

# Seasonal variability of crustal and marine trace elements in the aerosol at Neumayer station, Antarctica

By ROLF WELLER<sup>1\*</sup>, JANINA WÖLTJEN<sup>1†</sup>, CLAUDIA PIEL<sup>1</sup>, ROSA RESENBERG<sup>1</sup>, DIETMAR WAGENBACH<sup>2</sup>, GERT KÖNIG-LANGLO<sup>1</sup> and MICHAEL KRIEWS<sup>1</sup>, <sup>1</sup>Alfred Wegener Institute for Polar and Marine Research, Am Handelshafen 12, 27570 Bremerhaven, Germany; <sup>2</sup>Institut für Umweltphysik, University Heidelberg, Im Neuenheimer Feld 229, D-69120 Heidelberg, Germany

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## ABSTRACT

Atmospheric trace element concentrations were measured from March 1999 to December 2003 at the Air Chemistry Observatory of the German Antarctic station Neumayer, by inductively coupled plasma–quadrupole mass spectrometry (ICP–QMS) and ion chromatography (IC). This continuous five-year long record derived from weekly aerosol sampling revealed a distinct seasonal summer maximum for elements linked with mineral dust entry (Al, La, Ce, Nd) and a winter maximum for the mostly sea salt derived elements Li, Na, K, Mg, Ca and Sr. The relative seasonal amplitude was around 1.7 and 1.4 for mineral dust (La) and sea salt aerosol (Na), respectively. On average, a significant deviation regarding mean ocean water composition was apparent for Li, Mg and Sr, which could hardly be explained by mirabilite precipitation on freshly formed sea ice. In addition, we observed all over the year, a not clarified high variability of element ratios Li/Na, K/Na, Mg/Na, Ca/Na and Sr/Na. We found an intriguing co-variation of Se concentrations with biogenic sulphur aerosols (methane sulphonate and non-sea salt sulphate), indicating a dominant marine biogenic source for this element, linked with the marine biogenic sulphur source.

## 1. Introduction

The nearly completely ice covered Antarctic continent is virtually free of primary and secondary aerosol sources, whereas the Southern Ocean is by far the dominant source to the Antarctic aerosol body, making atmospheric sea salt and biogenic sulphur the major aerosol components (Minikin et al., 1998; Wagenbach et al., 1998). Terrestrial sources are limited to some insular rocky regions (on the Antarctic peninsula, in the coastal dry valleys and on high mountain ranges) and volcanic activity of Mt. Erebus. Nowadays, minor anthropogenic emissions, arising from fossil fuel combustion during research and tourism activities, may be considered as well. On the whole, these natural and anthropogenic sources constitute local or regional trace element emissions of mineral dust, sulphur and specific heavy metals, which are thought to be of minor importance for the overall aerosol budget of Antarctica. Therefore, Antarctica offers an outstanding place to study the background composition and the natural biogeochemical cycling of aerosol.

Apart from ion analyses, only limited trace element measurements have been conducted so far in Antarctic aerosol samples as: at South Pole (Zoller et al., 1974; Cunningham and Zoller, 1981; Tuncel et al., 1989), at the Antarctic peninsula (Dick, 1991; Artaxo et al., 1992) and at coastal areas (i.e. Neumayer Station; Görlach, 1988; Wagenbach et al. 1988). In recent years, the need for long-term background aerosol studies, especially addressing the trace element composition, has been recognized. Certain heavy metals (e.g. Pb, Cd, Cr) can be employed as valuable tracers for the growing impact of anthropogenic heavy metal emissions for remote Antarctica (Wolff and Suttie, 1994; Wolff et al., 1999; Planchon et al., 2002). Furthermore, mineral dust derived trace elements like Fe may act as micronutrients, affecting the biological activity of the ocean (Jickells et al., 2005), for example, the atmospheric CO<sub>2</sub> burial (Bopp et al., 2003; Wolff et al., 2006) and the emission of dimethyl sulfide (DMS; Turner et al., 2004), which is globally the most important precursor for natural sulphate aerosol. Finally, mineral dust and sea salt profiles retrieved from polar ice cores have proven to provide a wealth of palaeoclimatic information (e.g. Petit et al., 1999; Wolff et al., 2006; Fischer et al., 2007; Ruth et al., 2007). For improving the interpretation of these records, a better knowledge about long-range transported continental dust and regional derived sea salt would be needed, especially including the seasonality of their atmospheric loading and entry into the Antarctic

\*Corresponding author.

e-mail: rolf.weller@awi.de

†Now at: School of Environmental Sciences, University of East Anglia, Norwich NR4 7TJ, UK.

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continent. Concerning sea salt aerosol, the formation on freshly formed sea ice, associated with a significant sea salt fractionation, has been put forward as an alternative source (Rankin et al., 2000, 2002; Wolff et al., 2003) to the accepted process by wind induced bubble, bursting over open ocean water (Monahan et al., 1986). If the significance of this source proves true, it would entail a paradigm shift in the interpretation of sea salt profiles from polar ice cores (Wolff et al., 2003).

Here, we present atmospheric trace element records mainly associated with mineral dust and marine sources, which are continuously observed between 1999–2003, at the German Antarctic Neumayer station. Primarily focusing on seasonal aspects, the weekly filter samples were analysed by inductively coupled plasma–quadrupole mass spectrometry (ICP–QMS) for the trace element Li, Na, K, Mg, Ca, Sr, Al, La, Ce, Nd and Se. The ICP–QMS results are supported by our regular IC analyses, providing complementary information on the ionic aerosol composition with respect to methane sulphonate, sulphate,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ .

## 2. Methods

### 2.1. Measurement site and meteorological conditions

Aerosol sampling was made at the Air Chemistry Observatory, about 1.5 km south of Neumayer station ( $70^\circ 39'S$ ,  $8^\circ 15'W$ ). During the summer months, the bay and the nearby ice edge are mainly free of sea ice, and there is always open water present. Apart from a few nunataks about 100 km south of the station, there are no ice-free land surfaces near Neumayer, and the probability of contact with air masses from ice-free continents is small. In general, there are two different wind regimes: (1) strong synoptically affected winds are from the east, with infrequent geostrophically intensified switches to the west and (2) weak katabatic winds from southern directions. The air mass transport pattern to Neumayer station was investigated by Kottmeier and Fay (1998), and a more detailed picture on the climatology at Neumayer Station can be found in König-Langlo et al. (1998).

