Atmospheric methane sulfonate and non-sea salt sulfate records at the EPICA deep-drilling site in Dronning Maud Land, Antarctica

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Abstract

During three summer campaigns in January/February 2000, 2001 and 2002 the ionic composition of the aerosol at the EPICA deep-drilling site at Kohnen Station was measured in daily resolution. In 2000 and 2002 we observed mean (±std) non-sea salt sulfate (nss-SO_4^{2-}) concentrations of 353±100 ng m^{-3} and 320±250 ng m^{-3}, as well as methane sulfonate (MS) concentrations of 59±36 ng m^{-3} and 74±80 ng m^{-3}, respectively. For the summer campaign in 2001, significantly lower nss-SO_4^{2-} and MS levels of 164±150 ng m^{-3} and 19±12 ng m^{-3}, respectively, were typical. The mean MS/nss-SO_4^{2-} ratio ranged from about 0.1 to 0.2. MS and nss-SO_4^{2-} concentrations and their variability were roughly comparable to coastal stations at summer. Supported by air mass back trajectory analyses this finding documented an efficient long-range transport to Kohnen via the free troposphere. MS/nss-SO_4^{2-} ratios exhibited a strong dependence on the MS concentration with systematically higher ratios at higher MS concentrations, a peculiarity which is also evident in a firn core drilled at this site.

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1. Introduction

Secondary aerosol formation by biogenic precursors like algae derived dimethyl sulfide (DMS) [*Gondwe et al.,* 2003] or other volatile organic compounds emitted by terrestrial and marine flora [*Kavouras et al.*, 1998; *O'Dowd et al.,* 2002; *Claeys et al.,* 2004] play an important and decisive role in determining the Earths albedo. This is especially true for the Southern Hemisphere, where the emission of manmade aerosol is still much less dominant compared to the Northern Hemisphere [*Bates et al.,* 1992; *Spiro et al.,* 1992; *Curran and Jones,* 2000]. Considering the naturally derived aerosol load of the Southern Hemisphere, the atmospheric photo-oxidation of DMS leading to the final reaction products methane sulfonic acid (MSA) and sulfuric acid [*Yin et al.,* 1990; *Koga and Tanaka,* 1999; *Lucas and Prinn,* 2002] is believed to be the most important process [*Clarke et al.,* 1998; *Gondwe et al.,* 2003], although the contribution of secondary organic aerosol formation seems to be higher than previously assumed [*Kavouras et al.,* 1998; *O'Dowd et al.,* 2002].

Addressing the coupling between climate and biogeochemical cycles, polar ice cores provide an unique archive of climate proxies from which information about past changes of temperature, snow accumulation rate and atmospheric composition can be derived in adequate temporal resolution [e.g. *Legrand and Mayewski,* 1997]. In contrast to deposited sulfate, which comprises a composite signal of marine biogenic, sea salt, terrestrial, and volcanic sources, MSA is believed to be exclusively formed by photo-oxidation of algae derived DMS and, to a minor part, dimethyl disulfide [*Yin et al,* 1990]. Recently, *Meinardi et al.* [2003] identified DMS emission by biomass burning, but this process seems to be negligible compared to the marine source. Volcanic sulfate signals in ice cores have proven to be invaluable in assessing the climatic impact of large volcanic eruptions [e.g. *Robock and Free,* 1995; *Robock,* 2000] and in establishing a framework of time horizons [e.g. *Palmer et al.,* 2001]. Concerning the marine biogenic tracer MSA, extensive long-term aerosol measurements at coastal stations revealed that the main source region is primarily located south of 50°S with increasing contribution from more local sources south of 60°S [*Minikin et al.*, 1998]. Accordingly, methane sulfonate (MS) changes retrieved from Antarctic ice cores have been used to assess past bio-productivity of the southern ocean and the impact of El Nino events [*Legrand and Feniet-Saigne,* 1991] as well as to reconstruct past see ice extension [*Welch et al.,* 1993; *Curran et al.,* 2003]. However, the interpretation of MSA signals in ice cores is still ambiguous. This is due to the highly complex mechanisms controlling DMS emission from algae [*Andreae,* 1990; *Saltzman,* 1995; *Simó and Pedrós-Alió,* 1999; *Simó and Dachs*, 2002; *Toole and Siegel,* 2004], variable MSA yields from DMS photo-oxidation [*Ayers et al.,* 1996; *Koga and Tanaka,* 1999; *Gondwe et al.,* 2004], and finally post depositional losses and migration of MSA signals within annual firn layers [*Minikin et al.*, 1994; *Pasteur and Mulvaney* 2000; *Delmas et al.,* 2003; *Weller et al.,* 2004].

For a better understanding of non-sea salt sulfate (nss-SO_4^{2-}) and methane sulfonate (MS) records in central Antarctic ice cores in terms of atmospheric changes, investigating of their atmospheric concentrations of these compounds at the relevant ice core-drilling site is needed (e.g. in view of the present deep ice core drilling activities on Amundsenisen in the frame work of the European Project for Ice Coring in Antarctica (EPICA)). A basic motivation for aerosol studies is to elucidate whether the MS and biogenic sulfate signal at the drilling site is representative for the local polar South Atlantic or the sub polar Southern Ocean. Up to now, only very few and sporadic atmospheric measurements of sulfate and MS are available from continental Antarctica [*Tuncel et al.*, 1989; *de Mora et al.,* 1997; *Harder et al.,* 2000; *Arimoto et al.,* 2001 and 2004; *Udisti et al.,* 2004]. Here we present results from the first extensive aerosol-measuring program carried out during three summer campaigns at the EPICA drilling site in Dronning Maud Land (EDML, Kohnen Station). In evaluating the atmospheric variability of ionic aerosol species, we will focus on the Antarctic nss-SO_4^{2-} source apportionment and atmospheric sulfur transport to Kohnen. Based on a firn core retrieved at this site [*Traufetter et al.*, 2004], we address then the implication of our atmospheric findings on the interpretation of nss-SO_4^{2-} and MS profiles archived in firn and ice cores mainly with respect to the relevance of observed MS/nss-SO_4^{2-} ratios.

2. Measurement Techniques

2.1. Measurement Site and Meteorological Conditions

Fig. 1

Within the EPICA project an air chemistry program was conducted during 3 summer seasons at Kohnen Station, the deep drilling location in Dronning Maud Land (75°S, 0°E, 2892 m a.s.l., air pressure 672-675 hPa, Figure 1). The sampling campaigns cover the periods from 6 January to 6 February 2000 (EPICA V), from 11 January to 4 February 2001 (EPICA VI), and finally from 8 January to 11 February 2002 (EPICA VII) [*Piel,* 2004]. A relatively low snow accumulation rate of 71±21 kg m^{-2} yr^{-1} [*Oerter et al.,* 1999] and an annual mean temperature of –46°C characterize the sampling site. The mean wind speed and direction being about 4.6 m/s and 60°, respectively [*Reijmer*, 2001] characterize the glacio-meteorological condition of the sampling site. During the sampling periods, the temperature varied between -11°C and -42°C. In the present study, we rely on three dimensional five-day back trajectories calculated by the German Weather Service (Deutscher Wetterdienst, DWD) which are essentially based on the global model of the European Centre for Medium-Range Weather Forecasts (ECMWF).

During EPICA V, a battery driven aerosol sampler, supported by solar panels was set up, while during the following campaigns we used two specially designed line-powered samplers (ISAP® 1050, Schulze Automatisierungstechnik, Germany). The former sampler was equipped with a simple open-end filter holder, positioned face down about 2 m above ground, while the latter was operated with a PM_{10} filter holder mounted 2.2 m above the firn surface. One of the ISAP® 1050 samplers was provided with a small meteorological mast equipped with sensors for air pressure, wind velocity, wind direction and relative humidity. In order to minimize the impact of local pollution by vehicles and the base itself, the aerosol sampling experiment was set up about 300 m north-east of the main station. Because the main wind direction was within 60°±30° at >90% persistency, contamination from the base could be excluded for most of the time. The power supply for both ISAP® 1050 (2.5 kW) was provided by a cable from the main station, thus no fuel driven generator was operated in the immediate vicinity of the samplers. Contamination-free sampling was controlled by the permanently recorded wind velocity and wind direction. Potential impact of contamination, indicated by wind directions outside the 330° to 150° sector, and/or the wind velocities <1.0 m s^{-1} initiated an automatic instant interrupt of the sampling procedure, which was restarted after recurrence of clean air conditions.

2.2. Aerosol Sampling Methods and Analysis

During all three field campaigns, aerosol was sampled using a 2-stage filter system, consisting of a teflon and a nylon (Nylasorb) filter (all 1µm pore size) connected in series [*Piel,* 2004]. Roughly 40 m^3 (STP) of ambient air was probed over a typical collection period of 24 hours. The teflon filter collected all particulate compounds with efficiencies higher than 95% but allowed gaseous (acidic) species like HCl, HNO_3 to pass through to the nylon filter, where HCl and HNO_3 were collected with efficiencies of 70-80% and 90%, respectively. To investigate the amount of such acidic gases more accurately, we occasionally carried out with the same sampling system denuder experiments (eight samples collected from 8 Jan. to 9 Feb. 2002) during EPICA VII parallel to the above mentioned aerosol experiments. The denuder set-up consisted of two annular denuder tubes (ChemSpec company, USA) in series, followed by a teflon made cyclone (aerodynamic cut-off: 2.5 µm) and finally the commonly used teflon-nylon filter stack. The denuder tubes were coated with Na_2CO_3 (1 g Na_2CO_3 dissolved in 1 g glycerol, 50 ml milliQ-water, and 50 ml methanol). The so treated tubes were dried by a helium flow and subsequently capped and sealed in polythene bags. This coating trapped any acidic gas, such as HCl, HNO_3, and gaseous methane sulfonic acid (MSA) ahead of the filter stack. To achieve laminar flow conditions within the annular denuder, the airflow has to be reduced from 2 m^3 h^{-1} to 0.9 m^3 h^{-1} whereas the sampling period was increased to 2-3 days to improve the detection limit. For HCl and HNO_3 the denuder results agreed by about ±15% with the results from the nylon back-up filters of the coinciding aerosol filter samples, while for MSA the situation was different and will be discussed below.

