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Year-round chemical aerosol records in continental Antarctica obtained by automatic samplings

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ABSTRACT

Aimed at year-round recording of the chemical aerosol composition in central Antarctica, an unattended operating aerosol sampler was successfully deployed at the EPICA deep drilling site in Dronning Maud Land (Kohnen Station). Analyses of teflon/nylon filter packs consecutively collected over bi-weekly intervals during the February 2003 to December 2005 period allowed to evaluate seasonal concentration variations of methane sulphonate (MS), Cl^-, $NO_3{}^-$, non-sea salt (nss-)$SO_4{}^{2-}$ and Na^+, while $NH_4{}^+$ and mineral dust related ion results remained below detection limits. For MS and nss-$SO_4{}^{2-}$ distinct late summer maxima around 44 and 200 ng m^{-3}, respectively, were found, while (total) $NO_3{}^-$ showed a broad November maximum of about 52 ng m^{-3}. In contrast, the highest concentrations of Na^+ with peak values of up to 160 ng m^{-3} were observed during the winter half year. The seasonality of these species broadly coincided with long-term observations at the coastal Neumayer Station, including surprisingly comparable $NO_3{}^-$ levels. However, the biogenic sulphur and sea salt concentrations were lower at Kohnen by typically a factor of 2–3 and 10, respectively. The arrival of sea ice derived sea salt particles at Kohnen could not clearly detected, since even during mid-winter the nss-$SO_4{}^{2-}$ to Na^+ ratio was generally too high to unambiguously identify a sulphur depleted sea salt $SO_4{}^{2-}$ fraction.

1. Introduction

In addressing the coupling between climate and biogeochemical cycles, Antarctic ice cores provide an unique archive of climate and environmental proxies. Basically, these ice cores allow to infer past changes over several climatic cycles of local temperature, circulation patterns and of various atmospheric constituents in adequate temporal resolution (e.g. Legrand and Mayewski, 1997; EPICA Community Members, 2006; Wolff et al., 2006). However, particularly in view of aerosol related species, the detailed interpretation of their continental Antarctic ice cores records remained partly ambiguous in terms of net atmospheric changes (Wolff et al., 2003; Ruth et al., 2004; Hastings et al., 2005; Jonsell et al., 2005; Bigler et al., 2006). In order to reduce this deficit, at least for Holocene climate conditions, year round aerosol (and associated trace gas) observations are needed from the relevant ice core-drilling site. First of all, such atmospheric records should comprise the set of ion species, commonly recorded in ice cores under investigation, which cover sea salt, mineral dust, biogenic and volcanic sulphur components as well as nitrate and ammonium. While detailed long-term records of chemical aerosol species are available from coastal Antarctic stations as Neumayer (Wagenbach, 1996) and Durmont d'Urville (Jourdain and Legrand, 2001), only very scattered atmospheric observations are obtained so far at central Antarctic positions (Bodhaine et al., 1986). Since most of these inland records were restricted to austral summer with only few ion data obtained during polar night (Tuncel et al., 1989; de Mora et al., 1997; Harder et al., 2000; Arimoto et al., 2001, 2004; Udisti et al., 2004; Piel et al., 2006), representative seasonal cycles of ionic aerosol compounds in the central Antarctic boundary layer remained virtually unknown. However, in elucidating to what extend the glacio-chemical signals may be related to the respective atmospheric aerosol changes, seasonality matters for several reasons. First, since ionic firn impurities originate from dry and wet deposition of aerosols and water-soluble trace gases, their mean firn levels (and the overall wet deposited fraction) may be governed by the interference of the seasonal cycles of net snow accumulation and atmospheric concentrations, respectively. This effect would be particularly significant, if a strong seasonal aerosol contrast prevail, as seen at coastal sites, among others for sulphur and nitrogen species (Minikin et al., 1998; Wagenbach et al., 1998a,b). Second, some of the seasonal cycles observed in coastal aerosol records are not well understood yet

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and deserve to be contrasted to respective records from central Antarctic sites. This is especially true for the multi-mode nitrate cycle (Wagenbach et al., 1998b), ammonium (Legrand et al., 1998), the methane sulphonate (MS) to sulphate ratio (Legrand and Pasteur, 1998; Piel et al., 2006) and the cycle of sea salt versus sea ice derived sodium fraction (Rankin et al., 2002). For various reasons (snow and impurity redistribution, inadequate chronology) it would not be feasible to obtain such seasonal cycles at useful quality from high resolution snow pit studies at the inland sites.

Within the European Project for Ice Coring in Antarctica (EPICA), we attempted therefore to obtain year round data of the ionic aerosol composition by deploying an automated aerosol sampler at the EPICA drill site in Dronning Maud Land (EDML). Here, we present an overview on the first results gained from the sampling campaigns at the unmanned Kohnen drill camp between February 2003 and December 2005, which complete our extensive summer samplings performed during the drilling seasons 2000–2002 (Piel et al., 2006). Herewith, emphasis is on assessing the performance of the technical approach, the reliability of the year round records as well as on the feasibility to deploy them for deep ice core related firn/air investigations.

2. Techniques

2.1. Site description and sampling technique

Kohnen Station (75°S, 0°E), serving as summer camp during the EDML deep drilling activities, is located 2892 m a.s.l. with the nearest distance to the Atlantic sector coast of roughly 520 km (see Fig. 1). The glacio-meteorological site conditions are characterized by a relatively low net snow accumulation rate around 71 ± 21 kg m^{-2} yr^{-1} (Oerter et al., 1999), an annual mean temperature of −46 °C (typically ranging between −15 and −70 °C) and a moderate annual mean wind speed wind of about 4.6 m s^{-1} (mainly persisting from northeast) (Reijmer, 2001). The prominent origin of air masses reaching Kohnen Station is the South Atlantic as shown by a thorough back trajectory analysis (Reijmer et al., 2002)

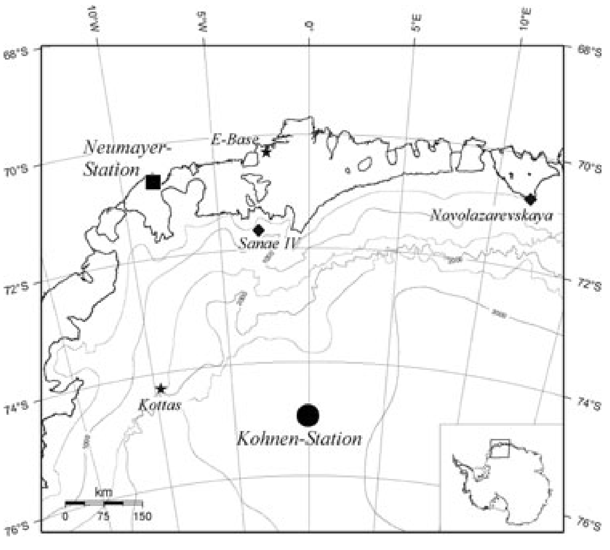

Fig. 1. Geographical position of the EPICA drill site in Dronning Maud Land (Kohnen Station) in relation to the Neumayer overwintering site.

