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

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Version 30.04.2008
ABSTRACT
Atmospheric trace element concentrations were measured from March 1999 through December 2003 at the Air Chemistry Observatory of the German Antarctic station Neumayer by inductively coupled plasma – quadrupol 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 sulfur aerosols (methane sulfonate and non-sea salt sulfate), indicating a dominant marine biogenic source for this element linked with the marine biogenic sulfur source.
1. Introduction

The nearly completely ice covered Antarctic continent is virtually free of primary and secondary aerosol sources while the Southern Ocean is by far the dominant source to the Antarctic aerosol body making atmospheric sea salt and biogenic sulfur the major aerosol components (Wagenbach et al., 1998; Minikin 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, sulfur, 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) and 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), e.g. the atmospheric CO$_2$ 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 sulfate aerosol. Finally,
mineral dust and sea salt profiles retrieved from polar ice cores have proven to provide a wealth of paleoclimatic 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 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 and 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 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 sulfonate, sulfate, Na\(^+\), NH\(_4^+\), K\(^+\), Mg\(^{2+}\), and 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° 39’ S, 8° 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 precleaned by soaking in HCl followed by rinsing with de-ionize water until virtually no enhancement of the electrolytical conductivity could be detected. The aerosol was continuously sampled at 120 m³ 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 µm at wind velocities between 4-10 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 through December 2003. These data were based on a sampling period of typically 7 days which corresponds to a probe volume of around 2×10⁴ m³ 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°-30° sector, wind velocity <2.0 m s\(^{-1}\) and/or CP concentrations (measured by a TSI CPC 3022A particle counter) >2500 cm\(^{-3}\) during summer, >800 cm\(^{-3}\) during spring/autumn and >400 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 one second (shut down of the pumps and closing the electromotive valves typically needed around 10 seconds). Sampling was restarted after recurrence of clean air conditions and a delay of two minutes. However, most of the data loss was provoked by blizzards and drifting snow (wind velocity >20 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 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 in order to quantitatively dissolve all mineral compounds, which is not been given by simple acidic (HNO\(_3\)) leaching (Lindberg and Harris, 1983; Reinhardt et al., 2003,
Table 5 therein). Thus these aliquots were subject to a pressurized digestion system (DAS 100, Picotrace) at 200°C in a mixture containing HNO₃ (suprapure, 65%, Merck, sub-boiling bi-distilled), HF (suprapure, 40%, Merck, sub-boiling bi-distilled) and H₂O₂ (suprapure, 30%, Merck). 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 (10⁴ ppb multielement verification standard 1 and 2, Perkin Elmer) which were generally applied in 1 ppb, 10 ppb, 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 (std) 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 (std) 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 approxi-
mately between ±8% and ±12% for element concentrations above three times the corresponding MDL. It increased from around ±(15-20)% approaching 3xMDL level to roughly (+50/-100)% close to the MDL. The final atmospheric concentrations (in ng m\(^{-3}\) or 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 minutes. All samples were analyzed for methane sulfonate (MS), Cl\(^-\), Br\(^-\), NO\(_3\)\(^-\), SO\(_4\)\(^{2-}\), Na\(^+\), NH\(_4\)\(^+\), K\(^+\), Mg\(^{2+}\), and 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 ±5% and ±11% for the components MS, Cl\(^-\), NO\(_3\)\(^-\), SO\(_4\)\(^{2-}\), Na\(^+\), K\(^+\), Mg\(^{2+}\), and Ca\(^{2+}\) and approximately ±27% for species Br\(^-\) and NH\(_4\)\(^+\). Non-sea salt sulfate (nss-SO\(_4\)\(^{2-}\)) concentrations were calculated by subtracting the concentration of the sea salt derived sulfate from the total SO\(_4\)\(^{2-}\) concentration (in ng g\(^{-1}\)). We used Na\(^+\) as sea salt reference species and the sulfate 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, HNO\(_3\), and NH\(_3\) were partly collected on the filter material and contributed to the reported Cl\(^-\), Br\(^-\), NO\(_3\)\(^-\), and NH\(_4\)\(^+\) concentrations.