Filters were pre-cleaned before arrival in Antarctica by successive washings in milliQ water (ie. 18.2 MΩ cm^{-1}), dried under vacuum, stored in airtight polyethylene (PE) beakers and finally sealed in polythene bags. After collection, the filters were placed directly into pre-cleaned, airtight sample vials, and were extracted and analysed using ion chromatography (IC) in our home laboratory in the Bremerhaven laboratory. Nylon filters were extracted with ≈20 ml milliQ water by soaking, shaking, followed by ultrasonic treatment for 3-5 minutes. Teflon filters were first wetted with isopropyl alcohol (less than 200 µl) and then extracted in the same way as the nylon filters. Blank determinations were performed regularly throughout the campaigns. In general, samples were analyzed for methane sulfonate (MS), Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+} by ion chromatographic (IC) analysis. For details concerning IC set up, accuracy and detection limit see *Göktas* [2002] and *Piel* [2004]. Extracts from denuder samples were highly loaded with carbonate which has to be removed by ion exchange cartridges (on-guard-H® cartridges, Dionex) to attain an appropriate analytical performance allowing these samples to be analyzed for anions only. 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 approximately ±10% to ±15% for the main components MS, Cl^-, NO_3^-, SO_4^{2-}, Na^+, and between ±20% and ±30% for the minor species NH_4^+, K^+, Mg^{2+}, and Ca^{2+}. The accuracy of the HCl, HNO_3 and MSA ascertainment from the denuder experiments was ±20%, ±25%, and ±40%, respectively.

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}), using Na^+ as sea salt reference species and the sulfate to sodium ratio in bulk sea water of $\alpha_{sulfate}$ = 0.252, i.e.:

$$(\text{nss-}SO_4^{2-}) = (SO_4^{2-}) - \alpha_{sulfate} \times (Na^+) \qquad (1)$$

On average, the sea salt sulfate contribution was only about 8% of the total sulfate concentrations. Due to the fact that our campaigns took place in austral summer and because of generally low sea salt contribution we did not consider the impact of sea salt fractionation by frost flower formation leading to significantly lower $\alpha_{sulfate}$ value (*Wagenbach et al.* [1998] and *Rankin et al.* [2000]). In a similar way the non-sea salt contribution of the cations Mg^{2+}, K^+, and Ca^{2+} was calculated using equation (1) with the standard mean ocean water (smow) ratios α_{Mg} =0.1206, α_K = 0.03595, and α_{Ca} = 0.03791.

The possibility of exchange reactions like mobilization of particle bound nitrate, chloride and potentially MS by sulfuric acid aerosol into the corresponding volatile acids must be considered when making filter measurements:

$$H^+ + NO_3^- \ (Cl^-, CH_3SO_3^-) \ \text{->} \ HNO_3 \ (HCl, CH_3SO_3H)$$

We found for all samples collected via the denuder/filter stack combination, that within the denoted uncertainties essentially no HNO_3, HCl, or MSA appeared on the nylon back up filters, indicating that the exchange reaction was not a problem for our samples. Additionally, the impact of a further potential exchange reaction (with $A^- = HSO_4^-$, NO_3^-, MS):

$$NaCl\ (s) + HA\ (g) \rightarrow NaA\ (s) + HCl\ (g)$$

could not be observed, most probably due to the relatively minor sea salt fraction(< 8% by mass) present in our samples.

In addition, high volume filters were independently sampled at a typical resolution of 2-3 days as dedicated to the study of air firn transfer of the cosmogenic and terrigenic radioisotopes ^{7}Be, ^{10}Be ^{36}Cl and ^{210}Pb, respectively. In the present work, we use the atmospheric ^{7}Be data to identify at DML the varying influence of air masses from the higher troposphere or lower stratosphere, respectively. ^{7}Be- analyses were performed at the University Heidelberg by γ-spectroscopy along with IC-analyses of the ion content following the procedure given by *Wagenbach et al.* [1988] for aerosol filters from the Neumayer Station. Mainly depending on the sampled air volume and the decay time before analyses, relative uncertainties range from 5-15% for ^{7}Be, whereas the analytical sulfate and MS uncertainties remained typically below 10%. An identical high volume sampling and analyses technique has been deployed during concurrent summer campaigns at the Antarctic Dome C drilling site, from which mean nss-SO_4^{2-} and MS values are reported here for inter-site comparison.

3. Results

3.1. Overview on the chemical aerosol composition of at Kohnen Station

First, we present a brief synopsis of our aerosol measurements performed during three summer campaigns at Kohnen Station. Table 1 lists the chemical composition of the aerosol samples. For each campaign the mean values ± standard deviation (std) of the corresponding ionic concentrations are given. Obviously, nss-SO_4^{2-} accounted for the main component of the aerosol mass (70%), followed by MS (12.9%), nitrate (7.4%), and NH_4^+ (2.8%). Due to the continental character of the sampling site, the sea salt contribution (i.e. the sum of Cl^-, Na^+,

Tab. 1

sea salt-K^+, -Mg^{2+}, and -Ca^{2+}), which constitutes nearly half of the total aerosol mass at coastal stations like Halley, Dumont d'Urville and NM, [*Wagenbach et al.,* 1998] contributed barely 8% to the total aerosol mass at Kohnen. The high acidity of the aerosol with H^+ accounting for about 77±4% of the total cation equivalents (Table 1) was found to be a characteristic feature. The H^+ concentration was calculated from the measured ion balance assuming that the difference between the anion and the cation equivalents corresponds roughly to the H^+ equivalents ($[\text{ion}]_e$ is given in μeq g^{-1}) as:

$$[H^+]_e = [MSA^-]_e + [Cl^-]_e + [NO_3^-]_e + [SO_4^{2-}]_e - [Na^+]_e - [NH_4^+]_e - [K^+]_e - [Mg^{2+}]_e - [Ca^{2+}]_e$$

Accordingly the results from the Nylon back-up filters and the denuder samples revealed that between 33% and 76% of the total nitrate and between 71% and 88% of total chloride were present as free acids HCl and HNO_3, respectively. The fractions of non-sea salt Mg^{2+}, -K^+ and -Ca^{2+} were roughly about 50% of their total amounts, indicating a significant terrestrial origin. However, absolute concentrations of these cations were often close to the analytical detection limit and clearly constituted only a minor fraction of the total aerosol mass.

3.2. Methane Sulfonate and Nss-Sulfate Data Presentation

Figures 2 to 4 show nss-SO_4^{2-} and MS concentrations as well as the molar ratio MS/nss-SO_4^{2-} (β_{MS}) derived from teflon/nylon filter samples demonstrating their high variability with standard deviations in the order of the mean values (see also Table 1). Nevertheless, during EPICA VI atmospheric nss-SO_4^{2-} and MS levels where about 50-70% lower compared to preceding and subsequent campaign. This inter annual variability was also evident in our data from Dome C and Neumayer measured during January 2000, 2001 and 2002. The hatched area in Figure 4 marks an extraordinary meteorological situation from 10-11 January 2002. During this period, a distinct low-pressure system entered central Dronning Maud Land asso-

Fig. 2

Fig. 3

Fig. 4

ciated with a heavy snowstorm and the highest ever-measured temperatures at this site of -11°C.

MS is virtually exclusively of marine biogenic origin, while nss-SO_4^{2-} can also have volcanic, stratospheric or terrestrial sources. In our case, the strong linear correlation between MS and nss-SO_4^{2-} (regression coefficient $r^2 = 0.84$, Figure 5) would point to a common major (i.e. biogenic) source for both sulfur components. Because neither MS nor nss-SO_4^{2-} can be assumed as independent variable, a bivariate regression is necessary [*Ayers,* 2001]. We used the so-called reduced major axis (RMA) regression as recommended by *Davis* [1986]. At first glance, the y-axis intercept $\varepsilon_{sulfate}$ of 141±15 ng m^{-3} suggests a significant fraction of background, non-biogenic nss-SO_4^{2-}. In fact, β_{MS} was strongly dependent on the MS concentration, showing higher values at higher MS concentrations (Figure 5b). An exponential fit through the data yielded the regression function ß$_{MS}$ = 0.027x$[MS]^{0.47}$. Interestingly, MS and nss-SO_4^{2-} data from Neumayer for the month January combined over the period 1983-2003 also showed a distinct dependency of ß$_{MS}$ on the MS concentration with an empirical regression function ß$_{MS}$(NM) = 0.064x$[MS]^{0.37}$.

Fig.5

In addition, our denuder experiments revealed that an apparently constant amount of MS corresponding to 5.5±2.9 ng m^{-3} (i.e. 4%-52% of the total MS signal) could be found in the extracts of the denuder tubes, indicating the existence of gaseous MSA in the atmosphere. Apart from the volatile acids HNO_3 and HCl, we detected no other components in these extracts, supporting the assumption that particle deposition and thus fake MSA on the denuder walls should be negligible. In contrast to HNO_3 and HCl, however, we could not observe MSA on the nylon back-up filters of our teflon-nylon filter combinations.