The automatic year round sampling of aerosol filters for subsequent ion analyses started at Kohnen in February 2003 based on a dedicated satellite-station and is still ongoing. Since the detailed outline of this sampling station will be given elsewhere, only the essential technical feature is briefly presented here. We installed the automated aerosol sampler inside a specially insulated 20′ container. The operating aerosol sampler has a continuous power consumption between 6 and 7 W at 12 VDC. Electric power was supplied by solar panels and a wind turbine, backed up with 1070 Ah nickel–cadmium batteries which have proven to be operative down to −50 °C. This ensured a continuous sampling and minimized outages due to wind velocities below around 3 m s^{-1} during polar night, when the power supply relies entirely on the wind turbine.

The automatic sampling basically follows the concept developed by Preunkert and Wagenbach (1998) and Preunkert et al. (2002), which rely on consecutive activation of individual filter holder/pump units. Apart from various measures to cope with temperatures down to −70 °C, substantial updates of the previous version (to be deployed at high alpine sites) mainly concerned the improvement of the automatic filter sealing during the pre- and post-sampling period and an all PFA (polyfluoralkoxy-copolymer) inline design. The sampling time was fixed to 15 d (corresponding to a typical air volume of 60 m^3 STP), which for the given power supply reflects a reasonable compromise between temporal resolution and analytical sensitivities (i.e. quantitative detection limits). In principle, ambient air was sucked in through a single inlet and was directed to 22 sampling units each consisting of a PFA inline filter holder, a one-way inlet and outlet valve and a miniature vacuum pump (carbon vane pump) as outlined in Fig. 2. The sampling line was about 2 m long (PFA, inner diameter 8 mm) and its orifice was fixed 1 m above the container top resulting in a total sampling height of around 5 m. To minimize the danger of passive sampling, we avoided permanent contact of the filters with ambient air by isolating each inline filter holder via squeezing valves at the entrance and outlet (Fig. 2). Appropriate working of the valves was ensured using silicon tubing for the pinching unit which remains flexible even at temperatures down to −50 °C. A programmable data logger managed the control of the procedure cycle. Two-stage filter systems were deployed at a ambient air flow rate of 3–4 l min^{-1}, which included an upstream teflon (Millipore, 47 mm diameter, 1 μm pore size) and a downstream nylon filter (Gelman Nylasorb, 47 mm diameter, 1 μm pore size). The teflon filter collected all particulate compounds with efficiencies higher than 95% but allows gaseous (acidic) species like HCl, HNO_3

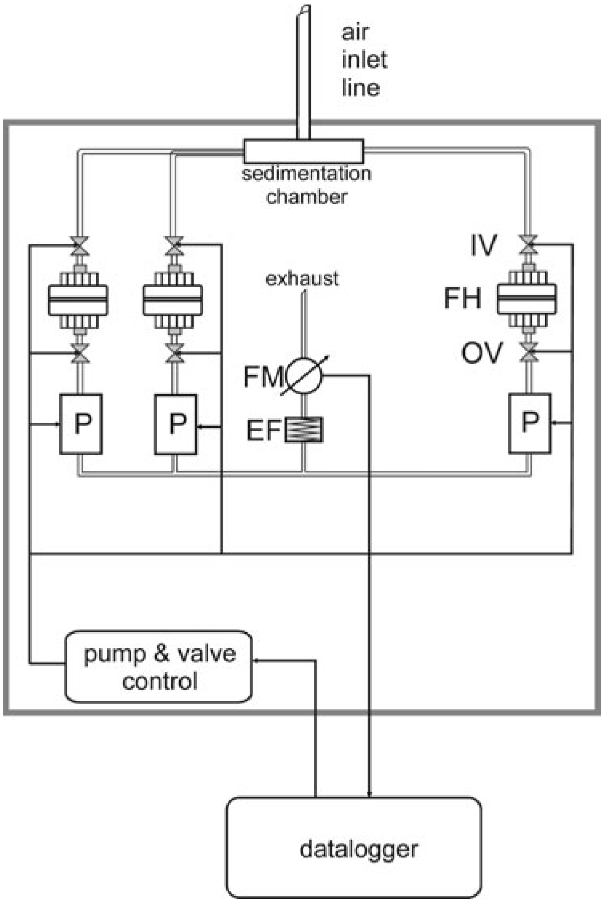

Fig. 2. Diagram of the technical layout of the automated aerosol sampler installed at EDML. Abbreviations: P, carbon vane pumps (22); EF, exhaust filter; FH, filter holders (22); FM, flow meter; IV, inlet valves (22) and OV outlet valves (22). To enhance clarity, only 3 out of 22 filter units are shown.

to pass through as becoming partly adsorbed on the nylon filter (Piel et al., 2006). It is expected that these volatile species, which may be possibly desorbed from the front filter during the rather long post sampling storage were sampled by the nylon back up filter as well. Consequently, we did not attempt to differentiate between the particulate fractions of nitrate and chloride, respectively, but report the total concentrations of these species.

For a comparison we referred to the 22 yr (1983–2005) record of continuous and ongoing aerosol sampling at Neumayer (e.g. Legrand and Pasteur, 1998; Wagenbach et al., 1998a,b). The mean seasonality of ion concentrations measured at this coastal site is of climatologic relevance due to the long observation period. A description of the sampling procedure at Neumayer is given in Wagenbach et al. (1988). In short, these data were based on a sampling period of typically 7 d, occasionally extended up to 2 weeks. In contrast to Kohnen, two Whatman™ 541 cellulose filters were used in series instead of a teflon/nylon combination.

