements such as

Ni, Cu, Zn and Pb may be questionable. However, from the SFU data it appeared that Cu, Zn and some other typical anthropogenic elements (i.e., As, Sb) were nearly always below the detection limit in the fine size fraction, but generally clearly observed in the coarse size fraction. This thus indicates that these metallic pollutant elements were indeed mainly associated with the coarse particles.

4. Discussion

The atmospheric aerosol over the remote central Arctic Ocean is likely to result from the combination of the following processes:

(i) mechanical generation of coarse mode sea-salt aerosols by bubble bursting at the sea surface and of windblown mineral dust on land, snow or ice surfaces;

(ii) long-range transport of fine mode biogenic materials from the open waters and along the ice edge zone of the Arctic seas and of anthropogenic aerosol particles from high-temperature sources on islands and/or land areas further to the south;

(iii) the generation of new particles from gaseous precursors and the growth of the existing aerosols by condensed and gaseous phase interactions, in particular during the cycling of air through clouds;

(iv) the removal of coarse particles by sedimentation and of fine mode aerosols by primarily wet deposition (fog or rain).

A major objective of the IAOE-91 was the quantification of the biogenic aerosol components which are related to the atmospheric natural sulfur cycle. For this purpose, sampling was performed over the central Arctic Ocean in summer, when the Arctic region is expected to be little influenced by polluted air masses. Nevertheless, even in summer some transport may occur from the large anthropogenic source regions on the Eurasian continent and from the less distant settlements within the Arctic region. In order to explain the concentration variability of the airborne particulate species over the 10 INWG periods and to understand the observed elemental mass size distributions, we examined the origin of the sampled air masses by means of 5-day (and for some

periods 10-day) backward, 3-dimensional trajectories. These trajectories were calculated with the model of McGrath (1989) at the European Centre of Medium-range Weather Forecasts (ECMWF) with the *Oden* as the arrival point and using 1000 hPa or surface pressure as arrival pressure. The clusters of trajectories for the INWG periods no. 8 and 4 are shown in Figs. 6, 7, respectively.

From the trajectory data for the entire expedition we also derived the transport time from the open sea, the time since last contact with land areas, and the time spent in the MBL since last subsidence from the free troposphere. The median

values of these various times for each of the 10 INWG periods are given in Table 6. A detailed description of the weather and air mass transport statistics during the IAOE-91 and a discussion on the reliability of the trajectory model and trajectories obtained are given by Nilsson (1996).

As indicated in Subsection 3.2, on the basis of their temporal variation over the 10 INWG periods, the airborne particulate elements can be divided in two distinct groups: on the one hand, the sea-salt elements and nss-S and I, which exhibited a roughly similar time trend with high values over the open ocean, and, on the other