Aerosol was collected on Whatman 541 cellulose filters, which were pre-cleaned by soaking in HCl, followed by rinsing with de-ionize water until virtually no enhancement of the electrolytic conductivity could be detected. The aerosol was continuously sampled at  $120 \text{ m}^3 \text{ h}^{-1}$  by two filters (diameter 240 mm) in series, using a ventilated electropolished stainless steel inlet stack (total height about 8 m above the snow surface), with a 50% aerodynamic cut-off diameter around 7–10  $\mu\text{m}$  at wind velocities between 4 and 10  $\text{m s}^{-1}$ . This high volume sampling technique is part of the continuous long-term observation programme, carried out since 1983 at Neumayer. Here, we refer to samples taken from March 1999 to December 2003. These data were based on a sampling period, typically, of 7 d, which corresponds to a probe volume of around  $2 \times 10^4 \text{ m}^3 \text{ STP}$ . A

more detailed description of the sampling procedure itself is given in Wagenbach et al. (1988).

Local pollution by vehicles and the base itself is a potential problem for many measurements concerning the background status of the Antarctic troposphere. To ensure contamination free air sampling, the Air Chemistry Observatory is situated in a clean air facility, approximately 1.5 km south of Neumayer. Due to the fact that northerly wind directions are very rare, contamination from the base can be excluded for most of the time. Additionally, the power supply (20 kW) is provided by cable from the main station; thus, no fuel driven generator is operated in the observatory vicinity. Finally, contamination-free sampling is controlled by the permanently recorded wind velocity, wind direction and by the condensation particle (CP) concentration. Contamination was indicated for each of the following criteria: wind direction within a  $330^\circ$ – $30^\circ$  sector, wind velocity  $< 2.0 \text{ m s}^{-1}$  and/or CP concentrations (measured by a TSI CPC 3022A particle counter)  $> 2500 \text{ cm}^{-3}$  during summer,  $> 800 \text{ cm}^{-3}$  during spring/autumn and  $> 400 \text{ cm}^{-3}$  during winter. The CP threshold values were chosen based on our more than 20-year long CP record from Neumayer, demonstrating that CP concentrations above the corresponding levels can usually be traced back to local pollution. In case of contamination, given by these criteria, an automatic interrupt of the sampling procedure was initiated within 1 s (shut down of the pumps and closing the electromotive valves typically needed around 10 s). Sampling was restarted after recurrence of clean air conditions and a delay of 2 min. However, most of the data loss was provoked by blizzards and drifting snow (wind velocity  $> 20 \text{ m s}^{-1}$ ). During such harsh weather conditions, aerosol sampling has to be switched off (due to the danger of snow entering the inlet), which entailed a downtime of roughly 10% of the observation period. Note, that  $< 2\%$  of data loss was actually caused by potential contamination.

### 2.2. Analytical methods

**2.2.1. ICP–QMS analysis.** Trace element analysis was performed by means of ICP–QMS (ELAN 6000, Sciex/Perkin Elmer), equipped with a cross-flow nebulizer as sample introduction system. The alignment of the instrument (plasma torch, ion lens, gas flow, nebulizer) was checked and adjusted before analysis, by daily performance solutions containing a mixture of  $10 \text{ ng g}^{-1}$  Mg, Ba, Ce, Pb and Rh. One half of each filter was used for trace element analysis, while another 1/6 of each filter was used for IC analysis (see below). For trace element analyses, we chose a total digestion of the samples to quantitatively dissolve all mineral compounds, which had not been given by simple acidic ( $\text{HNO}_3$ ) leaching (Lindberg and Harris, 1983; Reinhardt et al., 2003, table 5 therein). Thus, these aliquots were subjected to a pressurized digestion system (DAS 100, Picotrace) at  $200^\circ\text{C}$  in a mixture containing  $\text{HNO}_3$  (suprapure, 65%, Merck, Darmstadt, Germany, sub-boiling bi-distilled), HF (suprapure, 40%, Merck, Darmstadt, Germany, sub-boiling bi-distilled) and

Table 1. Instrumental ICP-QMS detection limits (IDL,  $n = 60$ ) and overall method detection limits (MDL,  $n = 49$ ), corresponding to a typical, total sampling volume of  $2.0 \times 10^4 \text{ m}^3$  (MDL for IC-analysis given in parenthesis)

Element ( $\text{pg m}^{-3}$ )	IDL	MDL
Li	0.12	0.21
Na	16	1800 (300)
Mg	0.44	300 (170)
K	32	330 (100)
Ca	5.0	1300 (140)
Sr	0.02	12
Al	10	220
La	0.005	0.07
Ce	0.002	0.17
Nd	0.006	0.09
Se	2.7	3.1

$\text{H}_2\text{O}_2$  (suprapure, 30%, Merck, Darmstadt, Germany). With this device, a series of 24 samples could be digested in parallel. Each series included one filter blank and a certified reference sample (NIST 1648 urban particulate matter). For calibration, we used commercially available standard solutions ( $10^4$  ppb multi-element verification standard 1 and 2, Perkin Elmer, Wiesbaden, Germany), which were generally applied in 1, 10 and 100 ppb concentrations (1 ppb corresponds to 1 ng of each element in 1 g solute). Each sample was spiked by 10 ppb Rh as internal standard to normalize the signal intensities and compensate instrumental sensitivity variations. The instrumental detection limits (IDL) were derived from 60 blank solutions and correspond to three times the standard deviation ( $SD$ ) of these blank values (Table 1). Based on the results of the NIST reference material, the retrieval for each element to be discussed here was generally between 95 and 100%. When analysing the filter samples of the years 2002 and 2003, we were frequently faced with abnormally elevated Al-blanks prohibiting further evaluation. Thus, the time-series of this period appeared fragmentary. Due to these unexplained analytical problem, we decided to use the consistently measured La as mineral dust tracer and reference element for calculating crustal enrichment factors.

The variability of the filter procedure blanks clearly governed the overall accuracy, as well as the analytical detection limits. These estimates were derived from the variation of 49 identically processed procedure blanks and include possible contributions by the previously cleaned filters and any effects arising from handling and storage. We conservatively estimated the method detection limits (MDL) as three times the standard deviation ( $SD$ ) of these overall blank values (Table 1). In addition to this blank induced uncertainty, relative ICP-QMS calibration errors were considered. In short, the combined uncertainty was found

to be approximately between  $\pm 8$  and  $\pm 12\%$  for element concentrations above three times the corresponding MDL. It increased from around  $\pm(15\text{--}20)\%$  approaching  $3 \times$  MDL level to roughly  $(+50\text{--}100)\%$  close to the MDL. The final atmospheric concentrations (in  $\text{ng m}^{-3}$  or  $\text{pg m}^{-3}$ ) were calculated from the blank corrected element amounts and the corrected sampled air volume to standard conditions (273.16 K and 1013 hPa).