2.2. *Filter analyses*

The filters were rigorously pre-cleaned at the Institute für Umweltphysik (IUP) by shaking them several days in steadily renewed de-ionized water (i.e. 18.2 MΩ cm^{-1}) until no significant enhancement of the electrolytic conductivity of the washing water could be observed. They were dried in a stream of particle free air, cleaned as well from contaminating trace gases by acidic, alkaline and activated carbon cartridges, respectively. The dry filter were subsequently loaded in a clean air laboratory face to face into PFA inline filter holders, which were capped by airtight stopcocks and finally sealed in aluminium lined polythene bags. After collection, the filters holders with the aerosol samples were again capped, sealed in polythene-aluminium bags and transported at −25 °C to our home laboratory in Bremerhaven. While we applied a common extraction of the nylon and teflon filters for the 2003 and 2004 sampling campaigns, the 2005 samples were extracted separately. The analytical procedure included wetting of the teflon filter by 100 μl 2-propanol, soaking and shaking in 20 ml milliQ water, followed by ultrasonic treatment for 15 min and subsequent ion chromatography (IC) analyses. In general, samples were analysed for methane sulphonate (MS), Cl^-, Br^-, $NO_3{}^-$, $SO_4{}^{2-}$, oxalate ($C_2O_4{}^{2-}$), Na^+, $NH_4{}^+$, K^+, Mg^{2+} and Ca^{2+}. According to this analytical procedure the IC blank levels were between 0.2 and 0.3 ng g^{-1}, except for Br^- (around 1 ng g^{-1}), $NH_4{}^+$ and Ca^{2+} (around 0.5 ng g^{-1}). Details of the IC set up, accuracy and detection limit of the IC procedure correspond to those reported by Göktas (2002) and Piel (2004).

2.3. *Uncertainties and data evaluation*

As expected, the variability of the filter blanks clearly governed the overall accuracy and thus the analytical detection limits as well. These estimates were derived from the variation of 17 identically processed procedure blanks which include possible contributions by the previously cleaned filters, and any effects arising from handling and long-term storage (Table 1). The latter, systematic effect appeared to dominate the overall blank and we conservatively estimated the detection limits (DL) as three times the standard deviation (*SD*) of these overall blank values, listed in Table 1. In addition to this blank induced uncertainty, relative errors of the flow meter ($<\pm10\%$) and the IC calibration error (±10% for oxalate, $NH_4{}^+$, Mg^{2+} and Ca^{2+} and ±5% for all other ions) were considered. In short, the combined uncertainty was found to be approximately ±15 to ±20% for ion concentrations above three times the corresponding detection limit (DL). It increased from around ±20 to ±40% approaching 3 × DL level to (−100/+50)% close to the detection limit. The concentrations for the cations K^+, Mg^{2+}, and Ca^{2+} were too low to calculate reliable non-sea salt (nss)-K^+, nss-Mg^{2+} and nss-Ca^{2+} values and bromide was below the IC detection limit of ~1 ng g^{-1} throughout, corresponding to 0.34 ng m^{-3}. In case of

Table 1. Blank variability in ng per 47 mm diameter filter, detection limits (DL) as well as mean ± *SD* of the ionic concentrations observed via automatic aerosol sampling at Kohnen (2003–2005) including the results from three separate summer seasons. Mean ± *SD* concentrations observed at Neumayer Station for the 1983–2005 period are given for comparison. The blanks denote the corresponding procedure blanks for filter combinations installed for the whole wintering-over in the sampler ($n = 17$). Detection limits were calculated for a typical sampling volume of 57 m^3 STD. Ammonium and oxalate results were most probably invalid due to contamination.

Ion	Blank (ng) Mean ± *SD*	DL (ng m^{-3})	Kohnen Mean ± *SD* (ng m^{-3})	Neumayer Mean ± *SD* (ng m^{-3})
MS	210 ± 45	2.7	17 ± 25	44 ± 75
$SO_4{}^{2-}$	210 ± 85	4.5	90 ± 91	150 ± 158
Cl^-	600 ± 150	8.9	38 ± 47	480 ± 664
$NO_3{}^-$	170 ± 55	2.9	25 ± 21	42 ± 32
Oxalate	350 ± 300	16	(35 ± 48)	Not analysed
Na^+	18 ± 5	0.28	24 ± 25	270 ± 330
$NH_4{}^+$	420 ± 360	19	(48 ± 44)	6.2 ± 6
K^+	8.0 ± 5	0.26	2.7 ± 2.2	11 ± 19
Mg^{2+}	24 ± 12	0.6	3.9 ± 4.0	41 ± 45
Ca^{2+}	280 ± 160	8.4	1.3 ± 5.7	12.5 ± 13

oxalate and $NH_4{}^+$ overall blanks and most of the atmospheric concentrations appeared suspiciously high compared to atmospheric concentrations typical for coastal Antarctica (Legrand et al., 1998), hence we tentatively attribute these results to a specific contamination problem. In addition overall blanks and their variability were unusually high for MS and Ca^{2+}. Here, a potential contamination during filter handling should be less critical compared to the ubiquitous ions Cl^-, $NO_3{}^-$, $SO_4{}^{2-}$ and $NH_4{}^+$. Especially Ca^{2+} blank values were suspect, which exceeded the Mg^{2+} and even Na^+ ones. Concerning MS, part of the procedure blank (about 20–30%) could be traced back to 2-propanol used for filter extraction causing a fake peak at the same elution time as MS. The remaining part may be due to passive sampling of gaseous MSA at the measuring site. For Ca^{2+} on the other hand, passive sampling should be negligible and we tentatively attribute the blanc problem to an unknown contamination during sample handling. While for MS only values observed from May to September were at or below the DL of 2.7 ng m^{-3} and thus seriously influenced by contamination, for Ca^{2+} this was unfortunately the case for nearly all samples. According to the overall uncertainties of the different ion records, we restrict the presentation and discussion of our results to the ions MS, Cl^-, $NO_3{}^-$, $SO_4{}^{2-}$ and Na^+. The final atmospheric concentrations (in ng m^{-3}) were calculated by summing up the blank corrected ion amounts of the teflon and nylon filter of each sample and corrected the sampled air volume to standard conditions (273.16 K and 1013 hPa).