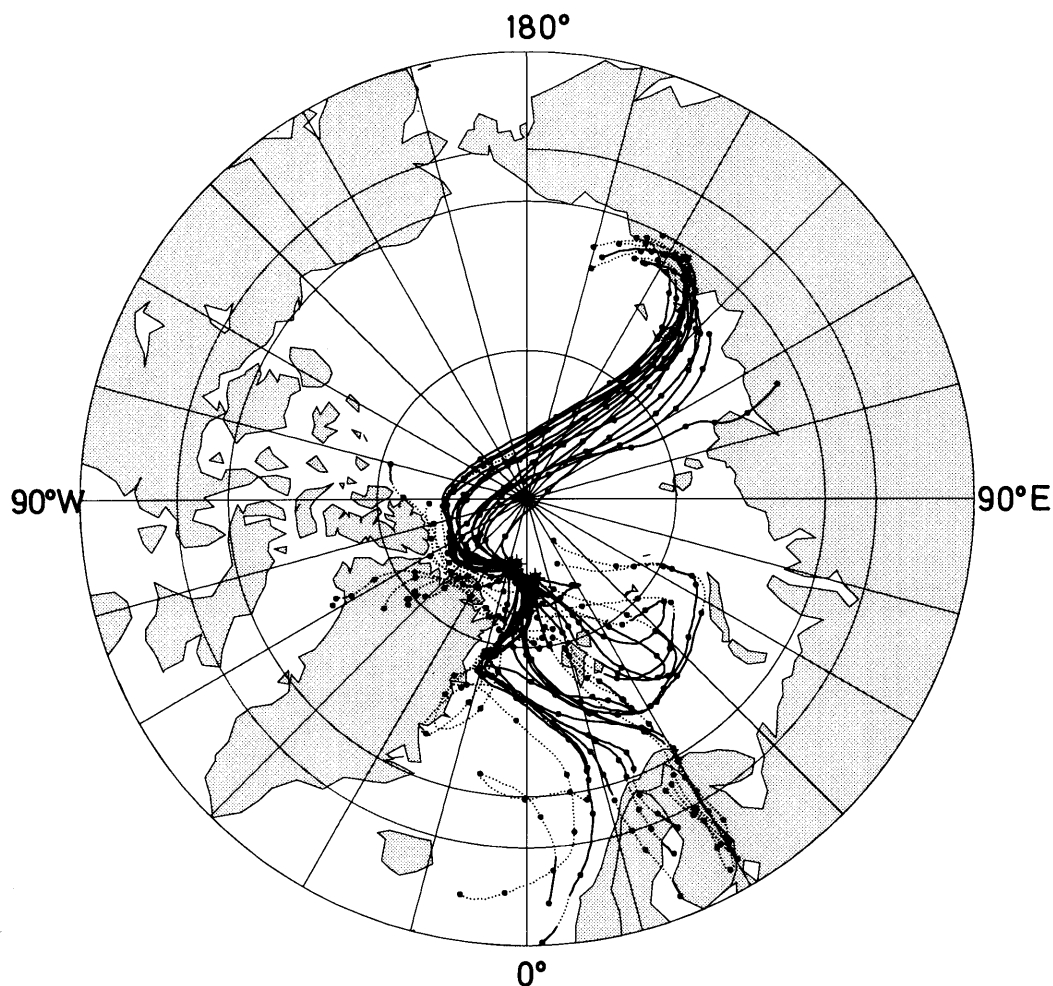


Fig. 6. Back trajectories (5 days, arrival pressure: 1000 hPa) for INWG sampling period no. 8; the dots along the trajectory indicate the air mass locations at 12-h intervals; full line: below 975 hPa, dotted line: above.