4. Discussion

4.1. MS and nss-SO_4^{2-} at Coastal and Continental Antarctic Sites

Comparing our measured MS and nss-SO_4^{2-} concentrations with values typically found at coastal and continental Antarctic sites during summer, the following picture emerges. Generally, nss-SO_4^{2-} levels observed at Kohnen were comparable to coastal stations like NM, Mawson, Palmer, Marsh, and Dumont d'Urville (a detailed representation can be found in *Minikin et al.,* [1998]). From Neumayer (NM), a continuous MS and nss-SO_4^{2-} record is available from 1983-1993 in 10-14 days resolution and from 1994 on in weekly resolution. At this site the January mean of the nss-SO_4^{2-} concentration (±std) for the years 1983-2002 was 385±170 ng m^{-3}. Table 2 presents a summary of aerosol MS and nss-SO_4^{2-} concentrations measured so far in continental Antarctica. Nss-SO_4^{2-} concentrations found at South Pole and Dome C during austral summer appear not consistent showing values roughly comparable to EDML [*Harder et al.,* 2000; *Arimoto et al.* 2001], or significantly lower [*Tuncel et al.,* 1989; *Arimoto et al.,* 2004; *Udisti et al.,* 2004]. The latter findings compare to results from the East Antarctic Plateau (78°S, 139°E) during summer by *de Mora et al.* [1997]. Concerning MS, coastal stations showed again comparable concentrations to Kohnen during summer, except NM where the January MS concentration (±std) for the years 1983-2002 was as high as 165±112 ng m^{-3}. In contrast, conspicuously lower MS levels around 7-31 ng m^{-3} were generally observed at all sites in continental Antarctica [*de Mora et al.,* 1997; *Arimoto et al.,* 2001 and 2004; *Udisti et al.*, 2004] (Table 2).

Tab. 2

Figure 6 shows the frequency distribution of MS and nss-SO_4^{2-} concentrations measured at Kohnen (n = 98 samples) and in January at NM for the years 1983-2002 (n = 66). Obviously, the MS concentration distribution at NM appears much broader with a mean at higher values, while the results for nss-SO_4^{2-} look similar. Furthermore for NM the relative standard deviation σ_{rel} = std/mean is higher for MS (σ_{rel}(MS) = 0.7) compared to nss-SO_4^{2-} ($\sigma_{rel}(SO_4^{2-})$ =

Fig.6

0.44) but analogous at Kohnen (σ_{rel}(MS) = 0.77, and $\sigma_{rel}(SO_4^{2-})$ = 0.66). According to the empirical relation between atmospheric lifetime and σ_{rel} by *Junge* [1974], this finding indicates a correspondingly shorter atmospheric residence time for MS in the polar marine troposphere during austral summer. A comparison of nss-SO_4^{2-} and MS concentrations measured simultaneously at NM and at Kohnen revealed that a linear regression, which was based on weekly averages corresponding to the sampling period at NM, explained only about 26% of the observed variance for both compounds. As expected, a correlation on this time scale is barely significant, but altogether at least the nss-SO_4^{2-} budget (i.e. mean and scatter of the concentrations) at Kohnen during summer was rather similar to coastal than to central Antarctic sites. Interestingly, our limited data set showed a consistent inter annual variability of MS and nss-SO_4^{2-} summer levels at Kohnen, Dome C and NM for the years 2000, 2001 and 2002 (Figure 7). We infer that in this case, transport processes could hardly be responsible for the low sulfur levels observed during austral summer 2001, but most probably the lower strength of the marine biogenic source of the Southern Ocean. However, one has to keep in mind that aerosol measurements from continental Antarctica are still extremely scarce and mostly limited to summer. Consequently, our implications are preliminary and need verification particularly by year-round measurements.

Fig. 7

4.2. Origin of Atmospheric Sulfur at Kohnen Station

4.2.1. Air mass history

In the following section, we evaluate the striking variability of the recorded nss-SO_4^{2-} and MS time series using the available 5-day back trajectory analyses. The most outstanding feature in these records occurred between 1 and 4 February 2001 and particularly between 10 and 15 January 2002. In the latter case both, the nss-SO_4^{2-} and MS concentrations increased by more than an order of magnitude within two days. These elevated MS and nss-SO_4^{2-} levels persisted for about two days and covered around 27% of the total atmospheric MS and 17% of the nss- SO_4^{2-} budget observed during EPICA VII. A vigorous frontal activity preceded the event in January 2002. Trajectory analyses document an air masses intrusion from the marine boundary layer (Figure 8). Although one might expect high biogenic sulfur levels in such air masses during summer, efficient removal of aerosols by wet deposition en route and below-cloud precipitation scavenging above the measuring site were the most plausible reasons for the observed low MS and nss-SO_4^{2-} concentrations during this event. After passage of the frontal system, the source region of the air masses changed to the free troposphere above continental Antarctica (Figure 8) accompanied by a coeval increase of MS and nss-SO_4^{2-} concentrations. Concerning the MS and nss-SO_4^{2-} concentrations peak in 2001, a distinct change of air mass origin from marine to continental regions was also indicated, though no preceding passage of a frontal system happened. Moreover, a specific examination of all five days back trajectories calculated for EPICA VII revealed that in case of MS concentrations above the mean value of 74.5 ng m^{-3}, air mass origins were largely within the free troposphere above the Antarctic continent (pressure level <700 hPa or at least 80 hPa lower than the corresponding surface pressure; Figure 9a). Lower MS concentration were typically associated with air mass advection from the marine boundary layer (pressure level >750 hPa, Figure 9b). In addition, we calculated covariance ellipses of the corresponding trajectory positions (longitude and latitude) five and three days before arrival at Kohnen (Figure 9c and 9d) according to *Kottmeier and Fay* [1998]. Covariance ellipses are based on a two dimensional normal distribution of the trajectory longitudinal (y-coordinate) and latitudinal (x-coordinate) positions. The semi-major axes describe the spread of the coordinates in North-South (standard deviation σ_x) and East-West (σ_y) direction around a common mean position. The angle ϕ between the major axis and the x-axis is defined by the covariance coefficient ($\rho_{xy} = (\sigma_{xy}/(\sigma_x\sigma_y)) = \tan\phi$). For a two-dimensional normal distribution of the coordinates, the area enclosed by the

Fig. 8

Fig. 9

covariance ellipses comprises 68% of the data (in our case about 50-60% of the respecting trajectory ensemble). Concerning EPICA V and VI an analogous analysis turned out to be barely conclusive, except during the described event in early February 2001. At least for EPICA VI we assign the lacking correlation to relatively constant and low sulfur levels. Nevertheless, our evaluation suggests a rather effective long-range transport mechanism of sulfur compounds via the free troposphere to Dronning Maud Land. This finding is consistent with results from the SCATE campaign conducted at Palmer Station in austral summer 1993/1994: Photo-oxidation of a large part of algae derived DMS occurred in the so-called buffer layer just above the marine boundary layer [*Davis et al.* 1998¸ *Jefferson et al.,* 1998]. Low aerosol concentrations within the buffer layer favour gas phase reaction pathways of the DMS photo-oxidation mechanism, decrease depositional removal of the reaction products [*Davis et al.*, 1998; *Jefferson et al.,* 1998], and consequently potentiate effective long range transport of reaction products like DMSO and SO_2.

Nevertheless, the ultimate source region of biogenic sulfur is the marine boundary layer and the observed correlation of high MS concentrations with 5 days back trajectory originating in the continental free troposphere would indicate a long-range transport to DML via the free troposphere. The ^{7}Be concentrations (see Figures 2-4) which are expected to be strongly enhanced in higher tropospheric or lower stratospheric air masses, exhibited at Kohnen a significant anti-correlation with MS, nss-SO_4^{2-} and $ß_{MS}$ values (correlation coefficients -0.44, -0.37, -0.52, respectively). This may substantiate the marine boundary layer properties of air parcels typically made up by relatively high biogenic sulfur and low ^{7}Be burdens. However, during the frontal passage of January 10-12, (displayed in Figure 4) trajectory evaluations assigned the origin of the associated air masses to the coastal marine boundary layer, but surprisingly, high ^{7}Be and exceptionally low biogenic sulfur levels prevailed during that episode at DML. This observation seems to contradict the above general picture, but during such frontal passages, intense small-scale uplifts of air masses are typical, which may not be adequately described by trajectory calculations. Thus, caution has to be taken when deriving air mass histories for this site by back trajectories during such extreme general weather situations.

4.2.2. Gaseous precursors and local MS and sulfate production.

Davis et al. [1998] estimated the atmospheric residence time of SO_2 in the marine boundary layer during summer to be around 8-24 hours, mostly due to removal by heterogeneous reactions. Within the free troposphere, the reaction OH + SO_2 is most probably the only relevant SO_2 loss process. Assuming an OH concentration of around 10^5 cm^{-3} and a reaction rate coefficient $k_0[M] = 1.2\times10^{-11}$ cm^3 s^{-1} (taken from *Sander et al.* [2003] for p = 680 mbar and T = 243 K) photochemical lifetime of SO_2 would increase to 8-9 days. OH-measurements at South Pole indicate that within a flat inversion layer, OH concentrations typically reached average values around 2×10^6 cm^{-3} during polar day [*Mauldin III et al.*, 2001 and 2004]. Consequently, down mixing of SO_2 from the free troposphere to the inversion layer above continental Antarctica could cause a photo-oxidation of SO_2 within less than a day. Hence, efficient long-range transport of SO_2 via the free troposphere and subsequent rapid photo-oxidation within the continental inversion layer might be a potential in situ sulfate source for central Antarctica. Observations by *Mauldin III et al.* [2004] indicated the occurrence of such processes during ISCAT 2000. Nevertheless, this campaign revealed that locally generated H_2SO_4 did not contribute significantly to nss-SO_4^{2-}. Unfortunately, SO_2 measurements during ISCAT 2000 were equivocal, suggesting values around 1 pptv [*Huey et al.*, 2004]. At Dumont d’Urville about 1.2±0.9 nmol m^{-3} were observed during January/February [*Jourdain and Legrand*, 2001], which would potentially correspond to 115±90 ng m^{-3} sulfate.