Non-sea salt sulphate (nss-$SO_4{}^{2-}$) concentrations were calculated by subtracting the concentration of the sea salt derived sulphate from the total $SO_4{}^{2-}$ concentration (in ng g^{-1}). We used Na^+ as sea salt reference species and the sulphate to sodium ratio in bulk sea water of $\alpha_{\text{sulphate}} = 0.252$ for November to February, and due to the potential impact of sea salt fractionation by frost flower formation $\alpha_{\text{sulphate}} = 0.07$ for winter (March–October) samples, that is:

$$\left(\text{nssSO}_4^{2-}\right) = \left(\text{SO}_4^{2-}\right) - \alpha_{\text{sulfate}} \times (\text{Na}^+) \qquad (1)$$

Note that due to low sea salt aerosol concentrations the impact of sea salt fractionation on the nss-$SO_4{}^{2-}$ budget at Kohnen was in most cases negligible, except during the sporadic occurrence of peaking sea salt aerosol loadings happened mainly during winter. A determination of sea salt Na^+ by correcting the mineral dust portion of the Na^+ signal according to Bigler et al. (2006) was not possible due to Ca^{2+} levels typically below the detection limit. However, even in the worst case, a mineral dust correction would change the Na^+ concentrations by less than about 5%.

3. Data presentation

Figures 3–5 give an overview of our EDML aerosol measurements for the ions MS, nss-$SO_4{}^{2-}$, Na^+ and $NO_3{}^-$. Note that for each component two samples taken in 2004 between September 21 and October 5 as well as between November 7 and 21 were removed because of inadequately low sampling volumes of 17 and 14 m^3, respectively. A total loss of the wind turbine controller caused a breakdown of aerosol sampling between mid of April to the end of October in 2003, while during 2004 we obtained reliable data from the periods February to the end of June and from mid of September to December. The reason for a data gap over 11 weeks in winter 2004 was again malfunction of the wind turbine leading to empty backup batteries, while during 2005 just one sample was lost in September. Due to maintenance of the system, no automatic samplings were performed in January. Each value shown in Figs. 3–5 represents a sampling period over 360 h

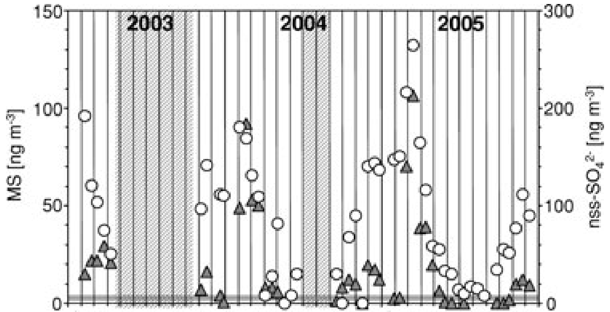

Fig. 3. Concentrations of MS (triangles) and nss-SO_4^{2-} (circles) observed during the years 2003, 2004 and 2005 at Kohnen Station. Hatched areas mark sampler down times due to power failure. Grey bars denote the detection limit for MS (2.7 ng m^{-3}) and nss-SO_4^{2-} (4.5 ng m^{-3}), respectively.

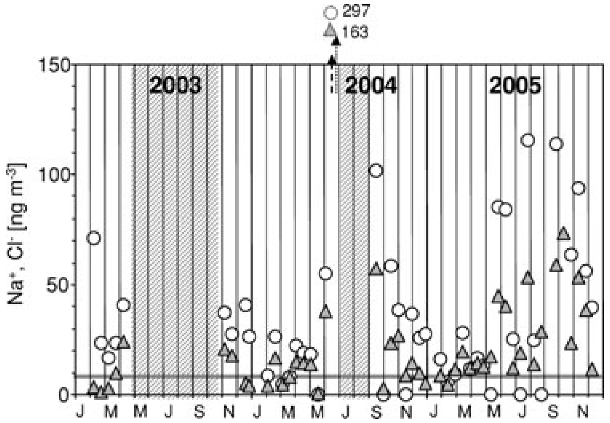

Fig. 4. Same as Fig. 2, but for Na^+ (triangles) and Cl^- (circles). The grey bar marks the 8.9 ng m^{-3} detection limit of Cl^- while that of Na^+ (0.28 ng m^{-3}) is not displayed.

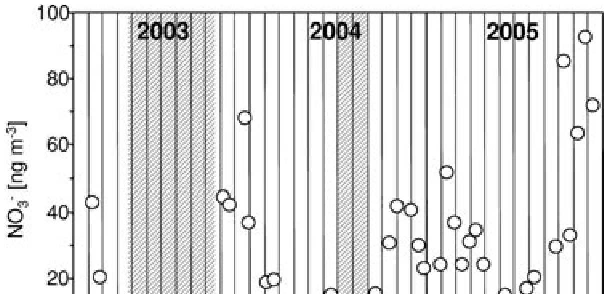

Fig. 5. Same as Fig. 2, but for NO_3^- with bold line denoting the 2.9 ng m^{-3} detection limit.

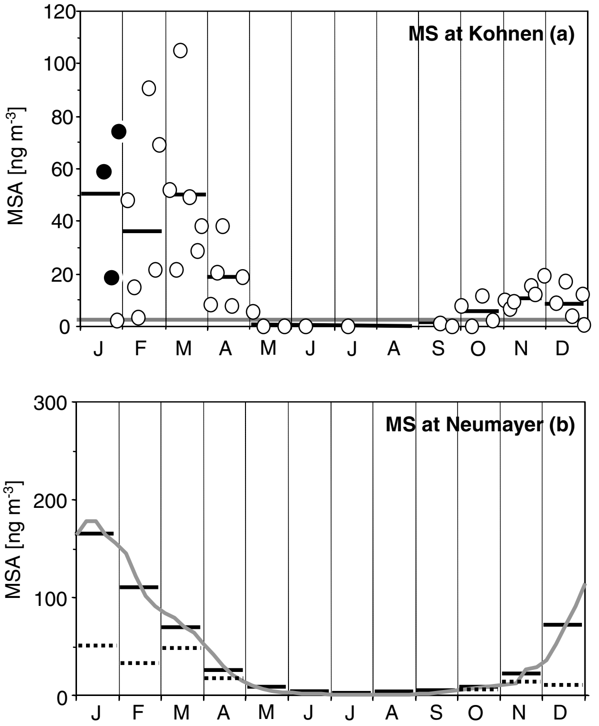

Fig. 6. Seasonal cycles of MS (open circles) at Kohnen (a) during the years 2003 to 2005, including mean results from 2000–2002 summer campaigns (filled circles) contrasted to the mean MS seasonality at Neumayer for the 1983–2005 period (b). Black bars represent monthly means from the corresponding site, dashed bold lines in (b) are again the monthly means from Kohnen for comparison. The bold grey line in (a) is the MS detection limit at Kohnen.