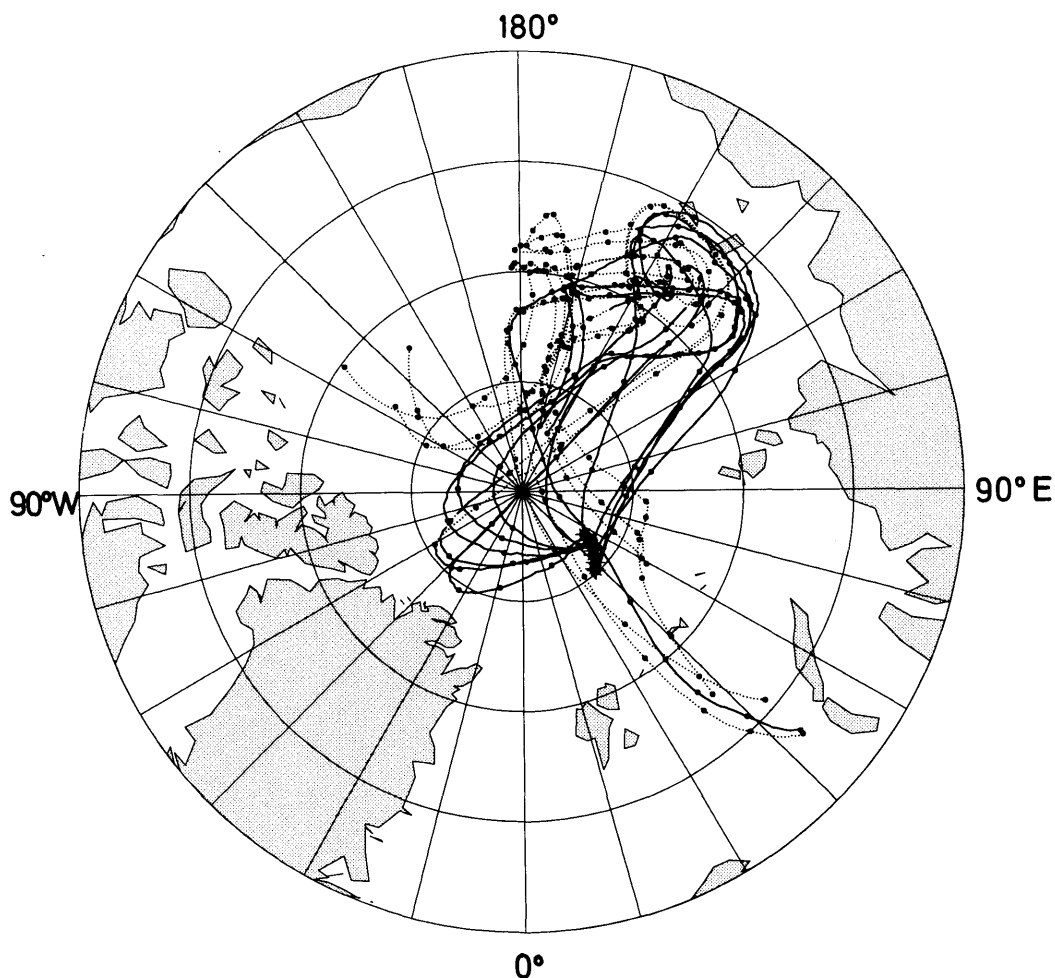


Fig. 7. Back trajectories (10 days; arrival pressure: 1000 hPa) for INWG sampling period no. 4; the dots along the trajectory indicate the air mass locations at 12-h intervals; full line: below 975 hPa, dotted line: above.

hand, the mineral dust and anthropogenic aerosol constituents, which showed a quite different pattern. On the basis of the fine-to-total ratios and of the detailed mass size distributions (Subsection 3.3) the various elements can be roughly divided into three groups: (a) nss-S and I, which are essentially associated with the submicrometer particles; (b) the sea-salt elements, with about equal proportions in the fine ($<2\text{ }\mu\text{m}$ EAD) and coarse ($2\text{--}10\text{ }\mu\text{m}$ EAD) size fractions; and (c) the crustal and anthropogenic elements, which are predominantly found in the coarse fraction. Interestingly, the size distribution data for the ocean subset are quite similar to those for the pack ice

subset. Before we proceed with the identification of the underlying factors (local versus distant sources) behind the observed multielemental signature for each of the 10 INWG samples, we like to emphasize that, due to the long sampling times, each sample represents a mixture of several air masses, although one type of air mass may have dominated.

4.1. Local marine and high Arctic sources

4.1.1. *Local marine sources.* The sea-salt levels for the ocean subset undoubtedly have to be ascribed to sea spray generation in the nearby open water. Also in the mostly pack ice covered

Table 6. Air back trajectory statistics for the INWG sampling periods (based on 5-day back trajectories)

INWG period no.	Median transport time (h) from, and fraction (%) of trajectories with any contact with					
	free troposphere		marine sources		crustal sources	
	(h)	(%)	(h)	(%)	(h)	(%)
1	62	79	0	100	60	84
2	119	31	3	100	34	100
3	84	60	21	90	81	65
4	80	69	82	85	> 120	23
5	> 120	25	55	70	> 120	40
6	89	68	34	100	74	68
7	> 120	39	58	92	101	69
8	87	70	49	97	79	86
9	43	93	> 120	39	> 120	25
10	36	78	> 120	28	> 120	22