2.2.2. *IC analysis.* The extraction of the aliquots for IC analysis included soaking and shaking in 50 ml MilliQ water, followed by ultrasonic treatment for 15 min. All samples were analysed for methane sulphonate (MS),  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ , by IC analysis. For details concerning IC set up, the determination of accuracy and detection limits, see Piel (2004). Errors were determined from the blank variability, the typical IC error (calibration error and baseline noise) and the error from the sample air volume. In short, the combined uncertainty was between  $\pm 5$  and  $\pm 11\%$  for the components MS,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  and approximately  $\pm 27\%$  for species  $\text{Br}^-$  and  $\text{NH}_4^+$ . Non-sea salt sulphate (nss- $\text{SO}_4^{2-}$ ) concentrations were calculated by subtracting the concentration of the sea salt derived sulphate from the total  $\text{SO}_4^{2-}$  concentration (in  $\text{ng g}^{-1}$ ). We used  $\text{Na}^+$  as sea salt reference species and the sulphate to sodium ratio in bulk sea water, of 0.252 for, November to February and due to the potential impact of sea salt fractionation by frost flower formation, a factor of 0.07, for winter (March–October) samples (Wagenbach et al., 1998). Note that with our sampling technique, gaseous HCl, HBr,  $\text{HNO}_3$  and  $\text{NH}_3$  were partly collected on the filter material and contributed to the reported  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  concentrations.

For the elements Na, K, Mg and Ca, an intercomparison with the corresponding concentrations measured by IC was possible. A reduced major axis regression (RMA) revealed a good agreement between ICP-QMS and IC for Na and Mg; however, the ICP-QMS systematically provided higher K and lower Ca concentrations (Table 2). For these two elements, the results from the IC-analytics were used throughout the paper, because they appeared more reliable. Apart from known problems associated with the detection of K and Ca by ICP-QMS (mainly

Table 2. Intercomparison of trace elements measured by IC versus ICP-QMS: results refer to a reduced major axis regression (RMA) with slope =  $m$ , y-axis intercept =  $b$ , regression coefficient =  $r^2$

Element	$m$	$b$ ( $\text{ng m}^{-3}$ )	$r^2$
Na	$1.00 \pm 0.05$	$24 \pm 35$	0.52
K	$0.76 \pm 0.04$	$-0.71 \pm 1.4$	0.43
Mg	$1.14 \pm 0.07$	$-5.94 \pm 6.5$	0.35
Ca	$1.51 \pm 0.09$	$-2.05 \pm 2.1$	0.42

interferences from Ar carrier gas of the plasma), a possible explanation in case of Ca may be the formation of hardly soluble  $\text{CaF}_2$  during digestion. The relatively high scatter of the data around the regression line, expressed by somewhat low regression coefficients  $r^2$  (Table 2), may partly be due to the fact that ICP-QMS and IC analyses were performed with different aliquots of the corresponding filters.

### 3. Results and discussion

#### 3.1. Classification of trace elements

We first calculated for each element M, the so-called crustal  $\text{EF}_{\text{crust}}$  and sea salt  $\text{EF}_{\text{ss}}$  enrichment factors, respectively as:

$$\text{EF}_{\text{crust}} = \frac{(\text{M/La})_{\text{aerosol}}}{(\text{M/La})_{\text{crust}}}, \quad \text{EF}_{\text{ss}} = \frac{(\text{M/Na})_{\text{aerosol}}}{(\text{M/Na})_{\text{ss}}}$$

For reasons discussed in the analytical section, we chose as marker for mineral dust La and refer to the crustal composition reported in Wedepohl (1995). Note that at Neumayer Ca is largely sea salt derived (see below) and thus an unfavourable tracer for mineral dust. For the corresponding  $\text{EF}_{\text{ss}}$ , we rely on standard mean ocean composition reported in Holland (1993). In Fig. 1, the results are presented for winter and summer. Because the ocean is well mixed, even small deviations from the

standard mean ocean composition indicate that either the given component was only partially associated with sea salt or a sea salt fractionation during aerosol formation/transport occurred. The situation is intrinsically much more complicated in case of mineral dust. First of all the crustal composition of the earth exhibits a pronounced variability (Wedepohl, 1995). Apart from this, weathering and mineral dust generating processes usually entail a distinct fractionation. Also the crustal element composition may significantly differ between mean crust, soil and the small (clay) particles being readily long-range transported. Here, we conservatively assume that  $\text{EF}_{\text{crust}}$  values above 10 point, at a negligible mineral dust source. The enrichment factors indicate crustal material as the main source for the elements Al, Nd and Ce, while, on the other hand, Li, K, Mg, Ca and Sr were primarily sea salt derived elements, though this dissection appears equivocal for Li. Selenium, in contrast, was found to be highly enriched relative to crust but also with respect to (sea salt) Na, pointing to anthropogenic or biogenic sources.

#### 3.2. Overview on the trace element concentrations measured at Neumayer station

Table 3 gives a compendium of the trace element concentrations measured 5 yr at Neumayer Station. In addition, individual time series of trace elements representative for sea salt aerosol

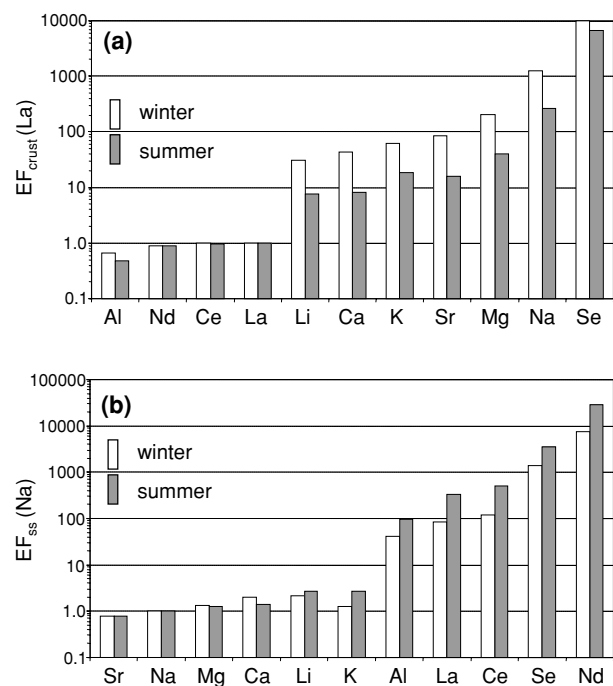


Fig. 1. (a) Mean element enrichment factors with respect to earth crust ( $\text{EF}_{\text{crust}}$ ) and (b) sea salt composition ( $\text{EF}_{\text{ss}}$ ) of Neumayer aerosol samples dissected for summer (November to March) and winter (April to October), respectively.