(15 d). Concerning the accuracy of the data, we omitted error bars for clarity and refer to the outline in Section 2.3. Table 1 summarizes mean and standard deviation for all ionic compounds measured at Kohnen. Due to missing data for the month January and the mentioned sampling gaps during winter, a bias in calculating annual mean and median concentrations from the whole data set would result. Hence, we included adequately weighted the results from three summer campaigns performed between January and early February in the years 2000, 2001 and 2002 (Piel et al., 2006) and padded missing winter data with the medium winter concentrations for the year 2005.

In Figs. 6–9, addressing the seasonality of the ionic aerosol compounds, we merged the results obtained by automatic sampling with those from the mentioned three summer campaigns. It is important to note that the values from these summer campaigns were consistent with those obtained during that season by the automated aerosol sampler. Also illustrated in Figs. 6–9 are the main seasonal cycles at the coastal Neumayer Station as to be compared with the Kohnen ones.

4. Discussion

4.1. MS and nss-SO_4^{2-}

Based on aerosol measurements conducted during three summer campaigns, Piel et al. (2006) reported on the origin of atmospheric sulphur at Kohnen in detail addressing the fraction of non-biogenic sulphur and the variability of MS/nss-SO_4^{2-}

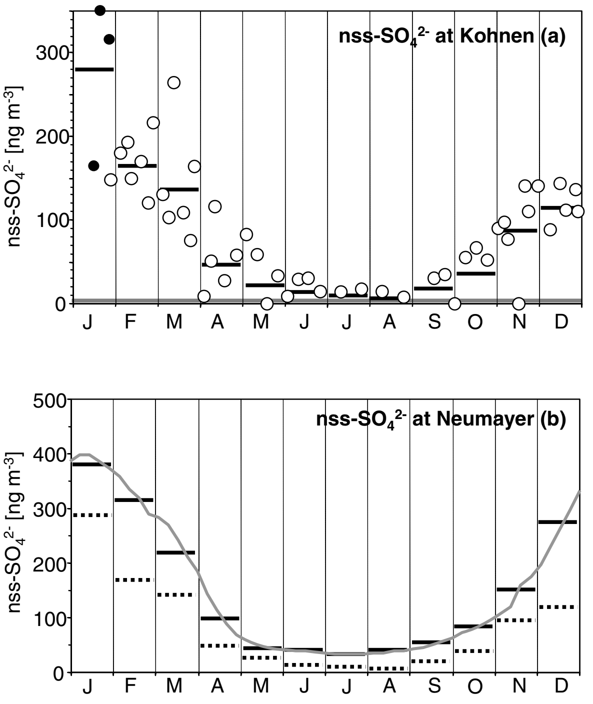

Fig. 7. Same as for Fig. 6, but for nss-SO$_4^{2-}$ concentrations (open circles: automated sampler, filled circles: separate summer campaigns)

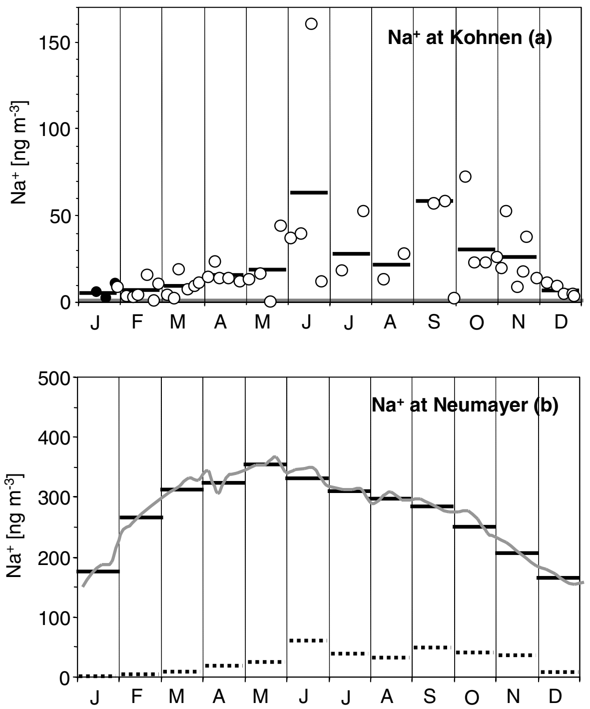

Fig. 8. Same as Fig. 6, but for Na$^+$ concentrations (open circles: automated sampler, filled circles: separate summer campaigns).

ratios β_{MS}. In completing this study, we focus here on seasonal aspects of the sulphur budget at Kohnen.

Comparison of the year-round MS and nss-SO$_4^{2-}$ concentrations at Kohnen with Neumayer revealed broadly the same seasonality for both species with corresponding maximum concentrations during austral summer. If we include our MS and nss-SO$_4^{2-}$ results of 51 ± 28 ng m^{-3} (mean ± *SD*) and 280 ± 100 ng m^{-3}, respectively, obtained during three composite summer campaigns at Kohnen, the resulting annual mean concentrations were found to be a factor of 2.6 and 1.6 lower, compared to the long-term means at coastal Neumayer (see Table 1). A more detailed comparison of the seasonality between these two sites is shown in Fig. 10. At Kohnen the summer MS maximum appeared less sharp and even the fall (i.e. March and April) MS concentrations were relatively high. Interestingly, only during summer MS concentrations were clearly lower at Kohnen, while during all other seasons they were roughly comparable to Neumayer. Thus the higher annual mean values at Neumayer were essentially caused by the summer maxima. The seasonal cycle of MS at Neumayer appears to be a composite of a flat maximum lasting from December to March superimposed by a sharp peak in January, which was obviously absent at Kohnen. As discussed by Minikin et al. (1998), particularly marine sources south of 60°S seem to dominate the MS level at Neumayer, while for nss-SO$_4^{2-}$ also long range transport of biogenic sulphur from more northern regions of the South Atlantic were relevant. We infer that the biogenic sulphur seen at Kohnen was more representative for the Southern Ocean as a whole, while at Neumayer also a regional impact from the Antarctic part of the South Atlantic was discernible, particularly for MS.