In addition, investigations at Dumont d'Urville revealed that air masses from central Antarctica, advected by catabatic winds showed enhanced concentrations of dimethyl sulfoxide (DMSO), an intermediate of the gas phase photo-oxidation of DMS [*Jourdain and Legrand,* 2001; *Legrand et al.,* 2001]. As mentioned above, we found gas phase $(MSA)_g$ concentrations of around 5.5±2.9 ng m^{-3} (mixing ratio 1.3±0.7 parts per 10^{12} by volume, pptv) in our denuder experiments. Compared to $(MSA)_g$ mixing ratios obtained by chemical ionization mass spectrometry during the SCATE (around 0.04 pptv, [*Jefferson et al.,* 1998]) and both ISCAT campaigns (around 0.005 pptv [*Mauldin III et al.,* 2001 and 2004]), our value was about two orders of magnitude higher. Again, results from ISCAT 2000 indicated that locally generated MSA did not contribute significantly to particulate MS [*Mauldin et al.,* 2004]. However, in the marine troposphere over the tropical/subtropical Pacific $(MSA)_g$ mixing ratios up to 4 pptv could be detected [*Jefferson et al.,* 1998; *Mauldin III et al.,* 2003]. Although there were no indications of possible experimental problems in the denuder experiments, our preliminary $(MSA)_g$ results are of restricted significance and clearly need farther verification.

Furthermore, part of MS budget could potentially be supplied by re-emitted $(MSA)_g$ from the firn layer. According to *Weller et al.* [2004], about 51%, i.e. 9.6±6 ng g^{-1} of the once deposited MS was lost at this site by MSA emissions from all annual snow layers younger than roughly about 5 years. In an equivalent manner, we can assume that all the loss occurred in the uppermost annual layer within one year. Following this approach and using an annual snow accumulation of 71 kg m^{-2} [*Oerter et al.,* 1999], yielded a MSA emission flux $\Phi_{em}(MS)$ of $(22\pm12)\times10^{-3}$ ng m^{-2} s^{-1}. *Bergin et al.* [1995] measured a dry deposition velocity of 0.024±0.023 cm s^{-1} for MS at Summit (Greenland) during summer. With an overall mean MS concentration of 45±37 ng m^{-3} at Kohnen during austral summer, the dry deposition flux of MS, $\Phi_{dry}(MS)$, should be around $(10.8\pm10)\times10^{-3}$ ng m^{-2} s^{-1}, comparable to the estimated emission flux $\Phi_{em}(MS)$. Consequently, recycled atmospheric MS by MSA emissions from the firn layer could potentially account for a significant fraction of the atmospheric MS budget during summer.

4.3. Non-Biogenic Sulfur and Variability of MS/nss-Sulfate Ratios

In assessing the amount and nature of non-DMS derived nss-SO_4^{2-} in Antarctica, *Minikin et al.* [1998] used the radioisotopes ^{10}Be, ^{7}Be, and ^{210}Pb, as well as crustal Mn along with nss-SO_4^{2-} in the coastal aerosol body at NM-Station. Thereby they arrived at a summer background level of around 25 ng m^{-3}, which was dominated by long-range transport of continental nss-SO_4^{2-}, whereas stratospheric air mass subsidence contributed only by 2 ng m^{-3}. Since the radioisotope levels at Kohnen were found to be not much different from typical summer values at NM (though being slightly higher), we may expect also some tens ng m^{-3} of background nss-SO_4^{2-} at DML. Unfortunately, the impact of non-eruptive volcanic sulfate from the only currently active Antarctic volcano Mt. Erebus remains highly uncertain, although a minor contribution corresponding to 10-30 ng m^{-3} has been estimated [*Radke,* 1982; *Rose et al.,* 1985; *Chuang et al.,* 1986]. From ^{210}Po tracer measurements *Arimoto et al.* [2004] cautiously suggested that Mt. Erebus accounted for about 15-30% of nss-SO_4^{2-} at South Pole, but emphasized the large uncertainties of this estimate. Thus, unless the Mt. Erebus contribution can be safely quantified, the non-DMS derived nss-SO_4^{2-} background of some tens ng m^{-3} expected for DML should be regarded as a lower limit. As already stated, β_{MS} is strongly dependent on the MS concentration (Figure 5b) and a simple appraisal of non-biogenic nss-SO_4^{2-} contribution by extrapolating a linear regression of the MS versus. nss-SO_4^{2-} data as shown in Figure 5a is inappropriate and would result in a unrealistically high non-biogenic nss-SO_4^{2-} values of around 140 ng m^{-3}.

MS/nss-sulfate ratios >0.2 (typically between 0.3 and 0.4) are characteristic for coastal Antarctic Stations during January (a detailed survey is given by *Legrand and Pasteur,* [1998] and recently *Gondwe et al.,* [2004] presented a global analysis), while results from field measurements in continental Antarctica manifested values below 0.2 [*Arimoto et al.,* 2004; *de Mora et al.,* 1997]. Generally, the correlation between MS and nss-SO_4^{2-} seems only significant for the summer months at coastal stations [*Legrand and Pasteur,* 1998] when Antarctic sulfur budget becomes dominated by the biogenic source and an uncertain correction for fractionation of sea salt sulfate by frost flower formation [*Wagenbach et al.,* 1998] is not necessary. There are at least two main reasons causing the observed high variability and partly poor correlation between MS and nss-SO_4^{2-}: Temperature dependence of β_{MS} and fractionation of MS and nss-SO_4^{2-} by chemical and deposition processes.

Previous investigations suggested an empirical relation between temperature and β_{MS} [*Bates et al.,* 1992; *Hewitt and Davison,* 1997] with higher β_{MS} values at lower temperature. Modelling studies demonstrated that the temperature dependence of the reaction rate coefficients of the complex gas phase photo-oxidation mechanism of DMS could partly be responsible for the observed empirical relation [*Ayers et al.,* 1996; *Koga and Tanaka,* 1999]. This simple temperature - β_{MS} relation may hold for sites where local MS and nss-SO_4^{2-} production by photo-oxidation dominates over advection of these compounds. The seasonality of β_{MS} measured in the southern Indian Ocean [*Baboukas et al.,* 2004] and at coastal Antarctic stations [*Legrand and Pasteur,* 1998], however, is clearly reverse to the predicted temperature - β_{MS} relation. For coastal Antarctica this indicates that during polar summer the dominant source region should be south of 60°S, while during spring and fall long range transport from warmer areas north of 50°S prevail [*Legrand and Pasteur,* 1998]. For Kohnen this would mean that the sub polar Southern Ocean north of 60°S should be the dominant source region even during summer.

However, a possible fractionation of MS and nss-SO_4^{2-} by deposition processes may complicate the situation. Although MS and nss-SO_4^{2-} showed a similar mass size distribution in coastal Antarctica [*Teinilä et al.,* 2000; *Rankin and Wolff,* 2003], higher MS/nss-SO_4^{2-} ratios were typically found in the coarse mode [*Berresheim et al.,* 1998; *Teinilä et al.,* 2000; *Rankin and Wolff,* 2003], implying a preferred loss of MS by dry deposition during long-range transport. In particular, the results gained from the SCATE campaign indicated a different impact of gas phase and liquid phase reaction mechanisms within the marine boundary layer and the buffer layer on β_{MS} [*Davis et al.,* 1998; *Jefferson et al.,* 1998]. Finally, as suggested before, part of the nss-SO_4^{2-} signal in summertime continental Antarctica might be the result of SO_2 photo-oxidation within the inversion layer. This process would entail low β_{MS} values, given that MSA and its precursors are less efficiently transported into continental Antarctica.

Obviously, β_{MS} is not a conservative factor as already pointed out by *Legrand and Pasteur* [1998]. Consequently, neither the amount of non-biogenic nss-SO_4^{2-} nor the source region of biogenic sulfur can be reliably derived from MSA/nss-SO_4^{2-} relation. In case of Dumont d'Urville and Vostok, recent atmospheric circulation model results based on the method of tracer retro-transport revealed that the prevailing meridional origin of MS and nss-SO_4^{2-} should be between 55°-60°S [*Cosme et al.,* 2005], consistent with our finding. However, similar model efforts would be necessary to clarify the main source region of biogenic sulfur for EDML.

4.4. Implication for Interpretation of MS and nss-SO_4^{2-} Signals in Firn Cores

In this chapter, we will briefly discuss our findings along with results derived from firn core B32-DML05 we retrieved at this site in the year 2000. This core has a total length of about 150 m and covers the period from 2000 to 165 AD in annual resolution. The upper section of the core (until 1951 AD) was actually sampled in sub-annual resolution. *Göktas et al.* [2002]

and *Traufetter et al.* [2004] thoroughly described the glacio-chemical characterization of the core as well as annual accumulation rates, dating and subtraction of volcanic sulfate signals. In contrast to aerosol data obtained during austral summer, there was virtually no correlation between MS and nss-SO_4^{2-} (r_{cor} = 0.08) in agreement with results from the East Antarctic Plateau [*de Mora et al.,* 1997]. Again, $ß_{MS}$ was strongly dependent on the MS concentration (linear regression r^2 = 0.44, Figure 10).

Fig. 10

Apart from depositional and post-depositional processes, which are described by *Göktas et al.* [2002], *Traufetter et al.* [2004], and *Weller et al,* [2004] for this site, the seasonality of MS and sulfate deposition can be asserted for the lack of correlation between MS and nss-SO_4^{2-} in the firn core. Results from a high-resolution snow pit excavated at Kohnen in 2000 revealed that MS and sulfate concentration maxima frequently occurred in late summer/fall [*Göktas et al.,* 2002]. We cautiously conclude that MS and nss-SO_4^{2-} profiles retrieved from ice cores drilled in Dronning Maud Land do not necessarily represent typical summer values and document the importance of long-range transport from sub-polar oceanic regions to this site. Thus, lacking correlation between MS and nss-SO_4^{2-} is probably the result of depositional processes as well as fractionation during long-range transport and not an indication for the prominence of non-biogenic sulfate.