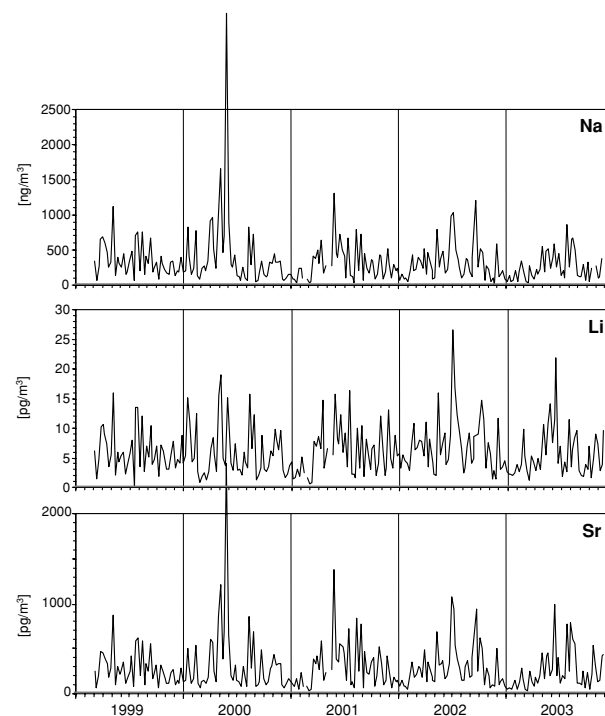


Fig. 2. Atmospheric Na, Li and Sr concentrations measured at Neumayer station at weekly time resolution. The grey bars mark the method detection limits.

Table 3. Summary of trace element composition of the aerosol measured during 5 yr (March 1999 to December 2003) at Neumayer Station via ICP-QMS, except for Ca and K, which were taken from IC-analysis. Atmospheric mean concentrations ( $\pm$  SD) refer to standard pressure (1013 hPa) and 273.16 K

Element	Overall mean	Winter Apr. to Oct.	Winter range	Summer Nov. to Mar.	Summer range
Li (pg m <sup>-3</sup> )	6.1 $\pm$ 4.1	6.9 $\pm$ 4.5	0.2–26.5	4.9 $\pm$ 3.1	0.17–15.0
Na (ng m <sup>-3</sup> )	330 $\pm$ 340	400 $\pm$ 400	41–3860	220 $\pm$ 160	0.3–820
Mg (ng m <sup>-3</sup> )	52 $\pm$ 66	62 $\pm$ 80	6.8–760	31 $\pm$ 22	0.17–10
K (ng m <sup>-3</sup> )	16 $\pm$ 15	17 $\pm$ 13	0.1 <sup>a</sup> –6.1	14 $\pm$ 17	0.1 <sup>a</sup> –12
Ca (ng m <sup>-3</sup> )	15 $\pm$ 15	19 $\pm$ 17	0.14 <sup>a</sup> –67	11 $\pm$ 8.6	0.14 <sup>a</sup> –26.4
Al (ng m <sup>-3</sup> )	1.0 $\pm$ 0.7	0.84 $\pm$ 0.6	0.22 <sup>a</sup> –3.2	1.3 $\pm$ 0.7	0.23–3.7
Sr (ng m <sup>-3</sup> )	0.29 $\pm$ 0.27	0.36 $\pm$ 0.31	0.012 <sup>a</sup> –2.6	0.19 $\pm$ 0.13	0.012 <sup>a</sup> –0.53
La (pg m <sup>-3</sup> )	0.86 $\pm$ 0.7	0.56 $\pm$ 0.5	0.07 <sup>a</sup> –3.1	1.32 $\pm$ 0.8	0.07 <sup>a</sup> –5.8
Ce (pg m <sup>-3</sup> )	1.6 $\pm$ 1.3	1.0 $\pm$ 0.8	0.17 <sup>a</sup> –5.5	2.5 $\pm$ 1.5	0.17 <sup>a</sup> –10.5
Nd (pg m <sup>-3</sup> )	0.7 $\pm$ 0.6	0.47 $\pm$ 0.45	0.09 <sup>a</sup> –2.7	1.1 $\pm$ 0.6	0.09 <sup>a</sup> –4.4
Se (pg m <sup>-3</sup> )	19 $\pm$ 18	16 $\pm$ 11	3.1 <sup>a</sup> –82	25 $\pm$ 24	3.1 <sup>a</sup> –160

<sup>a</sup>Method detection limit (MDL).

Table 4. Al, La, Na and Se concentrations ( $\pm$  SD) measured in Antarctic aerosol samples

Element	Winter	Summer	Sampling period	Site
Al (pg m <sup>-3</sup> )	–	570 $\pm$ 170	10/1970	SP (Zoller et al., 1974)
	300 $\pm$ 40	830 $\pm$ 410	1971/75/76/78	SP (Cunningham and Zoller, 1981)
	320 $\pm$ 110	730 $\pm$ 240	2/1979–11/1983	SP (Tuncel et al., 1989)
	–	194 $\pm$ 19	12/1984–02/1985	AP (Dick, 1991)
	9470 <sup>a</sup>	13290 <sup>a</sup>	1985–1988	AP (Artaxo et al., 1992)
La (pg m <sup>-3</sup> )	840 $\pm$ 600	1270 $\pm$ 700	3/1999–12/2003	NM, this study
	–	0.51 $\pm$ 0.37	10/1970	SP (Zoller et al., 1974)
	< 2	0.78 $\pm$ 0.25	1971/75/76/78	SP (Cunningham and Zoller, 1981)
	0.43 $\pm$ 0.11	0.56 $\pm$ 0.21	2/1979–11/1983	SP (Tuncel et al., 1989)
	0.56 $\pm$ 0.5	1.32 $\pm$ 0.8	3/1999–12/2003	NM, this study
Na (ng m <sup>-3</sup> )	–	7.2 $\pm$ 3.8	10/1970	SP (Zoller et al., 1974)
	40 $\pm$ 31	5.1 $\pm$ 1.7	1971/75/76/78	SP (Cunningham and Zoller, 1981)
	31 $\pm$ 14	8.7 $\pm$ 3.2	2/1979–11/1983	SP (Tuncel et al., 1989)
	869.9 <sup>a</sup>	1046.2 <sup>a</sup>	1985–1988	AP (Artaxo et al., 1992)
	–	27.6 $\pm$ 0.4	12/1984–02/1985	AP (Dick, 1991)
Se (pg m <sup>-3</sup> )	400 $\pm$ 400	220 $\pm$ 160	3/1999–12/2003	NM, this study
	–	5.6 $\pm$ 1.2	10/1970	SP (Zoller et al., 1974)
	6.9 $\pm$ 2.7	6.3 $\pm$ 6	1971/75/76/78	SP (Cunningham and Zoller, 1981)
	4.8 $\pm$ 0.8	8.4 $\pm$ 1.6	2/1979–11/1983	SP (Tuncel et al., 1989)
	118 <sup>a</sup>	122 <sup>a</sup>	1/1983–12/1984	AP (Artaxo et al., 1992)
	16 $\pm$ 11	25 $\pm$ 24	3/1999–12/2003	NM, this study

<sup>a</sup>Sum of fine and coarse mode.

AP, Antarctic Peninsula; SP, South Pole; NM, Neumayer.