Comparable to Neumayer we found a significant correlation between MS and nss-SO$_4^{2-}$ concentrations at Kohnen (Fig. 11). However, the inter-site difference in the seasonal biogenic sulphur maximum was also reflected in the individual MS/nss-SO$_4^{2-}$ ratios (β_{MS}) which reached at Kohnen its maximum of 0.33 during fall while at Neumayer a maximum value of 0.36 appeared during summer. Especially during winter, but also in spring and fall, at both sites the uncertainty of β_{MS} ratios were as large as the calculated values itself due to low MS and sulphate concentrations and difficulties to derive reliable nss-SO$_4^{2-}$ concentrations. The latter problem was mainly caused by the potentially varying and unknown impact of sea salt fractionation (Wagenbach et al. (1998a); Rankin et al. (2002)) entailing an uncertain value of $\alpha_{sulphate}$ needed in equation (1). Using $\alpha_{sulphate} = 0.07$, wintertime nss-SO$_4^{2-}$ persisted at 5–35 ng m^{-3} and were likely to be non-DMS related in view of MS remaining below the detection limit of 2.7 ng m^{-3}. Concerning the atmospheric sulphur inventory during winter at other inland sites, only atmospheric sulphur measurements were available, conducted at South Pole during the years 1979–1983 by Tuncel et al. (1989), whereas nss-SO$_4^{2-}$ South Pole data from July 1992 to December 1992 were reported by Harder et al. (2000). Winter concentrations of 5–50 ng m^{-3} (Harder et al., 2000) and 21 ± 13 ng m^{-3} (Tuncel et al., 1989) at South Pole were consistent with the level observed at Kohnen.

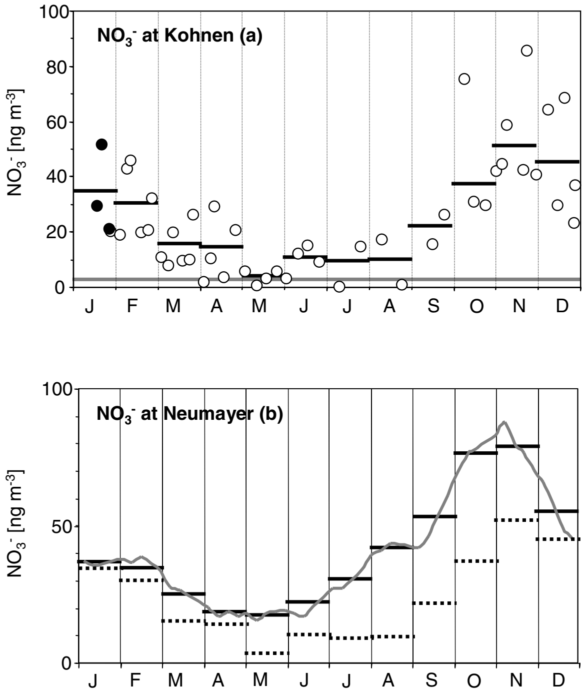

Fig. 9. Same as Fig. 6, but for NO_3^- concentrations (open circles: automated sampler, filled circles: separate summer campaigns).

4.2. Sea salt

The common mechanism producing sea salt aerosol is bubble bursting during whitecap formation caused by surface winds over open ocean waters (Monahan et al., 1986). For polar regions, the formation of sea salt aerosols by frost flowers on freshly formed sea ice has been put forward as alternative source (Rankin et al., 2000, 2002; Wolff et al., 2003). This assumption challenges a revision of the hitherto adopted interpretation that sea salt signals in ice cores should be a proxy for storminess and meridional transport (Petit et al., 1999).

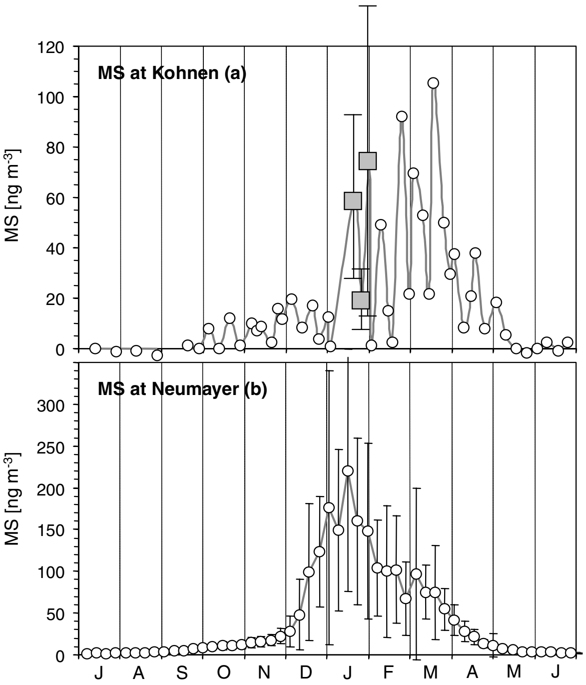

Fig. 10. Mean seasonality of atmospheric MS at Kohnen (a) and Neumayer (b). For Kohnen, the results from three additional summer campaigns were displayed by grey squares [error bars represent the standard deviation of the corresponding time series (Piel et al., 2006)]. The data from Neumayer (with standard deviation) comprise 22 yr of continuous observation (1983–2005).

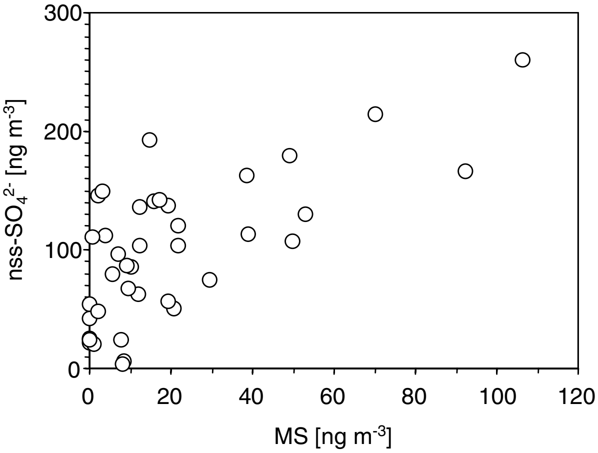

Fig. 11. Overall correlation of MS with nss-SO_4^{2-} concentrations (correlation coefficient $r = 0.72$).

