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Sea-salt aerosol in coastal Antarctic regions

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Abstract. Continuous year round records of atmospheric sea-salt concentrations have been recovered at three coastal Antarctic stations (Halley, Dumont D'Urville, and Neumayer) at temporal resolutions typically between 1 day and 2 weeks. The records were evaluated in terms of their spatial and seasonal variability as well as with respect to changes in the relative ion composition of airborn sea-salt particles. Annual mean sea-salt concentrations vary between 1400 ng m^{-3} at Dumont D'Urville, 850 ng m^{-3} at Neumayer, and 200 ng m^{-3} at Halley, respectively. They are thus considerably lower than the mean levels previously observed at the north tip of the Antarctic Peninsula but are, at their lower end, comparable to the level previously reported from Mawson. The representativeness of the atmospheric sea-salt data appears to be weak due to their high temporal variability, strong impacts of site specific aspects (such as site topography) but also due to the nonuniform sampling techniques applied so far. In accordance with the ice core evidence, the seasonal change in the atmospheric sea-salt load is found to be clearly out of phase with the seasonal cycle of the open water fraction offshore from the station as (with the exception of Dumont D'Urville) the lowest concentrations are generally observed during the local summer months. Major ion analyses of bulk aerosol and concurrently sampled fresh snow show a strong, systematic depletion of the SO_4^{2-} to Na^+ (Cl^-) ratios with respect to bulk sea water, which appeared to be confined to the local winter half year. During that time, sea-salt SO_4^{2-} was found to be depleted typically by 60–80% along with a concurrent Na^+ deficit, which is in accordance with the precipitation of mirabilite. No significant fractionation of Mg^{2+}, K^+, and Ca^{2+} between seawater and sea-salt particles is observed. Laboratory experiments failed to simulate the SO_4^{2-} fractionation in airborne seawater droplets or in the skin of seawater bubbles at low air temperatures. They gave, however, SO_4^{2-} depletion factors, similar to the field observation in air and snow, in the remaining brine of seawater which was partly frozen below $-8°C$ to an artificial sea ice surface. It is suggested therefore that the mobilization of brine from the sea ice surface constitutes an important sea-salt source in winter which may dominate the atmospheric sea-salt load at high latitudes of coastal Antarctica.

1. Introduction

Sea-salt particles produced by bubble bursting and wave crest disruptions provide by far the largest flux of primary aerosol particles to the marine atmosphere. The supramicron fraction of the marine aerosol body is controlled therefore by this oceanic source leading to boundary layer loads around 2–50 μg sea salt per m^3 which vary strongly as a function of wind speed [*Fitzgerald*, 1991]. Interest in atmospheric sea-salt particles was recently renewed due to their potential contribution to the indirect radiative forcing [*Latham and Smith*, 1990], as well as from their role in a series of heterogeneous air chemical processes as responsible for large fluxes of HCl and HBr [*McInnes et al.*, 1994; *Mozurkevich*, 1995], but also of reactive halogens [*Vogt et al.*, 1996], to the remote marine troposphere. In the context of the Antarctic troposphere, sea-salt particles are the only primary aerosols produced in relevant quantities within the south polar cell. They may add therefore a substantial fraction of seawater sulphate to the more interesting dimethyl sulfid derived sulphate inventory of this region. This contribution has to be estimated accurately via other seawater species. Further interest in Antarctic sea salt comes about since the Antarctic NH_x, level is normally extremely low [*Legrand et al.*, this issue]. Sea salt thus provides during modern times the only important alkaline counterpart to the otherwise dominating acidic components made up by non-sea-salt (NSS) biogenic SO_4^{2-}, methanesulfonate (MSA), and HNO_3. When sea-salt particles become externally mixed with these species [*Parungo et al.*, 1986], additional pathways may exist to carry biogenic sulphur and nitrate down to the ice sheet surface [*Moser et al.*, 1990].

A relatively large data set on the sea-salt content of modern and past Antarctic precipitation has been recovered from various ice core studies [*Legrand and Delmas*, 1988; *Clausen and Langway*, 1989; *Delmas and Legrand*, 1989]. The clear ice core evidence for higher sea-salt levels during glacial times was generally interpreted as indicating an intensified sea-salt production associated with higher cyclonic activity (higher storm-