(Li, Na, Sr) and mineral dust (Al, La, Ce, Nd) species are presented in Figs. 2 and 3. Generally, trace element concentrations at Neumayer exhibited a striking interannual and seasonal variability. Apart from the general sparseness of data available from other Antarctic sites, the intrinsic strong variability makes a coherent assessment of the intersite differences a difficult task.

Especially the extraordinarily high atmospheric Se and Al levels reported by Artaxo et al. (1992) remain unexplained (Table 4).

Görlach (1988) used acid extractable Mn and Wagenbach (1996) combined Mn and Al as mineral dust proxy at Neumayer. Converting the reported Mn from Görlach (1988) into corresponding La concentrations (using a mean crust

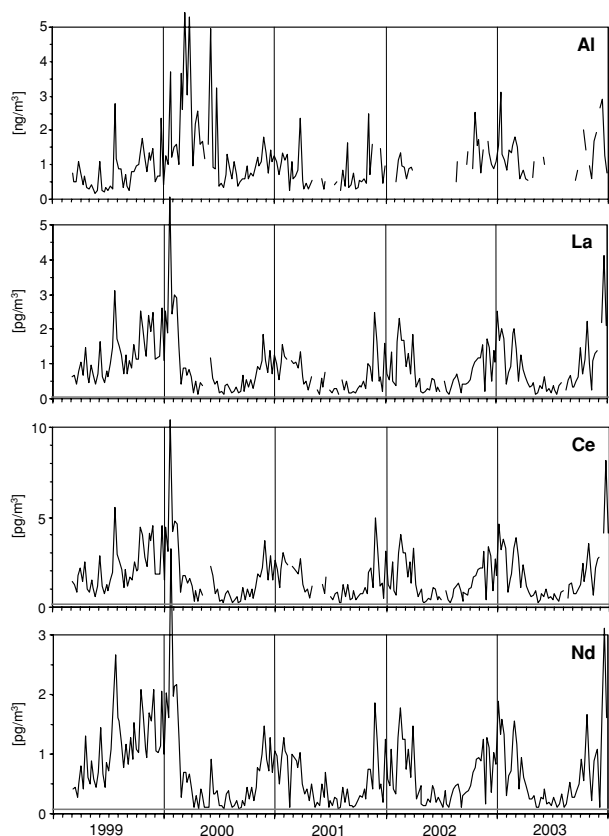


Fig. 3. Same as Fig. 2 but for Al, La, Ce and Nd.

composition given in Wedepohl (1995), i.e.  $Mn/La = 23.9$  resulted in a summer maximum of around  $1.1 \text{ pg m}^{-3}$  and a winter minimum of  $0.21 \text{ pg m}^{-3}$ . This is systematically lower (by  $0.21 \text{ pg m}^{-3}$  and  $0.35 \text{ pg m}^{-3}$ , respectively) but still in fair agreement with our La results (Table 3). A pronounced seasonal Al (i.e. mineral dust) maximum during austral summer was evident at all sites, with a mineral dust entry tentatively higher at coastal Neumayer compared with continental South Pole (Table 4). The data from the Antarctic Peninsula tip appeared contradicting, and the mentioned outstanding high Al values reported by Artaxo et al. (1992) might, most probably, be caused by sporadic local dust production from the rocky adjacencies. In contrast to the observed marginal gradient from coastal to continental Antarctica for mineral dust related trace elements, Na (i.e. sea salt) concentrations were about an order of magnitude higher at coastal sites.

### 3.3. Seasonal aspects

**3.3.1. Synopsis of the seasonality of the aerosol budget at Neumayer.** To assess the relative composition of the aerosol (by mass) and its seasonality, we included the relevant ionic compounds. Therefore, we considered the aerosol compounds sea salt (calculated from the measured Na) mineral dust (cal-

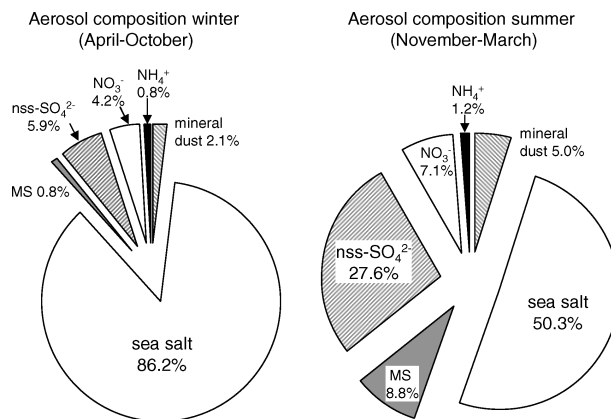


Fig. 4. Pi-diagram of the aerosol composition (weight percent referring to the sum of the measured species) at Neumayer during winter and summer, respectively.

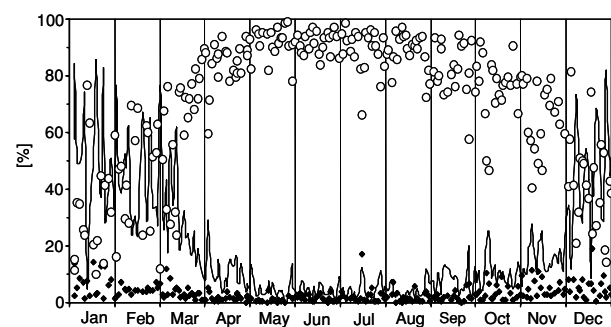


Fig. 5. Mean annual cycle of major mass fractions in Neumayer aerosol samples: sea salt (circles), biogenic sulphur (i.e. the sum of MS and  $nss-SO_4^{2-}$ , drawn line) and mineral dust (diamonds) portion.

culated from the measured La) and further MS,  $nss-SO_4^{2-}$ ,  $Cl^-$ ,  $NO_3^-$  and  $NO_4^+$  from the IC analyses. Clearly, the aerosol at Neumayer was dominated by sea salt particles (Fig. 4), even during summer when biogenic sulphur emissions reach their distinct annual maximum (Minikin et al., 1998), whereas mineral dust was generally a minor compound with a maximum mass fraction of about 5% during summer. Figure 5 shows, in more detail, the annual cycle of the compounds sea salt, mineral dust and biogenic sulphur (sum of MS and  $nss-SO_4^{2-}$ ). In terms of aerosol composition (biogenic, sea salt and mineral dust), the polar winter seemed confined between April and end October, with the turn of the seasons occurring in March/April and October/November.