In the following, we used Na^+ as a gauge for sea salt aerosol amount. Basically, Na^+ concentrations measured at Neumayer were an order of magnitude higher compared to Kohnen, which is clearly due to the source proximity at Neumayer. A broad seasonal maximum of Na^+ concentrations was evident at both stations during winter, but somewhat more pronounced at Kohnen (Fig. 8). Our findings were consistent with investigations by Hara et al. (2004) performed at the coastal Japanese Station Syowa and its continental counterpart Dome Fuji. These authors found at Dome Fuji maximum Na^+ concentrations of around 60 ng m^{-3} from May to November. Na^+ concentrations at Syowa were on average an order of magnitude higher. At South Pole, they decreased from roughly around 20–80 ng m^{-3} between July and October to typically less than 10 ng m^{-3} in November and December (Bodhaine et al., 1986; Harder et al., 2000). Except for Dumont d'Urville, a seasonal sea salt aerosol maximum during winter was generally observed in Antarctica (Hara et al. (2004) and references therein).

In order to assess the impact of potentially sea ice derived sea salt aerosol seen at Kohnen we compiled a ternary diagram of the SO_4^{2-}, Na^+ and Cl^- composition of the aerosol (Fig. 12). For presentation we followed the approach of Rankin et al. (2002) and normalized the data such that the composition corresponding

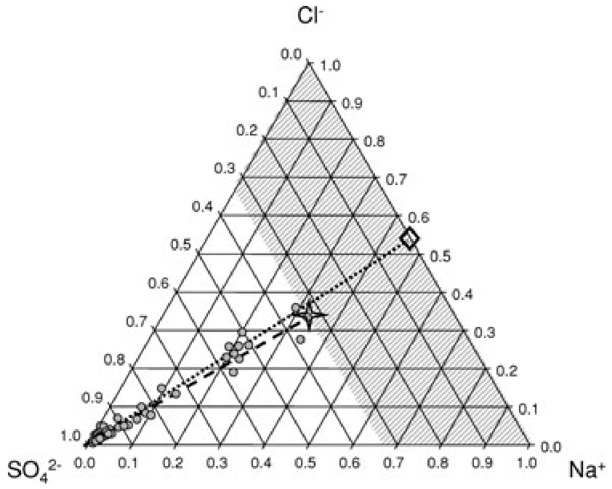

Fig. 12. Ternary diagram of the SO_4^{2-}, Na^+ and Cl^- aerosol composition at Kohnen. The data point positions, reflecting the relative composition are normalized such that the composition corresponding to pure seawater sea salt is localized in the centre of the diagram, marked by a star. The diamond marks the composition of totally fractionated sea salt with all sulphate initially precipitated as Mirabilite, while partly depleted sea ice sources sulphate would be located within the hatched area. Measured points are presented as grey circles. The dotted line represents the composition of fractionated sea salt aerosol plus additional nss-SO_4^{2-} and the broken one that of seawater sea salt plus additional nss-SO_4^{2-}.

to pure seawater sea salt is localized in the centre of the diagram:

$$
\begin{aligned}
\text{Na}^+\text{-ratio} &= \left([\text{Na}^+]/10.76\right)/([\text{Na}^+]/10.76 \\
&\quad + [\text{Cl}^-]/19.35 + \left[\text{SO}_4^{2-}\right]/2.712\Big) \\
\text{Cl}^-\text{-ratio} &= ([\text{Cl}^-]/19.35)/([\text{Na}^+]/10.76 \\
&\quad + [\text{Cl}^-]/19.35 + \left[\text{SO}_4^{2-}\right]/2.712) \\
\text{SO}_4^{2-}\text{-ratio} &= \left(\left[\text{SO}_4^{2-}\right]/2.712\right)/([\text{Na}^+]/10.76 \\
&\quad + [\text{Cl}^-]/19.35 + \left[\text{SO}_4^{2-}\right]/2.712\Big)
\end{aligned}
$$

where [ion] is the ion concentration in the aerosol sample in ng m^{-3}. The diamond in Fig. 12 marks the composition of totally fractionated sea salt (i.e. all sulphate precipitated as mirabilite, $Na_2SO_4 \cdot 10\ H_2O$). Within the hatched area sulphate depleted, that is, frost flower sea salt aerosol (with varying Cl^- portions) would be located. According to this ternary diagram, it seems that no fractionated sea salt had reached Kohnen Station during the observation period. However, this conclusion is surely ambiguous because even during winter a possible sea salt sulphate (ss-SO_4^{2-}) depletion could easily be compensated by nss-SO_4^{2-}, especially given the low sea salt aerosol level at Kohnen (Fig. 8; mean ± *SD*: 23.8 ± 25 ng m^{-3} Na^+). Generally, the composition of fractionated sea salt aerosol with a surplus of nss-SO_4^{2-} was consistent with the dotted line in Fig. 12, while the dashed line represents the composition of seawater sea salt plus a surplus of nss-SO_4^2. In view of the rather high uncertainty of our measured points both lines are too close together to differentiate between both processes. Therefore, the current Na^+ and SO_4^{2-} data from Kohnen did not allow to decide to what extent the winter time sea salt aerosol at central Antarctica has been fractionated and hence would originate from a potential sea-ice source. At South Pole and Dome F, sea salt concentrations during winter were well below 100 ng m^{-3} (see above), implicating that also at other continental sites an assessment of sea salt fractionation via sulphate depletion should remain ambiguous at least for weekly and longer sampling periods. At Neumayer, on the other hand, a significant Na^+ and sulphate depletion indicated the substantial role of sea ice as an additional sea salt source (Minikin et al., 1998; Wagenbach et al., 1998a).