5. Conclusion

Due to the lack of regional sources, the sulfur budget at Kohnen is entirely dominated by long-range transport of photo-oxidation products of DMS from marine areas and background non-biogenic sulfate. This is in contrast to the situation typical for coastal Antarctic stations, where at least during austral summer regional sources become more relevant. Our aerosol measurements carried out for the first time at Kohnen showed the consequences of this condition. First, MS and nss-SO_4^{2-} concentrations and their variability were virtually comparable to coastal stations and thus documented an efficient long-range transport to Kohnen, which is in strong contrast to sea salt compounds. We conclude that different transport mechanisms to Kohnen and different photo-oxidation processes of the corresponding precursors en route caused the variability MS and nss-SO_4^{2-} concentrations as well as the variability of β_{MS}. High MS concentrations were typically associated with elevated MS/nss-SO_4^{2-} ratios and air mass origins from the free troposphere over continental Antarctica. Their ultimate source region was the marine boundary layer, as farther supported by the overall anti-correlation between ^{7}Be and MS or nss-SO_4^{2-}. We speculate that in these cases, DMS photo-oxidation products were most probably immediately lifted above the buffer layer and efficiently advected via the free troposphere to continental Antarctica. Vice versa, low values of β_{MS} were typically associated with low MS and nss-SO_4^{2-} concentrations and advection of air masses within the marine boundary layer, where depositional removal dominated. From radionuclide measurements we infer for Kohnen during summer a non-biogenic nss-SO_4^{2-} contingent of some tens ng m^{-3} with a stratospheric contribution of about 2 ng m^{-3}.

We strongly point out that caution has to be taken when using MS or nss-SO_4^{2-} concentration profiles from ice cores drilled at this site as proxies for marine bio-productivity. Atmospheric transport efficiency of the compounds as well as seasonal and annual variations in snow accumulation and post depositional processes most probably dominate the concentration variability archived in firn and ice at this site. Even the seasonality of sulfur deposition is so far not yet established. We emphasize the need for long-term year-round aerosol and fresh snow measurements at the drilling site to clarify the seasonality of sulfur deposition, to examine whether the inter-annual variability of the compounds in aerosol are finally mirrored in firn. To meet this aim, we installed an automated aerosol sampler for year-round measurements at Kohnen Station.

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Table 1. Summary of the ionic composition of the aerosol measured during three summer campaigns at Kohnen Station. Atmospheric concentrations (±std) refer to standard pressure (1013 hPa) and 273.16K. Total-NO_3^- and total-Cl^- are the sum of the concentrations from the teflon and nylon filter samples.

Ionic component	EPICA V	EPICA VI	EPICA VII
	6 Jan. to 6 Feb. 2000	11 Jan. to 4 Feb. 2001	8 Jan. to 11 Feb. 2002
SO_4^{2-} [ng m^{-3}]	353±100	164±150	320±250
nss-SO_4^{2-}	99.2%	99.6%	99.5%
MS [ng m^{-3}]	59.0±36	19.0±12	74.5±80
MS/nss-SO_4^{2-}	0.156±0.06	0.103±0.080	0.203±0.08
total-NO_3^- [ng m^{-3}]	29.3±18	52.7±26	20.3±10
HNO_3 [ng m^{-3}]	22.2±18	17.6±15	10.5±6.3
total-Cl^- [ng m^{-3}]	28.3±21	4.3±3.1	9.7±7.4
HCl [ng m^{-3}]	24.9±16	3.7±1.8	6.9±4.3
Na^+ [ng m^{-3}]	12.0±6.7	2.4±1.9	5.9±5.3
Cl^-/Na^+	2.6±1.8	2.6±1.5	1.6±0.95
NH_4^+ [ng m^{-3}]	10.5±7.8	14.8±9.8	9.2±9.3
Mg^{2+} [ng m^{-3}]	1.1±0.5	0.5±0.5	1.7±1.7
nss-Mg^{2+}	6.4%	41.5%	48.2%
K^+ [ng m^{-3}]	2.1±0.8	0.5±0.3	0.4±0.3
nss-K^+	68%	73%	39.4%
Ca^{2+} [ng m^{-3}]	2.4±2.5	2.1±1.9	3.8±4
nss-Ca^{2+}	81%	96%	87%
H^+	81.5%	72.8%	76.9%

Table 2. Compendium of mean aerosol nss-SO_4^{2-} and MS concentrations (range in parentheses) measured in continental Antarctica.

site	MS [ng m^{-3}]	nss-SO_4^{2-} [ng m^{-3}]	β_{MS} = MS/nss-SO_4^{2-}	month/season	reference
EDML	59 (13-168)	353 (198-631)	0.156 (0.060-0.270)	Jan./Feb. 2000	
(75°S, 0°E)	19 (4-108)	164 (117-247)	0.103 (0.039-0.393)	Jan./Feb. 2001	*this work*
	74.5 (14-362)	320 (130-1150)	0.203 (0.078-0.460)	Jan./Feb. 2002	
South Pole	4.4 (1-12)	98 (40-150)	0.08	Nov. 2000/Jan. 2001	*Arimoto et al.*, 2004
	12 (6.8-23)	212 (140-300)	0.059	Dec.1998/Jan.1999	*Arimoto et al.*, 2001
	-	50-280	-	Nov./Dec. 1992	*Harder et al.*, 2000
	-	2-50	-	Jul.-Nov. 1992	*Harder et al.*, 2000
	-	124±108[a]	-	summer 1979-83[b]	*Tuncel et al.*, 1989
	-	18.8±11[a]	-	winter 1979-83[b]	*Tuncel et al.*, 1989
East Antarctic Plateau	21 (8.6-41.3)	88 (64.7-129)	0.187 (0.127-0.325)	Dec.1990/Jan.1991	*De Mora et al.*, 1997
(78°S, 139°E)					
Dome C	28.1 (11.5-107)	246 (182-459)	0.094 (0.048-0.234)	Jan.2000	*this work*
(75°S, 123°E)	7.1 (3.3-15.7)	148 (108-177)	0.052 (0.024-0.144)	Dec.2000/Jan.2001	*this work*
	46 (4-204)	306 (169-207)	0.15 (0.022-0.525)	Dec.2001/Jan.2002	*this work*
	3.1 (1.6-8.5)	110.3 (69.1-207)	0.028	Dec.2000/Jan.2001	*Udisti et al.*, 2004

[a] Data (±std) corrected for sea salt contribution according to equation (1), for winter $\alpha_{sulfate}$ = 0.07 was taken [*Wagenbach et al.*, 1998].

[b] average summer and winter values, respectively, are given for the sampling period 1979-1983.

FIGURES

Figure 1: Area of investigation in Dronning Maud Land, Antarctica.

Figure 2: MS (diamonds) and nss-SO_4^{2-} (circles) concentrations measured during EPICA V along with the calculated MS/nss-SO_4^{2-} ratio β_{MS} (triangles, top trace) and ^{7}Be activity (bold grey line, top trace). Error bars represent the estimated analytical accuracy; grey lines represent cubic spline fits through the data to guide the eye.

Figure 3: Same diagram as shown in Figure 2 for EPICA VI.

Figure 4: Same diagram as shown in Figure 2 for EPICA VII. The hatched area marks the period influenced by the passage of an intense low-pressure system.

Figure 5: Correlation of MS with nss-SO_4^{2-} concentrations (a) and MS versus MS/nss-SO_4^{2-} ratio β_{MS} (b). Results from all three summer campaign are combined (m = slope, b = intercept from RMA-regression). The line in (b) is an exponential fit with the given parameters.