**3.3.2. Seasonality of mineral dust and sea salt entry at Neumayer.** Figures 2 and 3 indicate that mineral dust and sea salt derived trace elements (Al, La, Ce, Nd and Li, Na, K, Mg, Ca, Sr, respectively) were characterized by distinct mean annual cycles. In Fig. 6, the mean seasonal cycle of the crustal and sea salt reference are displayed in monthly concentrations ( $\pm SD$ ). The seasonality was most pronounced for the crustal elements with a distinct concentration maximum from October to March,

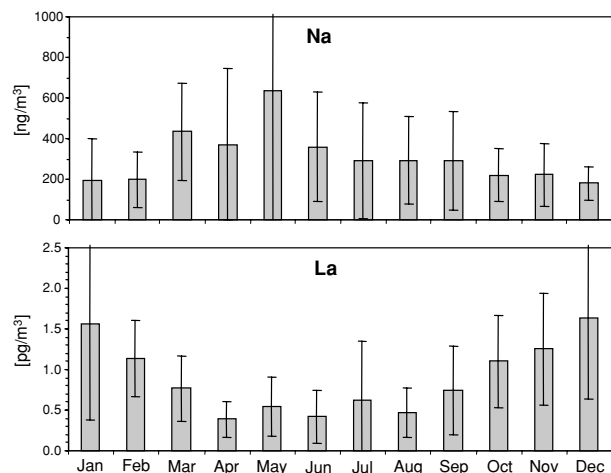


Fig. 6. Seasonality of monthly concentration mean of sea salt (Na) and mineral dust (La) reference elements. Values correspond to 5 yr of observation (i.e. about 20 samples per month). Error bars indicate the respective standard deviations.

whereas for sea salt aerosol, a broad maximum between April and September was evident. The mean relative seasonal amplitude, that is, the mean maximum normalized to the corresponding annual mean, was around 1.7 and 1.4 for mineral dust (La) and sea salt aerosol (Na), respectively. In addition, enrichment factors also exhibited a distinct seasonality, with higher  $EF_{\text{crust}}$  but lower  $EF_{\text{ss}}$  in winter and vice versa (Fig. 1). A possible reason for this finding might be the seasonality of dust and sea salt entry observed at Neumayer. During the seasonal maximum of atmospheric dust entry in summer and sea salt concentrations in winter, the corresponding enrichment factors were lowest due to the dilution of a given enrichment effect by enhanced crustal dust or sea salt material, respectively.

The observed seasonality for mineral dust appeared consistent with previous studies from Neumayer (Görlach, 1988; Wagenbach et al., 1988; Wagenbach, 1996), as well as South Pole (Cunningham and Zoller, 1981; Tuncel et al., 1989), where Mn and Al was used as tracer for mineral dust, respectively. A thorough evaluation of sea salt aerosol concentrations, measured at various coastal stations, was given in Wagenbach et al. (1998). In agreement with our findings, these authors reported a broad Na maximum during winter at Neumayer, which has also been observed at South Pole (Tuncel et al., 1989). In general, an annual cycle of aerosol components observed at remote, source-free sites can be attributed to a combination in the seasonality of the source strength and atmospheric transport processes. Whereas for sea salt aerosol regional or even local sources have to be considered, the source regions for mineral dust on the surrounding continents are more than 4000 km away, and consequently long-range transport, most probably via the free troposphere, is decisive (Genthon, 1992; Krinner and Genthon, 2003). It is believed that the main provenances for Antarctic mineral dust are

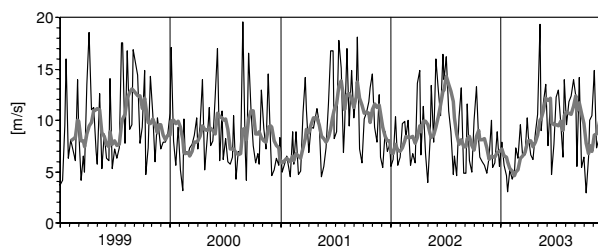


Fig. 7. Time-series of wind velocity at Neumayer during the sampling period displayed in the same temporal resolution as filter sampling (7 d, thin line), and six points moving average (bold grey line).

the Patagonian loess regions (Smith et al., 2003). The seasonal contrast of Patagonian dust fluxes seems, by far, not as distinct as those of the atmospheric rare earth element (equivalent to mineral dust) concentrations at Neumayer, though a broad maximum between October and March is discernible (Gaiero et al., 2003, fig. 14 therein). In addition to this somewhat ambiguous source strength seasonality, we may expect a clear annual cycle in the atmospheric mixing height above continents (typically maximum during summer). Since long-range dust transport to Antarctica is favoured via the mid-troposphere, a more effective transfer of dusty boundary layer into high altitudes during the summer half year would be consistent with a Neumayer summer maximum as well. This explanation is supported by measurements of a basically similar seasonality seen at this site for the long lived  $^{222}\text{Rn}$  decay product  $^{210}\text{Pb}$  (Wagenbach et al., 1988), known to have a rather constant (continental) emission rate and to be less effectively washed out than the typically coarse mode mineral dust particles. Therefore, the observed mineral dust maximum at Neumayer is probably a combined result of the seasonality in dust generation and the more efficient uplift of dust loaded air into the free troposphere in summer.

The most efficient global mechanism producing sea salt aerosol is bubble bursting during whitecap formation and dispersion of wave crests by surface winds over open ocean waters (Monahan et al., 1986). Thus, sea salt production exhibits a strong dependence on wind speed (Fitzgerald, 1991). Compatible with this perception is the fact that storminess and wind velocity exhibit a broad maximum during the winter months at Neumayer (Fig. 7). However, as for the individual data points, there was virtually no correlation between wind velocity and observed Na concentrations ( $r^2 = 0.07$ ). Note that this was also true for our low volume aerosol samples taken at daily resolution between October 2003 and February 2007 (teflon–nylon filter combinations, analysed by IC). It seems that the general weather situation over the South Atlantic was decisive and the most efficient sea salt production occurred during passing cyclones (Wyputta, 1997). However, the sea salt aerosol loading at Neumayer should also depend on the efficiency of the transport process, removal by wet deposition and the actual sea-ice cover. The interplay of these factors may have blurred a simple

correlation with the local wind speed. In this regard, however, we have to bear in mind that particles above an aerodynamic diameter of around 7–10  $\mu\text{m}$ , which may constitute a significant if not dominant fraction of the sea salt aerosol mass from nearby sources, were not adequately sampled due to the cut-off of our air inlet.

The formation of sea salt aerosols by frost flowers and associated processes suggested by Wolff et al. (2003) should be most active between March and September, consistent with the observed Na seasonality. Again it can be assumed that high wind velocities are still necessary to finally create sea salt aerosols by dispersion and mobilisation of frost flowers—a process which is actually not yet clarified.