4.3. Nitrate

To our knowledge, no atmospheric nitrate measurements are made up so far in continental Antarctica, except during austral summer. Representative year-round observations of total NO_3^- (Wagenbach et al., 1998b) and measurements of gaseous reactive nitrogen oxides (NO_y) (Weller et al., 2002) are available, however, at various coastal Antarctic sites. They indicated that the input of stratospheric nitrate may constitute the dominant sources there, including to some extent seasonal intrusions of stratospheric NO_y and sedimentation of polar stratospheric clouds (PSC).

Specifically at inland sites, part of the boundary layer nitrate is re-emitted from firn as HNO_3, which may impose a certain imprint on the atmospheric nitrate seasonality. For Kohnen, Weller et al. (2004) reported significant post depositional losses of nitrate (and MSA), most probably restricted to the summer months. Therefore, as shown by Piel et al. (2006) for MS, the measured total nitrate during austral summer at Kohnen may be partly attributed to re-emitted HNO_3 from upper firn layers. Indeed, denuder measurements during summer revealed that between 33 and 76% of the total nitrate was present there as free acid HNO_3 (Piel et al., 2006). Following this approach with a corresponding nitrate loss of about 26%, that is, 20 ± 12 ng g^{-1} (Weller et al., 2004) and considering an annual snow accumulation of 71 kg m^{-2}, yielded a HNO_3 emission flux $\Phi_{em}(HNO_3)$ of (45 ± 27) × 10^{-3} ng m^{-2} s^{-1}. This would be sufficient to replenish a 100 m thick local atmospheric inversion layer within 1 d to maintain a nitrate concentration of around 40 ng m^{-3} (neglecting any HNO_3 sinks). Thus re-emitted nitrate might have significantly influenced our Kohnen nitrate observations, at least during the summer half years.

Following Fig. 9, the seasonality of total nitrate at Kohnen agreed surprisingly well with long-term observations from Neumayer Station (Wagenbach et al., 1998b), though the absolute values were somewhat higher at Neumayer. In view of this systematic difference, we cannot rule out that HNO_3 may have been partly lost in the up-stream area of the automatic sampler or during filter storage, though the January means obtained by Piel et al.

(2006) did not significantly differ from the automatic sampling in December and February. Note however, that the Kohnen data reflect total nitrate, similar to Neumayer, where two Whatman™ 541 cellulose filters were used in series and where the relatively high sea salt load ensured total nitrate sampling even during high acid loads in summer (as discussed in Wagenbach et al.,1998b). Apart from the prominent nitrate maximum in November, secondary peaks during August to September and around February are regularly seen at Neumayer, which were attributed by Wagenbach et al. (1998b) to PSC and stratospheric air mass intrusions, respectively. While the nitrate minimum as well as the maximum in November and a secondary peak during January–February were also evident at Kohnen, there was no clear indication for a late winter peak. However, regarding our limited number of data points especially during this period the latter finding appears not conclusive, yet. The rather good correspondence of the seasonal nitrate cycles between Neumayer and Kohnen appears to be somewhat conflicting as suggesting the following implications:

(1) The latitudinal position of the sampling site relative to the Antarctic vortex (also associated with the height above sea level) may not play an important role. Given that in contrast to Neumayer, Kohnen is almost permanently below the Antarctic vortex, the seasonality of PSC sedimentation and stratospheric air mass intrusions should be of secondary importance in shaping the seasonal cycle of boundary layer nitrate.

(2) Because post depositional losses of NO_3^- are only significant at sites with annual snow accumulations below 100 kg m^{-2} (Röthlisberger et al., 2002; Weller et al., 2004), they are only relevant for inland sites. Thus, NO_3^- re-emissions do either not substantially contribute to the nitrate budget of the inland boundary layer, or instead, they are strong enough to impose an Antarctic wide impact seen at coastal sites as well. In this context it is worthwhile to mention, that although the extremely depleted δ^{15}N in atmospheric nitrate at Neumayer would be consistent with a significant nitrate source by re-emission (Wagenbach et al., 1998b), an almost negligible contribution on the nitrate budget of the entire Antarctic troposphere has been estimated by these authors.

5. Conclusion

We demonstrated that year-round aerosol chemistry records can be obtained from the Antarctic Plateau by deploying an unattended automated aerosol sampler, even though there was a higher probability of missing data during winter. Energy restrictions during polar night basically limited the sampling flow rate and thus the time resolution to bi-weekly samplings. Based on these constraints, including passive and post-sampling artefacts, reliable ion records of biogenic sulphur species, sea salt and total nitrate could be obtained, while the filter blank variability needs still to be improved to gain meaningful mineral dust related ion records.

On the one hand, the main feature of the seasonal cycles at the Kohnen inland position are found to be broadly in agreement with respective long-term observations from the coastal Neumayer Station. Except in the case of total nitrate, this general finding might have been expected, though the atmospheric concentration levels at the inland site were unknown. On the other hand, evidences for small, nevertheless important intersite differences could be revealed, emphasizing the need for long-term aerosol chemistry records from central Antarctic positions to interpret related ice core records. Among others, the differences of the Kohnen records relative to coastal ones mainly comprise: (1) a higher summer/winter contrast in the sea salt level, and (2) a less confined summer maxima of biogenic sulphur species, which extended more far into late summer/fall. Both observations might be related to the obviously less proximate situation of Kohnen Station to the principal sources of these marine aerosol components, underlying the importance of atmospheric transport not only for the absolute atmospheric levels, but also for the seasonal changes.

Based on the bi-weekly sampling interval it was not possible to clearly identify the arrival of depleted ss-SO_4^{2-}, which would help to indicate the relative importance of the sea ice related source at this position. It is evident, that this finding is due to a nss-SO_4^{2-} to Na^+ ratio generally too high for clearly detecting the depletion. Although a much higher sampling resolution may help to capture events with a lower and hence more favourable nss-SO_4^{2-} to Na^+ ratio, this attempt would be hardly feasible by an automatic sampler.

Obviously, ionic signals archived in firn do not straightforwardly depend on the atmospheric loading of the boundary layer at the drilling site but are, among others, also governed by various deposition processes. In conclusion, deploying year round aerosol records as exemplarily presented here, a dedicated improvement of related ice core interpretations needs to consider concurrent observations from snow accumulation records by, for example, automated weather stations, which should be backed up by subseasonal resolution snow pit data. For this attempt, the seasonalities of the atmospheric loads as well as of the precipitation strongly matters, since their interference eventually determines the mean firn levels as well as its relation to the deposition processes involved.

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