central Arctic Ocean the contribution from locally generated coarse mode sea-salt aerosols must be taken into consideration. During a part of the INWG sampling period no. 6 a low pressure system was passing over the sampling area, with high wind speeds causing substantially larger open leads than normal (up to 40% for a short period). It is therefore quite likely that local coarse mode sea-salt contributed substantially to the high levels of the sea-salt elements in this period no. 6 (see Fig. 4). During the INWG periods no. 3–5 and no. 7–9, on the other hand, the ice cover was much more closed, and this resulted in a much reduced local source strength of sea-salt. As a consequence, the sea-salt elements Na and Cl exhibited low levels in these periods, with period no. 8 forming an exception, however.

We already indicated above that the time trend of nss-S showed much resemblance with that of the sea-salt elements. The nss-S levels during the INWG sampling periods no. 1, 2 and 10, when the *Oden* was in the open waters of the Fram Strait area, were much larger than those for the samples collected in the pack ice (see Table 4 and Fig. 4). Furthermore, nss-S was predominantly associated with the submicrometer size fraction. This all suggests that the nss-S was from marine biogenic origin and that it was formed through gas-to-particle conversion of gaseous sulfur species.

Iodine showed a similar temporal variation as the sea-salt elements and nss-S, but, in contrast to these latter species, its concentration in the ocean subset was in general not higher than in the samples taken north of the ice edge. Nevertheless, the

similarity in the time trends seems to indicate that iodine, like these other species, is of marine origin. The fact that iodine is essentially associated with the fine size fraction suggests that it results from gas-to-particle conversion of marine biogenic precursor gases. Previous investigations on iodine in the Arctic arrived at similar conclusions. Barrie and Barrie (1990) found peak concentrations for particulate iodine at Alert in April/May and in early fall (August–October). The latter peak was tentatively attributed to secondary blooms of marine biota in late summer. Particulate iodine also exhibited separate spring and fall peaks in central Alaska (Sturges and Shaw, 1993), but the fall peak only occurred in October–November. Also here was the particulate iodine believed to be from marine biogenic origin.

4.1.2. The possibility of a local high Arctic source of anthropogenic metals to the atmosphere. The somewhat unexpected coarse mode association of the anthropogenic metals and metalloids (see Table 5 and Fig. 5) seems to point towards a local wind-generation source process, and from the time trends in Fig. 4, it appears that such source should have been particularly important in the INWG periods 4, 5 and 8. In Fig. 8 we have plotted the coarse fraction (2–10 μm EAD) concentrations of the anthropogenic metal Sb and of the crustal element Fe on a map with the cruise track. The large arrow on the map indicates the area which is influenced by continental river run-off from the Siberian coast and the peripheral seas, as a result of the transpolar drift of the sea ice towards the Fram Strait area (Gordienko