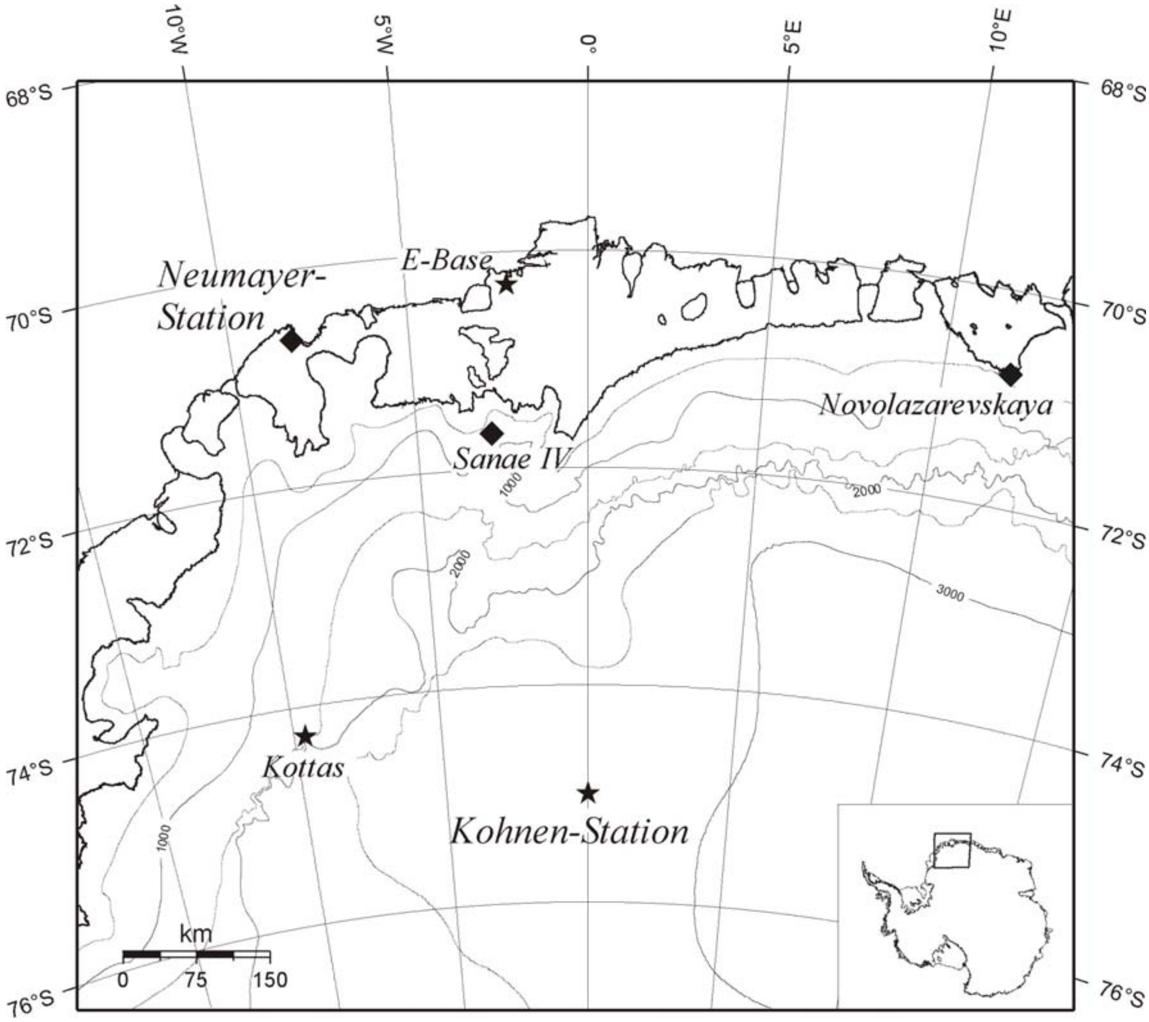
Figure 6: Frequency distribution of the measured MS (a) and nss-SO_4^{2-} (b) concentrations. Grey bars represent NM data, open bars the results from Kohnen. The drawn lines are fitted lognormal probability density functions (pdf) to the corresponding data sets; in (b) the hatched line represents the fit for the Kohnen data. Parameters for the pdf are: $\mu_{MSA} = 129$, $\sigma_{MSA} = 102$ for NM; $\mu_{MSA} = 33$, $\sigma_{MSA} = 32$ for Kohnen; $\mu_{sulfate} = 334$, $\sigma_{sulfate} = 230$ for NM; $\mu_{sulfate} = 250$, $\sigma_{sulfate} = 116$ for Kohnen (μ and σ are mean and standard deviation for the lognormal pdf).

Figure 7: Notched box plots of the MS and nss-SO_4^{2-} concentrations measured during January and February at Kohnen, Neumayer, and Dome C. 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.

Figure 8: Surface 5-day back trajectories during passage of the low-pressure system (arrival date of the air mass at Kohnen: 10 January 2002, (a), 11 January 2002, (b)) and during the nss-SO_4^{2-} and MS peak at 14 January 2002 (arrival time at Kohnen: 00:00, (c), 12:00, (d)). The pressure level of the trajectories arrived at Kohnen was between 670 and 650 hPa.

Figure 9: Origin of surface 5-day back trajectories during EPICA VII representative for MS levels above 74.5 ng m^{-3}, n=60 (a) and below 74.5 ng m^{-3}, n=150 (b). Also shown are the corresponding mean trajectories covariance ellipses (c) and (d), relating to air mass origin five days (plain) and three days (grey) before arrival at Kohnen.

Figure 10: MS versus MS/ nss-SO_4^{2-} ratio β_{MS} measured in firn core B32-DML05.



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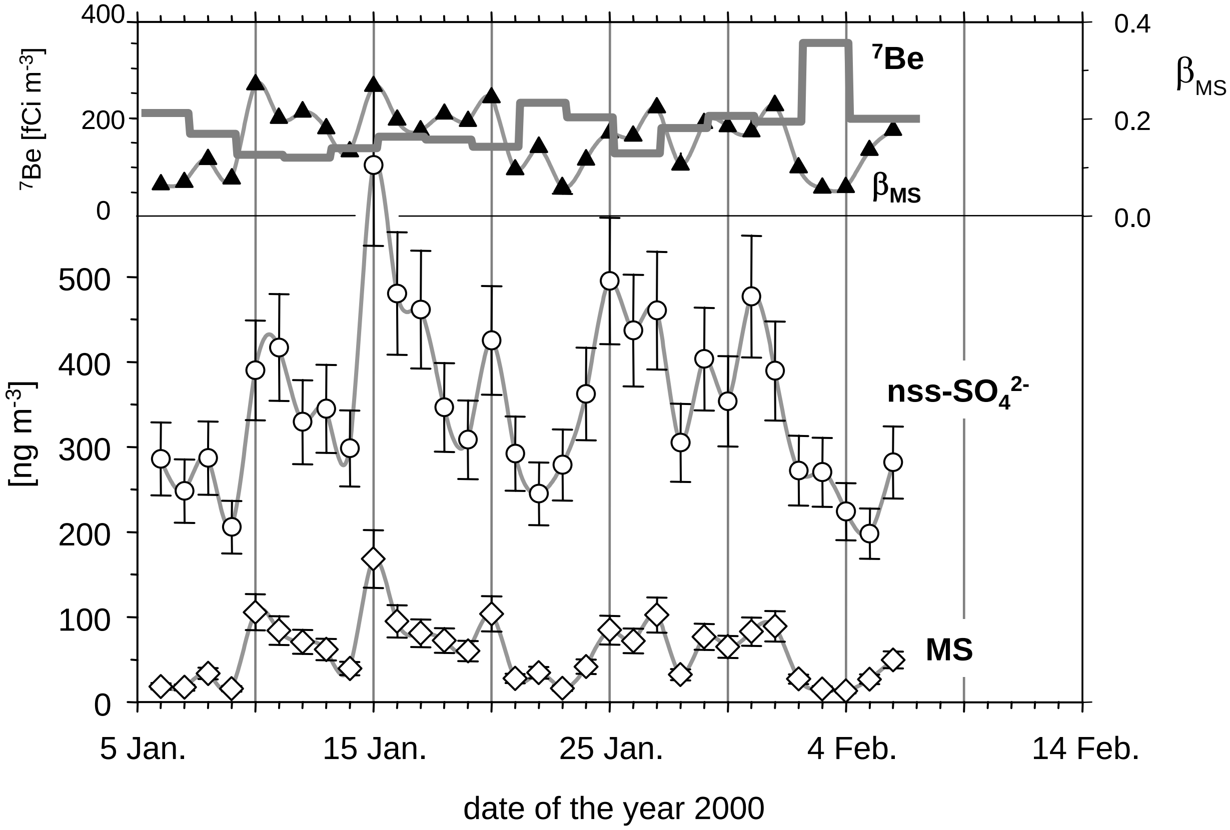

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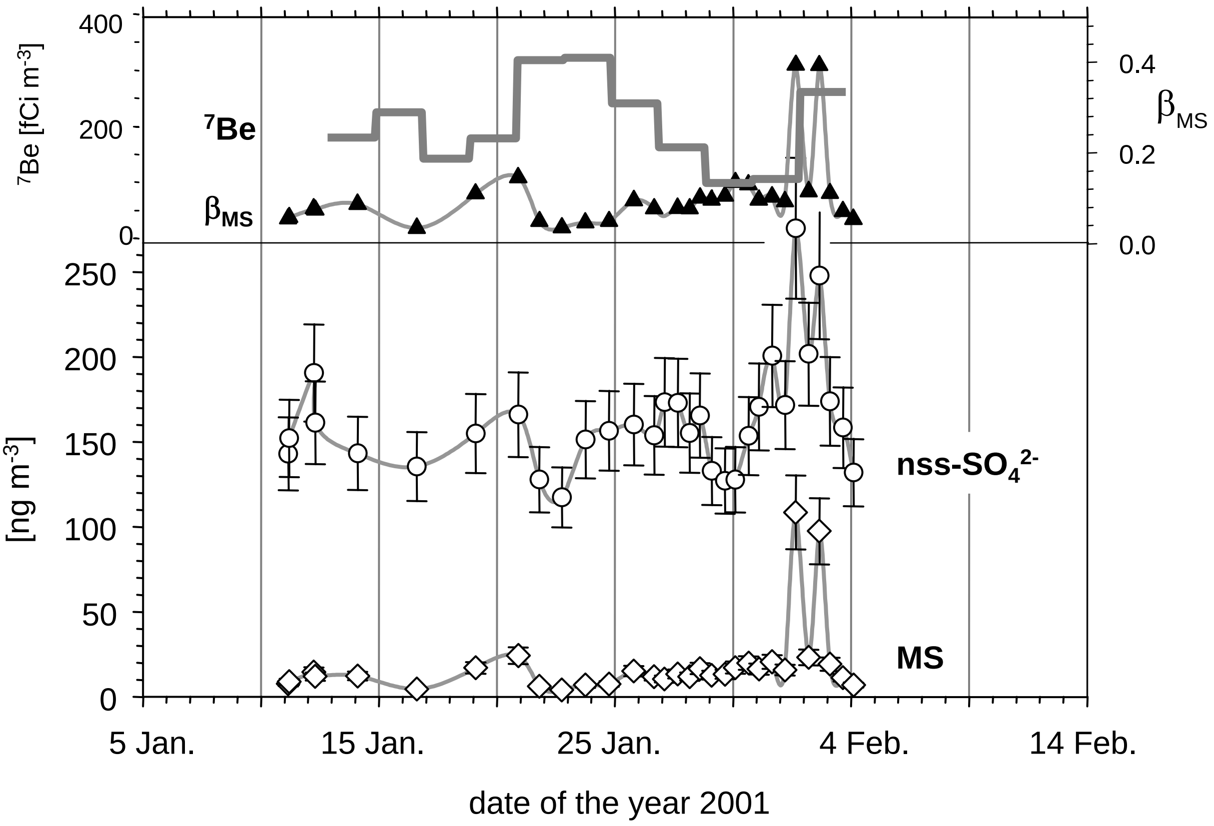