For the elements Na, K, Mg, and Ca an inter-comparison 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, while 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 interferences from Ar carrier gas of the plasma), a possible explanation in case of Ca may be the formation of hardly soluble 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 EF$_{\text{crust}}$ and sea salt EF$_{\text{ss}}$ enrichment factors, respectively as:

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

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 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 $EF_{\text{crust}}$ 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 five years at Neumayer Station. In addition individual time series of trace elements representative for sea salt aerosol (Li, Na, Sr) and mineral dust (Al, La, Ce, Nd) species are presented in Figures 2 and 3. Generally, trace element concentrations at Neumayer exhibited a striking inter-annual 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 inter-site 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 composition given in Wedepohl (1995), i.e. $\text{Mn/La} = 23.9$) resulted in a summer maximum of around 1.1 pg m$^{-3}$ and a winter minimum of 0.21 pg m$^{-3}$. This is systematically lower (by 0.21 pg m$^{-3}$ and 0.35 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 to 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 gradi-
ent 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

In order 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 (calculated from the measured La) and
further MS, nss-SO$_4^{2-}$, Cl$^-$, NO$_3^-$, and NH$_4^+$ from the IC analyses. Clearly, the aerosol at Neu-
mayer was dominated by sea salt particles (Fig. 4), even during summer when biogenic sulfur
emissions reach their distinct annual maximum (Minikin et al., 1998), while 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 sulfur (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

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cycles. In Figure 6 the mean seasonal cycle of the crustal and sea salt reference are displayed in monthly concentrations (± standard deviation). The seasonality was most pronounced for the crustal elements with a distinct concentration maximum from October through March, while for sea salt aerosol a broad maximum between April and September was evident. The mean relative seasonal amplitude, i.e. 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_{crust} but lower EF_{ss} in winter and vice versa (Figure 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. While 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 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, Figure 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 dependency 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 µm, 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.

3.3.4. Sea salt fractionation

There is some evidence that during wind induced sea salt aerosol generation over open ocean waters, a fractionation of major ions (Na$^+$, Mg$^{2+}$, K$^+$, Cl$^-$, and SO$_4^{2-}$) relative to bulk seawater is negligible, except for 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°C solid Na$_2$SO$_4$·10H$_2$O (mirabilite) crystallizes, followed by CaSO$_4$·2H$_2$O (gypsum), and NaCl·2H$_2$O (hydrohalite) precipitation at -22.2°C and -22.9°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 $EF_{ss}$ 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 (EF_{ss}(Mg) = 1.16, and EF_{ss}(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 EF_{ss}(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, while 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 Na_{ss} based EF_{ss}(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 ssNa reference during winter (Figure 8). It is important to note that in terms of analytical accuracy departures beyond ±20% (in the worst case, at very low concentrations, beyond ±50%) from standard mean ocean water (SMOW) should be regarded as significant. Another, but hardly conceivable reason for the scatter of EF_{ss}(ssM) could be more than an order of magnitude higher crustal M/La ratios (M = 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 EF_{ss}(ssM) from SMOW, Figure 8 reveals that ssLi and ssMg were enriched by a factor 2.2 and 1.2, respectively, while ssSr was
depleted throughout ($EF_{ss}(ssSr) = 0.72$). For $ssK$ and $ssCa$ the (median) deviation from SMOW was not significant, except for the winter values of $ssCa$ ($EF_{ss}(ssCa)_{winter} = 1.34$). In double-logarithmic plots of $ssM$ ($M = Li, K, Mg, Ca, Sr$) 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 $EF_{ss}(ssM)$ 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 (Figures 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 biosphere dominate the global budget of atmospheric Se by around 60%, while 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 sulfide (DMS) emission. It was found, that the sulfur 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 nss-SO$_4^{2-}$ ($r$(MS) = 0.66; $r$(nss-SO$_4^{2-}$) = 0.67). The
covariation of Se and MS time series is shown in Fig. 10. Even the inter-annual 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±1.6 pg m$^{-3}$
during summer (winter concentration: 4.8±0.8 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 sampling efficiency of total Se is not well specified. Inspecting
some of our Whatman 541 back-up 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 SeO$_2$ can be chemically transformed into water soluble se-
lenite (SeO$_3^{2-}$) and selenate (SeO$_4^{2-}$) 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 extend
volatile organic and inorganic Se species (e.g. DMSe, Se, SeO$_2$) are retained and likely
chemically transformed on the used filter material during the typical sampling interval of 7
days. 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 (Figure 10). Hence we
tentatively assign wintertime atmospheric Se levels at Neumayer mainly to the global back-
ground 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 to 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. Conclusion

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 years 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. Pro-
vided 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.