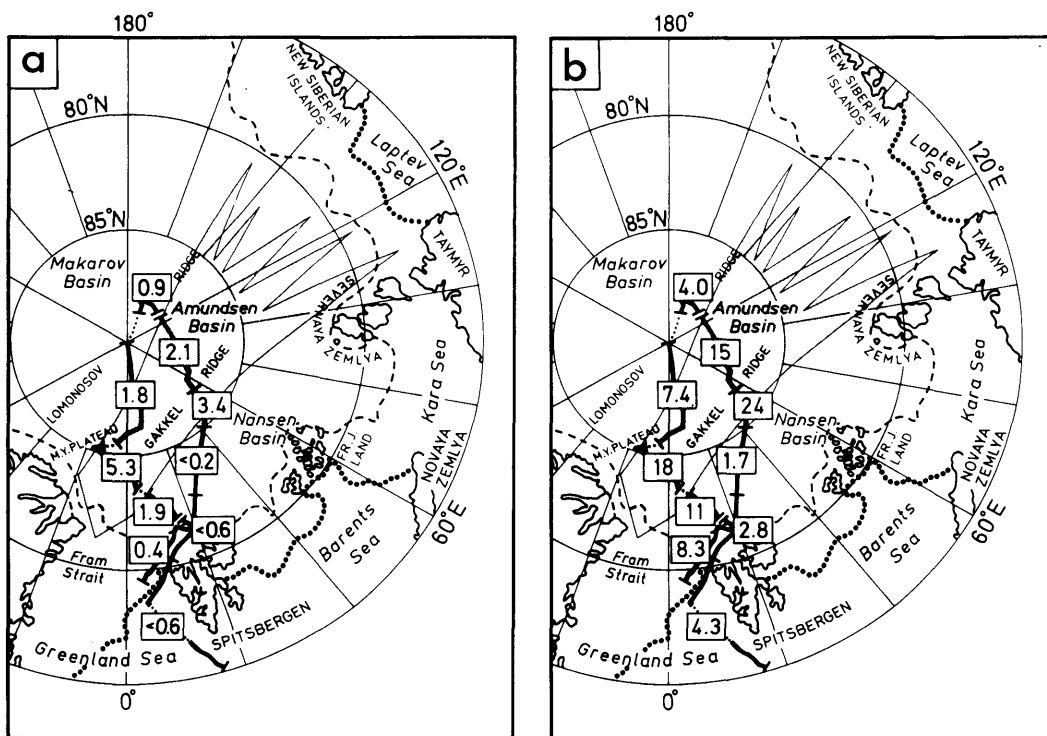


Fig. 8. Atmospheric concentrations (ng/m³ STP) in the coarse size fraction (2–10 μm EAD) for Sb (a) and Fe (b) in relation to the position of the *Oden* during the sampling. The large arrow indicates the area which is influenced by continental river run-off from the Siberian coast and the peripheral seas, as a result of the transpolar drift of the sea ice towards the Fram Strait area.

and Laktionov, 1969; Vinje, 1982; Colony and Thorndike, 1985). The ice surface in this area, and particularly near the river deltas in the shallow Siberian shelf sea, is covered with numerous clay spots and with various pollution effluents (Stig Westerlund, private communication, 1994). During an expedition with the R/V *Polarstern* icebreaker in July and August 1987, Pfirman et al. (1989) found that the ice north of 83°N was very much affected by particle-rich surface accumulations, and analyses of samples scraped off from the accumulations indicated that they contained lithogenic sediments (including also coal and heavy minerals) and biogenic materials. Large patches of particle-laden ice have also previously been reported by many Arctic researchers (e.g., Clark and Hanson, 1983). As indicated by Reimnitz and Kempema (1987) and Reimnitz et al. (1987), coarse shelf surface sediments, organic matter and river effluents can be incorporated into

the sea ice as a consequence of freeze-up storms and the formation of anchor ice. The latter rises to the surface, in the process lifting materials that are attached to it. It is quite intriguing that the highest levels for both Sb and Fe are observed in that area that is influenced by the Siberian river run-off (INWG periods 4, 5 and 8), and that elevated levels are also seen at the edge of this area (INWG periods 7 and 9), but that the concentrations outside the marked area (INWG periods 1–3, 6 and 10) are generally low. Although this may seem speculative, we like to put the hypothesis forward that the elevated concentrations of both the anthropogenic metals and the crustal elements are at least to some extent the result of local mechanical windblown generation of coarse aerosols from the river effluent materials which are present on or at the surface of the ice.

An alternative explanation for the coarse mode association of the anthropogenic metals is that

these metals mode were deposited as fine mode anthropogenic aerosols on the ice during Arctic haze episodes in late winter, and are then re-injected into the atmosphere as coarse mode windblown aerosols. However, this process does not explain why the atmospheric levels are particularly enhanced in the river run-off area.