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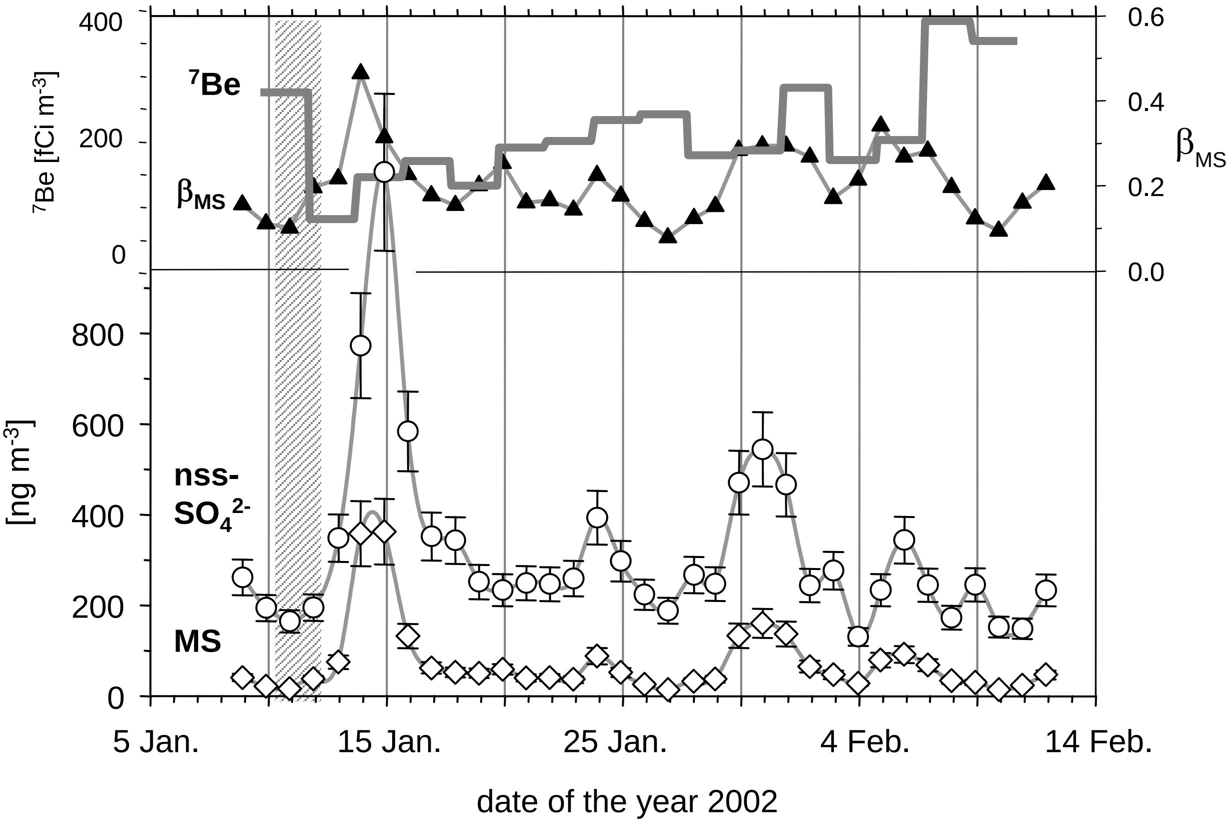

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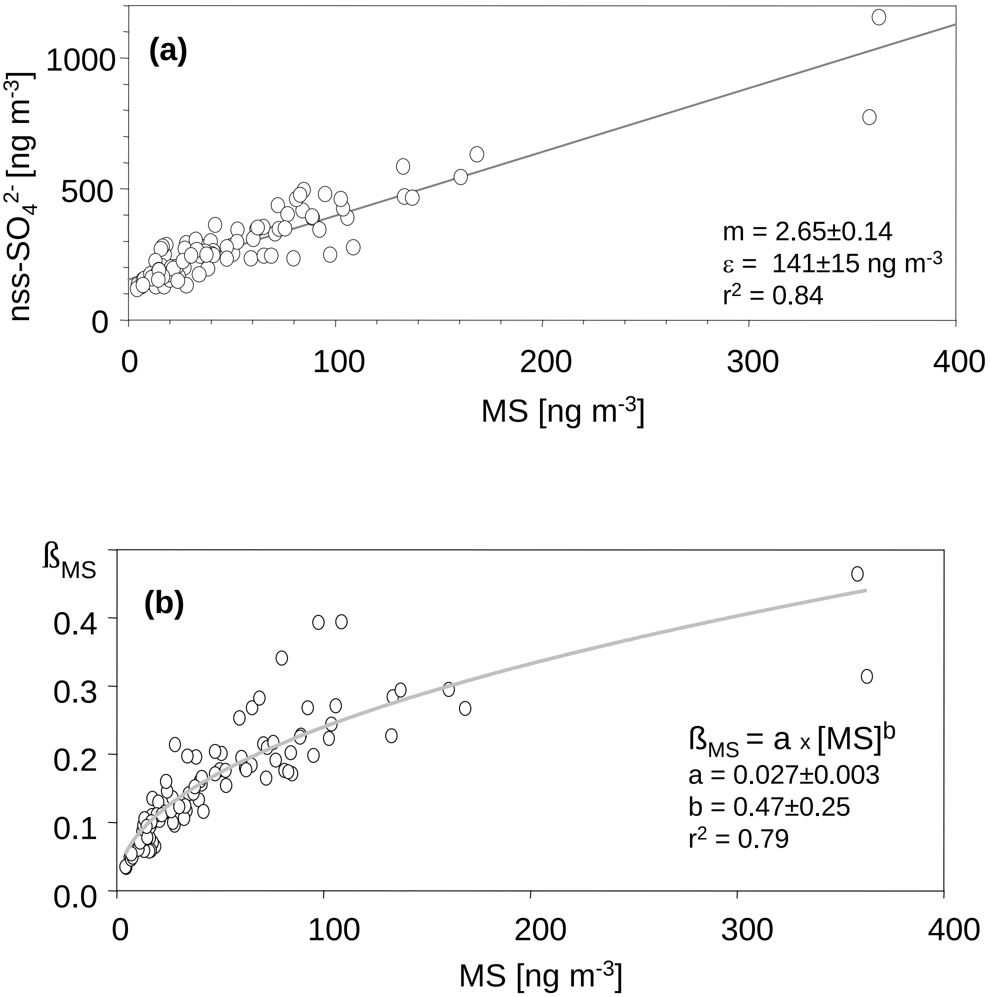

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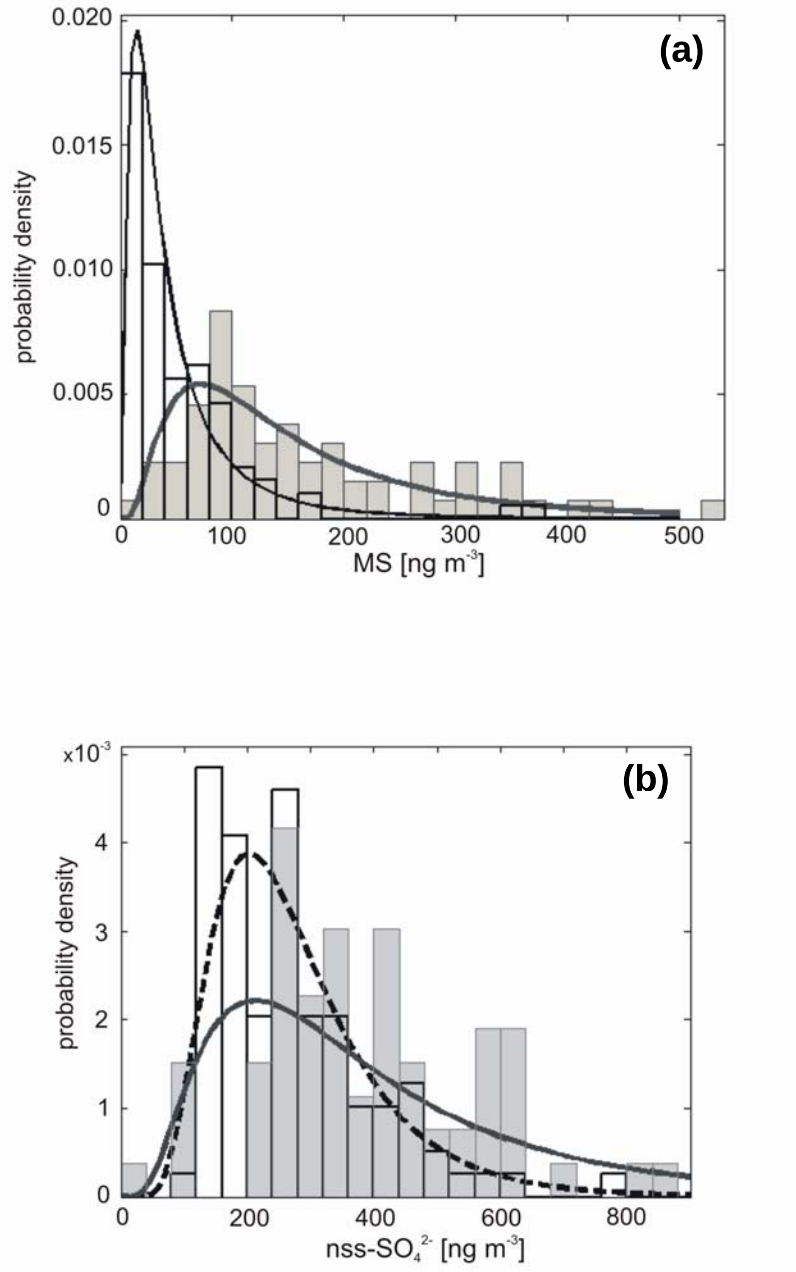