Acknowledgements. The authors would like to thank the technicians and scientists of the Neumayer overwintering crews of the years 1999-2003. Helpful comments and suggestions on the manuscript by an anonymous reviewer is greatly appreciated. This is AWI publication no. xy. Data are available from Pangaea (doi:10.1594/PANGAEA.691456).
References


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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 $2.0 \times 10^4$ m$^3$. (MDL for IC-analysis given in parenthesis)

<table>
<thead>
<tr>
<th>Element</th>
<th>IDL [pg m$^{-3}$]</th>
<th>MDL [pg m$^{-3}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>0.12</td>
<td>0.21</td>
</tr>
<tr>
<td>Na</td>
<td>16</td>
<td>1800 (300)</td>
</tr>
<tr>
<td>Mg</td>
<td>0.44</td>
<td>300 (170)</td>
</tr>
<tr>
<td>K</td>
<td>32</td>
<td>330 (100)</td>
</tr>
<tr>
<td>Ca</td>
<td>5.0</td>
<td>1300 (140)</td>
</tr>
<tr>
<td>Sr</td>
<td>0.02</td>
<td>12</td>
</tr>
<tr>
<td>Al</td>
<td>10</td>
<td>220</td>
</tr>
<tr>
<td>La</td>
<td>0.005</td>
<td>0.07</td>
</tr>
<tr>
<td>Ce</td>
<td>0.002</td>
<td>0.17</td>
</tr>
<tr>
<td>Nd</td>
<td>0.006</td>
<td>0.09</td>
</tr>
<tr>
<td>Se</td>
<td>2.7</td>
<td>3.1</td>
</tr>
</tbody>
</table>

Table 2. Inter-comparison 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 = $r^2$.

<table>
<thead>
<tr>
<th>Element</th>
<th>m</th>
<th>b [ng m$^{-3}$]</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>1.00±0.05</td>
<td>24±35</td>
<td>0.52</td>
</tr>
<tr>
<td>K</td>
<td>0.76±0.04</td>
<td>-0.71±1.4</td>
<td>0.43</td>
</tr>
<tr>
<td>Mg</td>
<td>1.14±0.07</td>
<td>-5.94±6.5</td>
<td>0.35</td>
</tr>
<tr>
<td>Ca</td>
<td>1.51±0.09</td>
<td>-2.05±2.1</td>
<td>0.42</td>
</tr>
</tbody>
</table>
Table 3. Summary of trace element composition of the aerosol measured during five years (March 1999 through December 2003) at Neumayer Station via ICP-QMS, except for Ca and K which were taken from IC-analysis. Atmospheric mean concentrations (±std) refer to standard pressure (1013 hPa) and 273.16 K.

<table>
<thead>
<tr>
<th>element</th>
<th>overall mean</th>
<th>winter range</th>
<th>summer range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li[pg m$^{-3}$]</td>
<td>6.1±4.1</td>
<td>6.9±4.5</td>
<td>0.2–26.5</td>
</tr>
<tr>
<td>Na[ng m$^{-3}$]</td>
<td>330±340</td>
<td>400±400</td>
<td>41-3860</td>
</tr>
<tr>
<td>Mg[ng m$^{-3}$]</td>
<td>52±66</td>
<td>62±80</td>
<td>6.8-760</td>
</tr>
<tr>
<td>K[ng m$^{-3}$]</td>
<td>16±15</td>
<td>17±13</td>
<td>0.1*-6.1</td>
</tr>
<tr>
<td>Ca[ng m$^{-3}$]</td>
<td>15±15</td>
<td>19±17</td>
<td>0.14*-6.7</td>
</tr>
<tr>
<td>Al[ng m$^{-3}$]</td>
<td>1.0±0.7</td>
<td>0.84±0.6</td>
<td>0.22*-3.2</td>
</tr>
<tr>
<td>Sr[ng m$^{-3}$]</td>
<td>0.29±0.27</td>
<td>0.36±0.31</td>
<td>0.012*-2.6</td>
</tr>
<tr>
<td>La[pg m$^{-3}$]</td>
<td>0.86±0.7</td>
<td>0.56±0.5</td>
<td>0.07*-3.1</td>
</tr>
<tr>
<td>Ce[pg m$^{-3}$]</td>
<td>1.6±1.3</td>
<td>1.0±0.8</td>
<td>0.17*-5.5</td>
</tr>
<tr>
<td>Nd[pg m$^{-3}$]</td>
<td>0.7±0.6</td>
<td>0.47±0.45</td>
<td>0.09*-2.7</td>
</tr>
<tr>
<td>Se[pg m$^{-3}$]</td>
<td>19±18</td>
<td>16±11</td>
<td>3.1*-82</td>
</tr>
</tbody>
</table>

* method detection limit (MDL)
Table 4. Al, La, Na, and Se concentrations (±std) measured in Antarctic aerosol samples.