Still another explanation is that the anthropogenic metallic elements result from long-range transport from Eurasian source regions to the high Arctic, but that there is an extensive atmospheric processing of the primary anthropogenic aerosol particles during summer, whereby those fine particles become attached to coarse mode sea-salt and/or mineral dust particles, so that an internally mixed aerosol is formed. That atmospheric processing, particularly in clouds, can indeed lead to internally mixed particles was demonstrated in a study by Andreae et al. (1986) on the remote marine aerosol. In that particular study, electron probe microanalyses indicated that sea-salts, silicates and sulfates had become internally mixed. The atmospheric (cloud) processing may well be at the origin of the coarse fraction association of the anthropogenic metallic elements for several of our sampling periods, in particular for the open ocean subset (periods no. 1, 2 and 10). However, it does not explain the particular pattern of Fig. 8. More important, as will be discussed in Subsection 4.2.2 below, some of the highest Sb and Fe levels were observed in air which had not been in contact with large continental or anthropogenic source regions during the last 5 to 10 days prior to its arrival at the *Oden*.

4.2. *Transport from sources within the Arctic and long-range transport from distant sources*

4.2.1. *Characterization of the INWG sampling periods with regard to atmospheric transport, and cloud processes during transport.* Nilsson (1996) concluded that the air masses during the IAOE-91 were predominantly from marine origin, and had been advected mainly from over the Atlantic Ocean and from the open seas which surround the central Arctic Ocean. This was the case for the INWG sampling periods no. 1–8. The second most important air mass origin appeared to be the free troposphere. Such origin was most common at the end of the expedition (end of September and beginning of October), when the air subsided from the free troposphere north of the ice edge zone (this

was the case for INWG periods 9–10). Also, in the beginning of August (first part of INWG period 1) subsiding free tropospheric air was sampled, but at that time the air subsided from Greenland. In general, during the 5-day (or 10-day) back trajectories, the air masses remained confined to the Atlantic sector and to the central Arctic Ocean north of 70°N, and it occurred only rarely that an endpoint of a trajectory was deep within the continent. Only 6% of the IAOE-91 air mass trajectories ended in regions which were suspected to be polluted, most of these trajectories were noted during two episodes of transport from Scandinavia and Russia. One of these episodes is described in detail by Bigg et al. (1996) and Covert et al. (1996).

In the INWG sampling periods no. 2–8 the air mass remained essentially within the MBL during the 5 days prior to arrival. During this advection over the pack ice, the aerosol particle population may have been seriously affected by both mixing processes and cloud-aerosol interactions. Nilsson and Bigg (1996) found that the fogs were in general an inefficient sink for the aerosol particles. But the stratus clouds above in combination with the mixing processes described by Nilsson (1996) and Bigg et al. (1996) should most likely have had a significant effect on the size distribution of the aerosols in the surface layer.

4.2.2. *Transport from anthropogenic sources.* The anthropogenic metals had their highest concentrations in the high Arctic (i.e., in the INWG periods no. 4, 5 and 8), and their mass was essentially contained in the coarse size fraction, which was rather unexpected. As can be seen from the trajectory cluster for INWG period no. 8 in Fig. 6, long-range transport from anthropogenic sources in northern Europe may have contributed considerably for this sample no. 8, which exhibited the highest levels of anthropogenic metals. For the other samples, however, such potential continental source regions were virtually always at more than 5 days transport distance, with only few exceptions. As an example, Fig. 7 gives the trajectory cluster for INWG period no. 4, which had the second highest mass concentrations of anthropogenic metals. All trajectories of Fig. 7 remain confined to the central Arctic Ocean north of 70°N, and only on a few occasions is there some indication of possible air mass transport from northern Russia/Siberia. Consequently, any polluted air from this region would have been very

much diluted by the air masses which had been over the central Arctic Ocean for more than 5 days. The same was true for INWG period no. 5. Thus, while the high levels of anthropogenic metals for INWG period no. 8 could be explained by long-range transport, such explanation can hardly be invoked for the elevated pollution metal levels in periods no. 4 and 5. As we indicated above, both the observed time trends and the coarse particle association of the metallic pollutants can be explained by the local aeolian generation of coarse mode particles on the ice-covered area which is influenced by Siberian river run-off. Most likely, this same process was also a major source process for the crustal elements in the high Arctic.