**3.3.3. Sea salt fractionation.** There is some evidence that during wind induced sea salt aerosol generation over open ocean waters, a fractionation of major ions ( $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ ) relative to bulk sea water is negligible, except for  $\text{Ca}^{2+}$ , which appeared significantly enriched (Keene et al., 2007). On the other hand, sea ice formation entails considerable sea salt fractionation, which could influence sea salt aerosol composition if freshly formed sea-ice acts as a significant source. Below  $-6.3^\circ\text{C}$ , solid  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  (mirabilite) crystallizes, followed by  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (gypsum) and  $\text{NaCl} \cdot 2\text{H}_2\text{O}$  (hydrohalite) precipitation at  $-22.2$  and  $-22.9^\circ\text{C}$ , respectively (Marion and Farren, 1999). A complete mirabilite precipitation, probably the dominant fractionation process on freshly formed sea-ice, would lead to a Na depletion of about 11.8% by mass. Assuming simply that no fractionation would occur for the sea salt compounds Li, K, Mg and Sr, a corresponding increase of the enrichment factors  $\text{EF}_{\text{ss}}$  to around 1.12 should be expected in sea salt aerosol for this species during winter when sea salt fractionation is most probable. In fact, Rankin et al. (2000) found Mg and Ca enrichment factors in frost flower samples near Halley station ( $\text{EF}_{\text{ss}}(\text{Mg}) = 1.16$  and  $\text{EF}_{\text{ss}}(\text{Ca}) = 1.15$ ), roughly compatible with mirabilite precipitation but indicating, if at all, a negligible gypsum precipitation. Also analyses of individual aerosol particles sampled at the coastal Syowa station evidenced fractionated Mg-rich (and Ca-rich) sea salt particles (Hara et al., 2005).

Combining our ICP–QMS and IC results allows to determine sea salt fractionation for an extended number of sea salt related trace elements. In our approach, we first corrected Li, K, Mg, Ca and Sr concentrations for the minor crustal contribution (which were generally between 1 and 8%) to derive enrichment factors  $\text{EF}_{\text{ss}}(\text{ssM})$  exclusively for the sea salt portion of these elements. To be consistent, we generally referred ssK and ssCa values to ssNa all taken from IC analyses, whereas for the other elements (Li, Mg, Sr) we relied on the ICP–QMS results and related them to ssNa also determined by ICP–QMS. In this way, we circumvent potential discrepancies caused by systematic analytical differences of both methods (see Section 2.2.2).

All  $\text{Na}_{\text{ss}}$  based  $\text{EF}_{\text{ss}}(\text{ssM})$  values were strikingly variable throughout the year and, except Ca, did not exhibit a significant seasonality as would have to be expected from a depleted

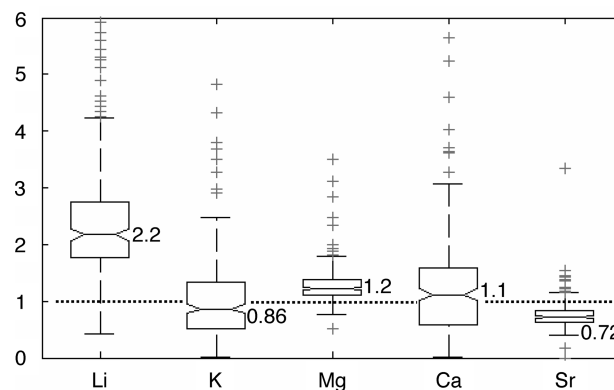


Fig. 8. Notched box plots for enrichment factors respecting standard mean ocean water composition for the sea salt portion of Li, K, Mg, Ca and Sr. Lines in the middle of the boxes represent sample medians (values are given aside), lower and upper lines of the boxes are the 25th and 75th percentiles, whiskers show the range of the sample values while outliers are marked by '+' signs. The widths of the notches indicate the confidence interval of the median.

ssNa reference during winter (Fig. 8). It is important to note that in terms of analytical accuracy departures beyond  $\pm 20\%$  (in the worst case, at very low concentrations, beyond  $\pm 50\%$ ) from standard mean ocean water (SMOW) should be regarded as significant. Another, but hardly conceivable reason for the scatter of  $\text{EF}_{\text{ss}}(\text{ssM})$  could be more than an order of magnitude higher crustal M/La ratios ( $M = \text{Li, Na, K, Mg, Ca, Sr}$ ) than reported by Wedepohl (1995), which would strongly increase the crustal corrections and thus the uncertainty of the calculated ratios. Concerning the medium departures of  $\text{EF}_{\text{ss}}(\text{ssM})$  from SMOW, Fig. 8 reveals that ssLi and ssMg were enriched by a factor 2.2 and 1.2, respectively, whereas ssSr was depleted throughout ( $\text{EF}_{\text{ss}}(\text{ssSr}) = 0.72$ ). For ssK and ssCa, the (median) deviation from SMOW was not significant, except for the winter values of ssCa ( $\text{EF}_{\text{ss}}(\text{ssCa})_{\text{winter}} = 1.34$ ). In double-logarithmic plots of ssM ( $M = \text{Li, K, Mg, Ca, Sr}$ ) versus the ssNa reference, it becomes apparent that departures from SMOW occurred equally over the whole measured concentration range, and that for ssLi, ssMg, and ssSr, the data points were displaced from the SMOW-line (Fig. 9). Obviously, the high variability of  $\text{EF}_{\text{ss}}(\text{ssM})$  in general, as well as the median departures from SMOW for ssLi and ssSr cannot be explained by mirabilite precipitation alone. Finally, the scatter of the enrichment factors (Figs. 8 and 9) were strikingly higher than the results from recent laboratory investigations on sea salt aerosol formation over a realistic air/sea interface (Keene et al., 2007). In summary, our results suggest that in the present case, additional unknown fractionation processes occurred during sea salt aerosol production over the whole year at the interface air/sea or air/sea-ice or subsequently during atmospheric transport and sampling.

**3.3.4. Source and seasonality of atmospheric Se..** It is believed that natural sources like sea spray, volcanoes and the



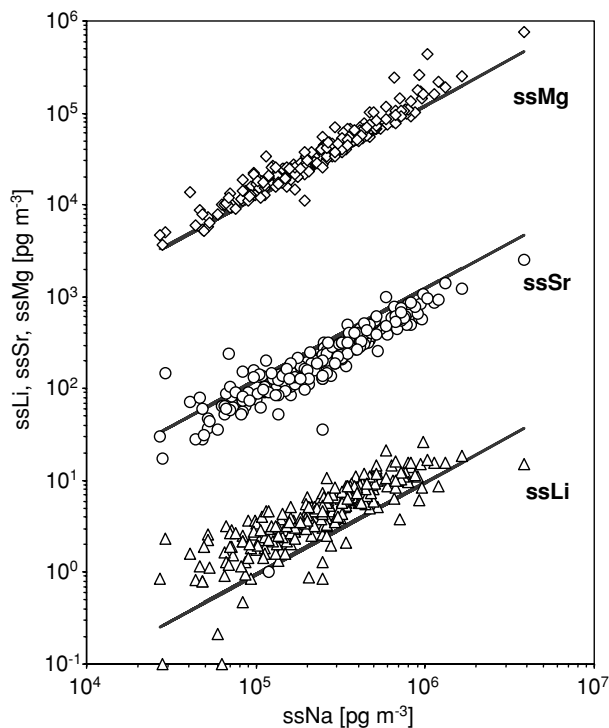


Fig. 9. Double-logarithmic plot of ssLi, ssMg and ssSr vs. ssNa. Bold grey lines represent the relation for standard mean ocean water.