<table>
<thead>
<tr>
<th>element</th>
<th>winter</th>
<th>summer</th>
<th>sampling period</th>
<th>sitea</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al [pg m⁻³]</td>
<td>300±40</td>
<td>830±410</td>
<td>10/1970</td>
<td>SP (Zoller et al., 1974)</td>
</tr>
<tr>
<td></td>
<td>320±110</td>
<td>730±240</td>
<td>1971/75/76/78</td>
<td>SP (Cunningham &amp; Zoller, 1981)</td>
</tr>
<tr>
<td></td>
<td>9470b</td>
<td>13290b</td>
<td>1985-1988</td>
<td>AP (Artaxo et al., 1992)</td>
</tr>
<tr>
<td></td>
<td>840±600</td>
<td>1270±700</td>
<td>3/1999 – 12/2003</td>
<td>NM, this study</td>
</tr>
<tr>
<td>La [pg m⁻³]</td>
<td>-</td>
<td>0.51±0.37</td>
<td>10/1970</td>
<td>SP (Zoller et al., 1974)</td>
</tr>
<tr>
<td></td>
<td>&lt; 2</td>
<td>0.78±0.25</td>
<td>1971/75/76/78</td>
<td>SP (Cunningham &amp; Zoller, 1981)</td>
</tr>
<tr>
<td></td>
<td>0.43±0.11</td>
<td>0.56±0.21</td>
<td>2/1979 – 11/1983</td>
<td>SP (Tuncel et al., 1989)</td>
</tr>
<tr>
<td></td>
<td>0.56±0.5</td>
<td>1.32±0.8</td>
<td>3/1999 – 12/2003</td>
<td>NM, this study</td>
</tr>
<tr>
<td>Na [ng m⁻³]</td>
<td>40±31</td>
<td>5.1±1.7</td>
<td>10/1970</td>
<td>SP (Zoller et al., 1974)</td>
</tr>
<tr>
<td></td>
<td>31±14</td>
<td>8.7±3.2</td>
<td>1971/75/76/78</td>
<td>SP (Cunningham &amp; Zoller, 1981)</td>
</tr>
<tr>
<td></td>
<td>869.9b</td>
<td>1046.2b</td>
<td>2/1979 – 11/1983</td>
<td>SP (Tuncel et al., 1989)</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>27.6±0.4</td>
<td>12/1984 – 02/1985</td>
<td>AP (Artaxo et al., 1992)</td>
</tr>
<tr>
<td></td>
<td>400±400</td>
<td>220±160</td>
<td>3/1999 – 12/2003</td>
<td>NM, this study</td>
</tr>
<tr>
<td>Se [pg m⁻³]</td>
<td>-</td>
<td>5.6±1.2</td>
<td>10/1970</td>
<td>SP (Zoller et al., 1974)</td>
</tr>
<tr>
<td></td>
<td>6.9±2.7</td>
<td>6.3±6</td>
<td>1971/75/76/78</td>
<td>SP (Cunningham &amp; Zoller, 1981)</td>
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<tr>
<td></td>
<td>4.8±0.8</td>
<td>8.4±1.6</td>
<td>2/1979 – 11/1983</td>
<td>SP (Tuncel et al., 1989)</td>
</tr>
<tr>
<td></td>
<td>16±11</td>
<td>25±24</td>
<td>3/1999 – 12/2003</td>
<td>NM, this study</td>
</tr>
</tbody>
</table>

*aAP = Antarctic Peninsula, SP = South Pole, NM = Neumayer |
bsum of fine and coarse mode
**FIGURES**

*Fig. 1:* (a) Mean element enrichment factors with respect to earth crust (EF\textsubscript{crust}) and (b) sea salt composition (EF\textsubscript{ss}) of Neumayer aerosol samples dissected for summer (November through March) and winter (April through 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.

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

*Fig. 4:* Pie 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 sulfur (i.e. the sum of MS and nss-SO\textsubscript{4}\textsuperscript{2-}, drawn line), and mineral dust (diamonds) portion.

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

*Fig. 7:* Time series of wind velocity at Neumayer during the sampling period displayed in the same temporal resolution as filter sampling (seven days, thin line), and 6 points moving average (bold grey line).

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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.

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

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.
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Figure 3: Same as Figure 2 but for Al, La, Ce, and Nd.
Aerosol composition summer (November-March)

- Mineral dust: 5.0%
- Sea salt: 50.3%
- nss-SO$_4^{2-}$: 27.6%
- NO$_3^-$: 7.1%
- NH$_4^+$: 1.2%

Aerosol composition winter (April-October)

- Mineral dust: 2.1%
- Sea salt: 86.2%
- nss-SO$_4^{2-}$: 5.9%
- MS: 0.8%
- NO$_3^-$: 4.2%
- NH$_4^+$: 0.8%

**Figure 4:** Pie diagram of the aerosol composition (weight percent referring to the sum of the measured species) at Neumayer during winter and summer, respectively.
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