Fine elemental carbon (EC) is an excellent indicator for combustion sources. As seen in Fig. 4, EC exhibited the highest levels in the last three INWG periods, nos. 8–10. This observation is consistent with the apparent influence of direct long-range transport from anthropogenic sources in northern Europe and Russia for INWG sample no. 8 and with a free tropospheric air mass origin which is influenced by more distant anthropogenic sources, for samples no. 9–10 (see also Table 6).

It cannot be excluded that anthropogenic sources within the Arctic itself may have contributed during short periods. This has been exemplified by Bigg et al. (1996) by the observation of a plume from Spitsbergen over the central Arctic Ocean. However, such episodes contributed rarely to the particulate mass and, they generally lasted for much shorter periods than the INWG sampling times. Furthermore, for the anthropogenic metals a single fine mode or a bimodal mass size distribution would have been expected, and this was clearly not the case.

4.2.3. Transport from crustal sources. The mineral dust elements were mainly found in the coarse mode (see Table 5 and Fig. 5). The MMADs for these elements in both the ocean and pack ice subsets were of the order of 4–5 μm , whereas these for the sea-salt elements were only 2–3 μm (Fig. 5). Considering that the median transport time from land areas was about 4–5 days (see Table 6), the mineral element MMADs are not inconsistent with a continental source, although they are somewhat at the high side. However, the fact that the mineral elements exhibit larger MMADs than the sea-salt elements Na and Cl, even in the ocean subset, seems to argue

against their long-range transport origin. As explained above, a substantial fraction of the mineral dust elements in the high Arctic may well be from nearby local origin.

4.2.4. Transport from the marine source. When the median transport times from the marine source (Table 6) are related with the time trends for nss-S, I and the sea-salt elements, it appears that the most elevated levels for these species are seen in the INWG periods with the shortest transport time (i.e., periods 1 and 2). This strongly suggests that nss-S, I and the sea-salt elements are all from marine origin. This suggestion is confirmed by the fact that nss-S and the various sea-salt elements, including Na, Cl, K, Ca and Br, exhibited clearly higher concentrations in the ocean subset than in the pack ice subset (Table 4).

Sulfur was mainly associated with the fine particle size fraction, which suggests a gas-to-particle conversion process. The gaseous source itself could either be marine, i.e., the biological production of DMS, or anthropogenic, i.e., fossil fuel combustion and smelting activities. On the basis of the air mass trajectories and of the similarity of the time trends of nss-S and the sea-salt elements, but dissimilarity with the trends of fine mode EC, crustal elements and anthropogenic metals, we can now conclude that the dominant source of sulfur for the INWG periods no. 8–10 must have been anthropogenic (advection of polluted air through the free troposphere), whereas the marine biogenic sulfur source must have dominated for the INWG periods no. 1–7. This agrees well with the conclusions drawn by Leck and Persson (1996b) and Leck et al. (1996).

5. Summary and conclusions

The intercomparisons of the IAOE-91 atmospheric particulate data, as obtained from various sampler types and by using different analytical techniques, indicated that there was generally reasonable agreement. However, the PCI sampler had a tendency to give lower values than the other collection devices, in particular for the sea-salt elements and for the samples with higher mass loadings. It was concluded that the low PCI data are most likely the result of sampling artifacts, i.e., bounce off effects and wall losses. It was further suggested that the PCI samplings may have suf-

fered from contamination problems for the heavy metals, especially for Zn.