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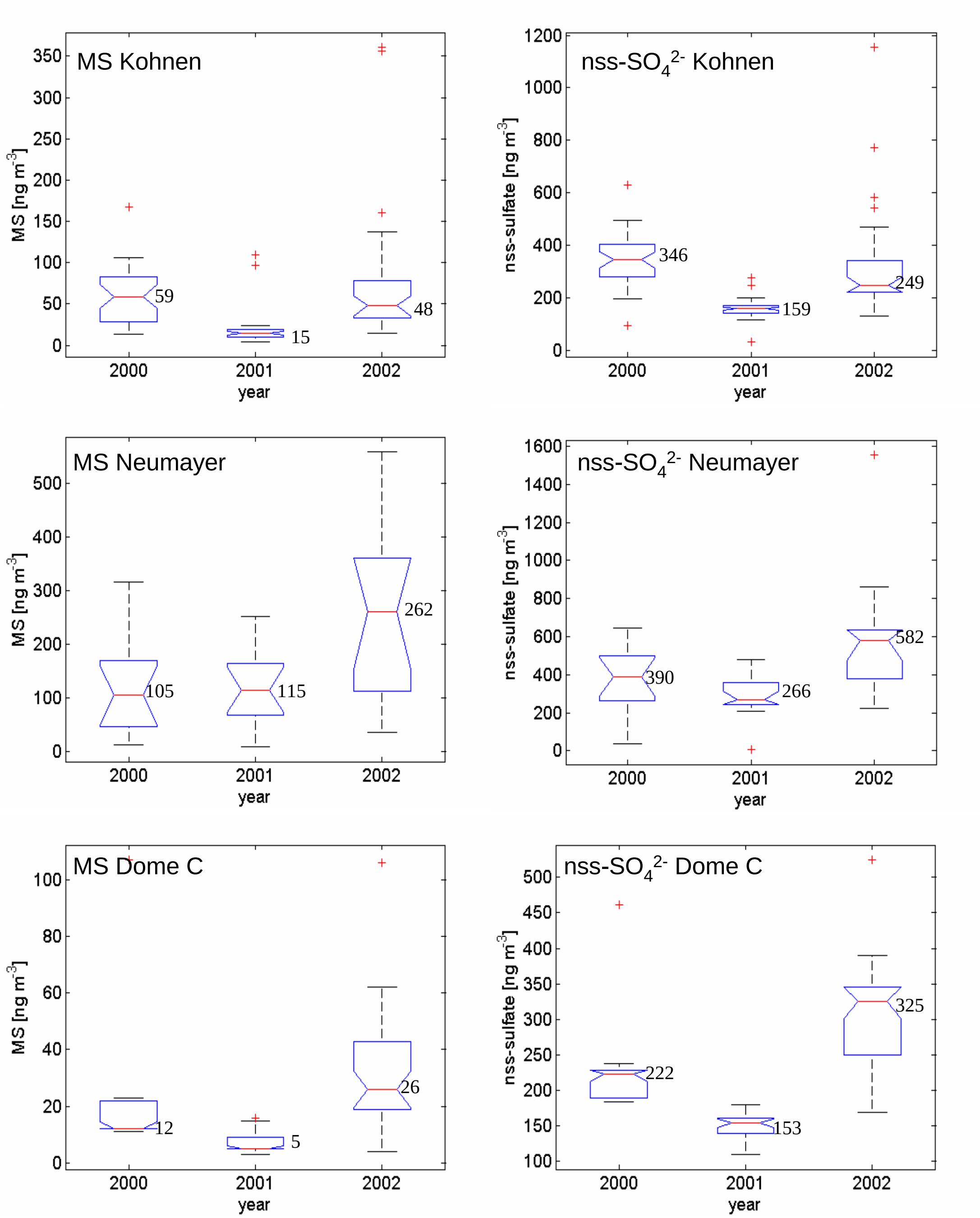

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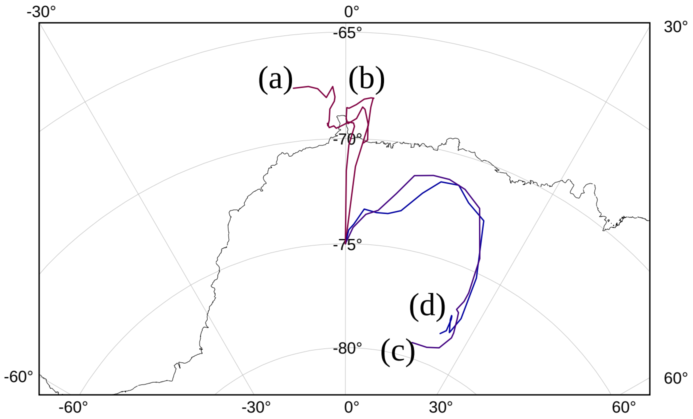

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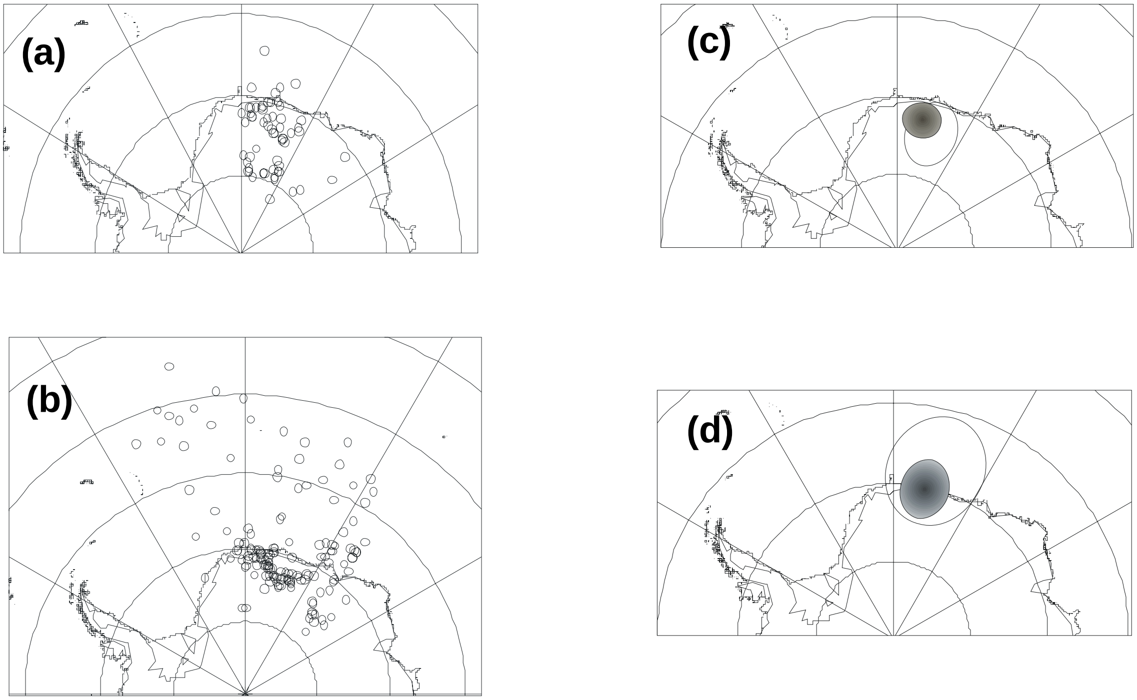

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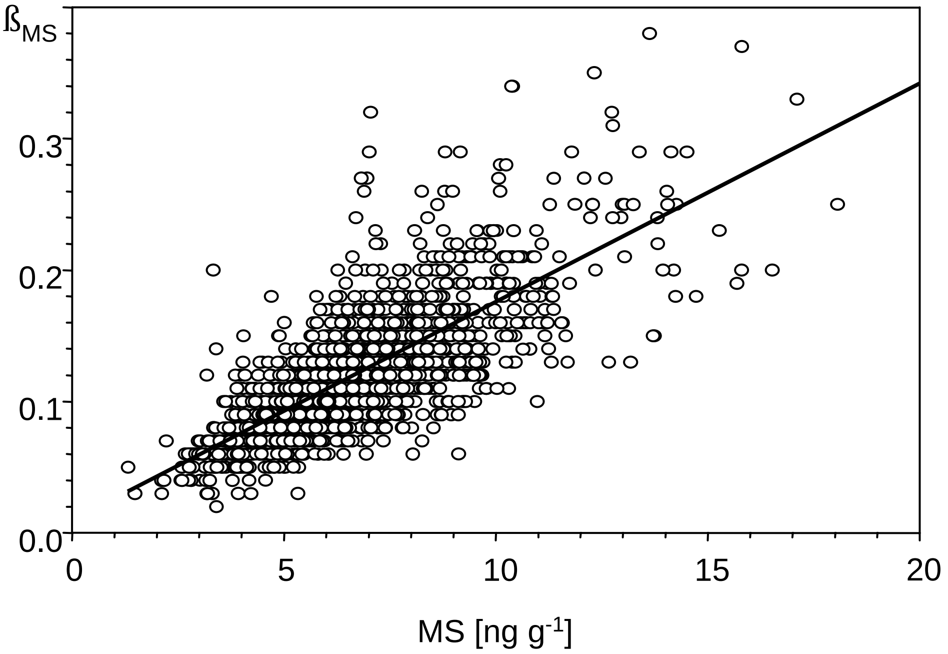

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