biosphere dominate the global budget of atmospheric Se by around 60%, whereas the remaining anthropogenic sources (basically fossil fuel combustion and mining) are mainly concentrated in the Northern Hemisphere (Mosher and Duce, 1987). As noted by Mosher (1986), the natural and anthropogenic Se cycles are closely linked through the biosphere. The distinct seasonal Se concentration maximum during summer observed at Neumayer suggests a potential biogenic source. Amouroux et al., (2001) have demonstrated that the production of gaseous selenium species coincided with phytoplankton blooms, responsible for dimethyl sulphide (DMS) emission. It was found, that the sulphur atom in DMS can be substituted by selenium (Mosher et al., 1987; Amouroux et al., 2001). Consequently, atmospheric Se should be closely coupled to the DMS turnover. In fact, we observed a significant correlation between Se and the end products of photochemical DMS oxidation, MS and  $\text{nss-SO}_4^{2-}$  ( $r(\text{MS}) = 0.66$ ;  $r(\text{nss-SO}_4^{2-}) = 0.67$ ). The co-variation of Se and MS time-series is shown in Fig. 10. Even the interannual variability largely coincided. Atmospheric Se concentrations found at South Pole were significantly lower (Table 4) but showed the same seasonality with maximum values of  $8.4 \pm 1.6 \text{ pg m}^{-3}$  during summer (winter concentration:  $4.8 \pm 0.8 \text{ pg m}^{-3}$ ; Tuncel et al., 1989), in accordance with a prominent marine biogenic source, which should be less discernible in continental Antarctica.

Apart from this overall consistent picture, there remain several open questions. First of all, we have to consider that the

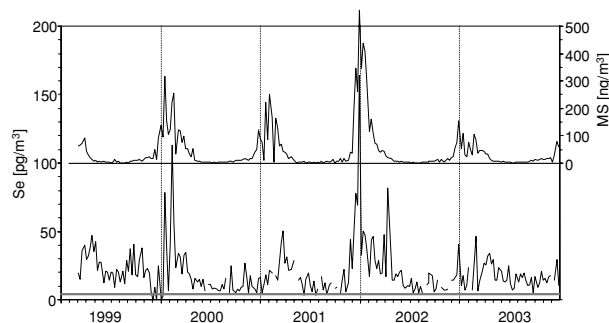


Fig. 10. Time-series of Se and MS (shifted y-axis) concentrations, measured at Neumayer. The grey bar marks the method detection limit for Se.

sampling efficiency of total Se is not well specified. Inspecting some of our Whatman 541 backup filter showed no Se concentrations above the typical blank value, in agreement with results by Mosher et al. (1987), who used Whatman 41 filters. In contrast, Mosher (1986) reported on low sampling efficiencies (65–45%) for this filter type in his thesis. Apart from this, knowledge on speciation of atmospheric Se is poor. Apparently, DMSe, elemental Se, as well as  $\text{SeO}_2$  can be chemically transformed into water soluble selenite ( $\text{SO}_3^{2-}$ ) and selenate ( $\text{SO}_4^{2-}$ ) in the atmosphere (Wen and Carignan, 2007). In marine environments, an enrichment of Se-compounds in sub-micron aerosol particles (mainly sea salt particles) was suggested (Wen and Carignan, 2007). It is not clarified to what extent volatile organic and inorganic Se species (e.g. DMSe, Se,  $\text{SeO}_2$ ) are retained and likely chemically transformed on the used filter material during the typical sampling interval of 7 d. Another issue are considerable Se background concentrations, measured during polar night (at Neumayer and South Pole) when regional biogenic activity ceases. This is in contrast to negligible MS concentrations generally observed during winter (Fig. 10). Hence we tentatively assign wintertime atmospheric Se levels at Neumayer mainly to the global background load of Se. According to Cunningham and Zoller (1981), the atmospheric load of volatile elements like As and Se at South Pole could also be influenced by volcanic emissions. These authors ascribed a distinct Se peak in their time-series to the explosive eruption of Ngauruhoe volcano in New Zealand that happened in 1975. In our case, however, the contribution of volcanic Se emissions should be, if at all, of minor importance due to the distance of the sole presently active but calm volcanoes Mt. Erebus and Mt. Melbourne. Above all, the observed seasonality of the Se signal at Neumayer can hardly be explained by volcanic impact but might partly be responsible for background Se concentrations. Interestingly, wintertime Se levels at Neumayer were about a factor of three higher compared with South Pole, where the impact of Mt. Erebus should be more pronounced. For mineral dust derived trace elements (Al, La), a similar but weaker gradient is apparent (Table 4), suggesting that the more pronounced and deeper stable inversion layer at South Pole hampers down mixing of long-range transported trace

compounds. In addition, further minor, yet unexplained Se sources (local contamination, still active regional biogenic emissions) possibly have to be considered at Neumayer.

## 5. Conclusions

In contrast to the ionic composition of Antarctic aerosol, corresponding continuous long-term observations of atmospheric trace element concentrations are so far restricted to South Pole and Neumayer. Even from these sites, complete year round data records do not cover more than 5 yr in series. Our results revealed a distinct and contrary seasonality of mineral dust and sea salt load at Neumayer, which, along with previous results, seems to be valid for coastal, as well as continental Antarctica. At coastal sites, mineral dust load appeared somewhat more pronounced. More observations from different sites are necessary to establish a potential difference between continental and coastal Antarctica in trace element entry. Provided that mineral dust is widely uniformly distributed in the free troposphere above Antarctica, this could give us some information on the role of the stable inversion layer, which is most pronounced in continental Antarctica, as a barrier against air mass down mixing. This would be especially interesting to scrutinize and constrain models addressing aerosol deposition in Antarctica. Another interesting point was the striking variability of the measured ssM/ssNa ratios for M = Li, K, Mg, Ca and Sr, suggesting that apart from sea salt formation in sea ice covered regions itself, sea salt aerosol fractionation processes are not sufficiently clarified. As a consequence we are still lacking a tracer to reliably assess sea salt production on sea ice, a crucial point for the interpretation of sea salt records in polar ice cores. Marine biochemistry was most probably the dominant source for Se. An interesting open question is, how much Se is persistently deposited in polar snow and may serve as a proxy for biogenic activity in polar ice cores. Clearly, more investigations on the atmospheric photochemistry of marine biogenic selenium, as well as the chemical nature of particulate atmospheric Se are required.

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