In the high Arctic very low atmospheric levels were generally found for the particulate mass (PM) and the various particulate species. The median concentrations of total ($<10\text{ }\mu\text{m EAD}$) PM, S, Na and Al were 870, 32, 20 and 13.5 ng/m^3 STP, respectively. These medians for PM and Na are only about 5 times larger than the average summer levels for these species at the geographic South Pole (Maenhaut et al., 1979), and for S, the high Arctic data are even lower than the levels at the South Pole. This clearly indicates that the high Arctic planetary boundary layer during summer is only very little influenced by natural and anthropogenic aerosols (and aerosol precursors). For the fine fraction ($<2\text{ }\mu\text{m EAD}$), the IAOE-91 levels could be compared with other Arctic summer data. The Ymer-80 data of Lannefors et al. (1983) were quite similar to the IAOE-91 data, but it should be indicated that only 12 particulate species were measured in the Ymer-80 expedition versus about 50 in the current study. The fine fraction concentrations of S and the sea-salt elements for the IAOE-91 open ocean samples were of the same order as those found at the Ny Ålesund sea level and Zeppelin mountain stations, but about 5–10 times larger than in the IAOE-91 high Arctic sample subset. On the other hand, for the fine fraction of the mineral dust elements (Al, Fe), considerably lower (5 to 10 times) levels were noted in both the IAOE-91 ocean and high Arctic (pack ice) subsets than at Ny Ålesund. This suggests that the latter site is influenced by mineral dust from local origin, but there may also be a substantial difference in fine/coarse separation between the IAOE-91 and Ny Ålesund sampling devices.

A surprising finding was that the typical anthropogenic metals and metalloids (e.g., Zn, As, and Sb) were essentially associated with the coarse ($>2\text{ }\mu\text{m EAD}$) size fraction. Furthermore, the highest levels of these elements and of the mineral dust elements were found in air which in general had not been in contact with large continental or anthropogenic source regions during the last 5 or even 10 days prior to its arrival at the *Oden*. Intriguingly, these highest levels were observed when the ship was in the pack ice in an area which was influenced by continental river run-off from the Siberian coast. It is tentatively suggested

that the elevated concentrations of both the anthropogenic metals and the crustal elements are at least to some extent the result of local mechanical windblown generation of coarse aerosols from the river effluent materials which were present on or at the surface of the ice. However, considering the limited number of sampling periods in the current study (only 10), further work will be needed to check this hypothesis.

Of the various species measured, only three (i.e., elemental carbon (EC), S and I) were predominantly associated with the fine size fraction. EC, which is an excellent indicator for combustion sources, exhibited the highest levels near the end of the IAOE-91, when there was direct long-range air mass transport from anthropogenic source areas in northern Europe and Russia or when the air subsided from the free troposphere and was likely influenced by distant anthropogenic source regions. Iodine and nss-S showed a similar temporal variation as the sea-salt elements, suggesting that they were predominantly from marine origin, but because of their fine particle association, the nss-S and I must have been formed from gaseous precursors. From relating the observed atmospheric nss-S levels to the origin of the air mass, as deduced from back trajectories, and from inter-comparing the nss-S time trend with the trends of various other particulate species, it was concluded that the nss-S was mainly from anthropogenic origin near the end of the IAOE-91, but that the marine biogenic DMS source must have dominated during the first month and a half of the expedition.

6. Acknowledgments

The authors are grateful to the crew of the icebreaker *Oden* (chartered from the Swedish National Maritime Administration by the Swedish Polar Research Secretary) for their assistance and cooperation. The authors are also highly indebted to Keith Bigg for operating several of the aerosol collectors during the expedition, and to Jan Cafmeyer for technical assistance in the preparation of the sampling devices and in the sample analyses in Gent. W.M. and G.D. acknowledge support from the Belgian "Nationaal Fonds voor Wetenschappelijk Onderzoek", the "Interuniversitair Instituut

voor Kernwetenschappen", the "Instituut tot Aanmoediging van het Wetenschappelijk Onderzoek in Nijverheid en Landbouw", and the Impulse Programme "Global Change" supported by the Belgian State, Federal Office for Scientific, Techni-

cal and Cultural Affairs. C.L., E.D.N. and J.H. were funded by the Swedish Natural Science Research Council (contract E-EG/GU 9906-303/E-EG 3922-313) and the Knut and Alice Wallenberg Foundation.

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