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iness) overcompensating the much larger sea ice extent during that time [*Petit et al.*, 1981]. Similarly, the sea-salt variability over the last 200 years has been attributed by *Peel and Mulvaney* [1992] to concurrent change in the regional sea ice and circulation pattern. Year-round observations of atmospheric sea-salt concentrations that would be needed to corroborate these pictures are, however, sparse. Discontinuous records from South Pole over the years 1979–1983 are the only such data from central Antarctica and were extensively used to study the episodic intrusion of maritime air masses to the plateau [*Bodhaine et al.*, 1986]. At coastal Antarctica, where the sea-salt source of the polar ocean is seen much more strongly, records exists back to 1983 at Neumayer [*Wagenbach et al.*, 1988] and back to 1987 at Mawson [*Prospero et al.*, 1991]. They are supplemented by shorter observations at the tip of the Antarctic Peninsula [*Savoie et al.*, 1993] which are, however, less representative for the marginal ice sheet regions. As reviewed by *Wagenbach* [1996], no conclusive picture could be derived so far from these records on their link to the annual sea ice cycle, making the principal source area responsible for highly elevated sea-salt concentrations during winter essentially unknown. Furthermore, there is still a serious uncertainty about the occurrence and the underlying process leading to the enormous depletion of sulphate in airborne sea-salt particles seen in aerosol and precipitation at almost all coastal sites [*Legrand and Delmas*, 1985; *Ivey et al.*, 1986; *Gjessing*, 1989; *Mulvaney and Peel*, 1988; *Wagenbach et al.*, 1988; *Minikin et al.*, 1994]. In a collaborative effort the aerosol chemical observations at Neumayer (NM) have been extended to the stations Halley (HB for Halley Bay) and Dumont D'Urville (DDU) in order to increase the spatial coverage of such observations and to deduce a detailed picture on the link between atmospheric and glacio-chemical changes [*Wolff et al.*, this issue (a)]. In this paper the atmospheric sea-salt records recovered at these stations will be discussed mainly in terms of their spatial and seasonal variability as well as with respect to the apparent sulphate fractionation observed between airborne sea-salt particles and seawater.

2. Sampling Sites and Methods

A general overview of the climatological situation at all three sites under investigation is given by *König-Langlo et al.* [this issue]. Sampling techniques and analytical methods used by the different groups involved are summarized by *Wolff et al.* [this issue (a)]. In the following section, only a brief outline of these aspects is presented, concentrating on details relevant for the sea-salt component of the Antarctic aerosol body. In Figure 1 the geographical locations of the stations are shown together with a zoomed view of their position relative to the (mean) coast line and the prevailing wind direction. Details on the site specific sampling and analytical techniques for sea-salt aerosol are given in Table 1.

NM and HB which are both situated on ice shelves of the Atlantic sector are subject to a similar surface wind pattern dominated by zonal winds most frequently from easterly directions. Apart from the lower mean annual wind speed at HB (6.2 m s^{-1} versus 8.9 m s^{-1} at NM), the following main distinguishing features may be relevant for the local atmospheric sea-salt load as (1) the more southerly position of HB (by 5°) leading to a shorter and delayed open water season as well as to a relatively high sea ice fraction during summer and (2) the generally larger distance to the ice edge at HB which may decrease the influence of the very local sea-salt source. For example, the ice shelf fetch for the most frequent easterly winds at NM may be as low as 6.5 km, whereas going eastward from Halley, no regional ice edge is reached.

DDU differs considerably from the situation of the two ice shelf stations in being placed on a small island 1 km offshore from the coastline and in being subject to strong meridional downslope winds throughout the year (mean annual wind speed ~9.5 m s^{-1}). For a detailed description of the site, see *Legrand et al.* [this issue]. Because of its position at 66°S in the Pacific sector, a longer open water season and a smaller maximum sea ice extent is seen at DDU in comparison to HB and NM. Hence the general conditions for aerosol sampling at DDU are quite similar to those at Mawson (Indian Ocean sector) where aerosol-chemical records were previously obtained by *Savoie et al.* [1993] over several years.

Aerosol collection was achieved at HB and DDU by continuous low volume sampling using open-face filter holders protected by a wind shield. In contrast to NM, no interruption of the sampling procedure related to wind direction or wind speed was applied here. At NM, aerosol sampling was performed in a special clean air satellite station as described by *Wagenbach et al.* [1988] with no major changes except that the station was moved in 1992 8 km to the southeast and that a newly constructed clean air station was established there in 1994 essentially applying the same sampling technique. On the basis of the different sampling methods outlined in Table 1, the following systematic effects may be important in assessing the comparability of the sea-salt loads observed at the three sites:

1. Because of the relatively large geometric mean mass diameter of locally produced sea-salt aerosol of the order of 10 μm [*O'Odowed et al.*, 1997], the particle cutoff of the air intake systems critically controls the observed sea-salt load. Since isokinetic sampling could not be applied, sea-salt concentrations are expected to be generally underestimated, especially during high wind speeds. At NM (where an actively ventilated high volume stack operates as a kind of virtual impactor) the particle cutoff diameter is empirically estimated at around 6 μm suggesting that the large sea-salt particle mode is not completely sampled.

2. No such information is available for the HB and DDU open-face sampling systems, but the much lower filter face velocity applied here (if compared to the NM sampling head) suggests an even lower cutoff diameter, especially during high wind speed events. At all three sites, aerosol scavenging in the near-surface layer by drifting snow might further contribute to the underestimation of the ambient sea-salt level. Being mainly dependent on the site specific snow drift frequency (e.g., 40% at NM), this effect is expected to be less important at DDU (island position), especially during summer. On the other hand, for a given comparable snow drift situation, NM data are least affected since the air intake is placed at 7–9 m above the snow surface instead of 2 m at the other sites and since the pumps are automatically switched off during heavy snow drift periods. This fractionating sampling at NM provides the most obvious difference from the otherwise continuous collection modes at HB and DDU because situations with extremely high or low wind speeds as well as with northerly winds (putting the sampling site downwind from the main station) are a priori excluded.

Laboratories in charge of the design of the collection procedure and sample analyses were the British Antarctic Survey for HB, the Laboratoire de Glaciologie et Géophysique de

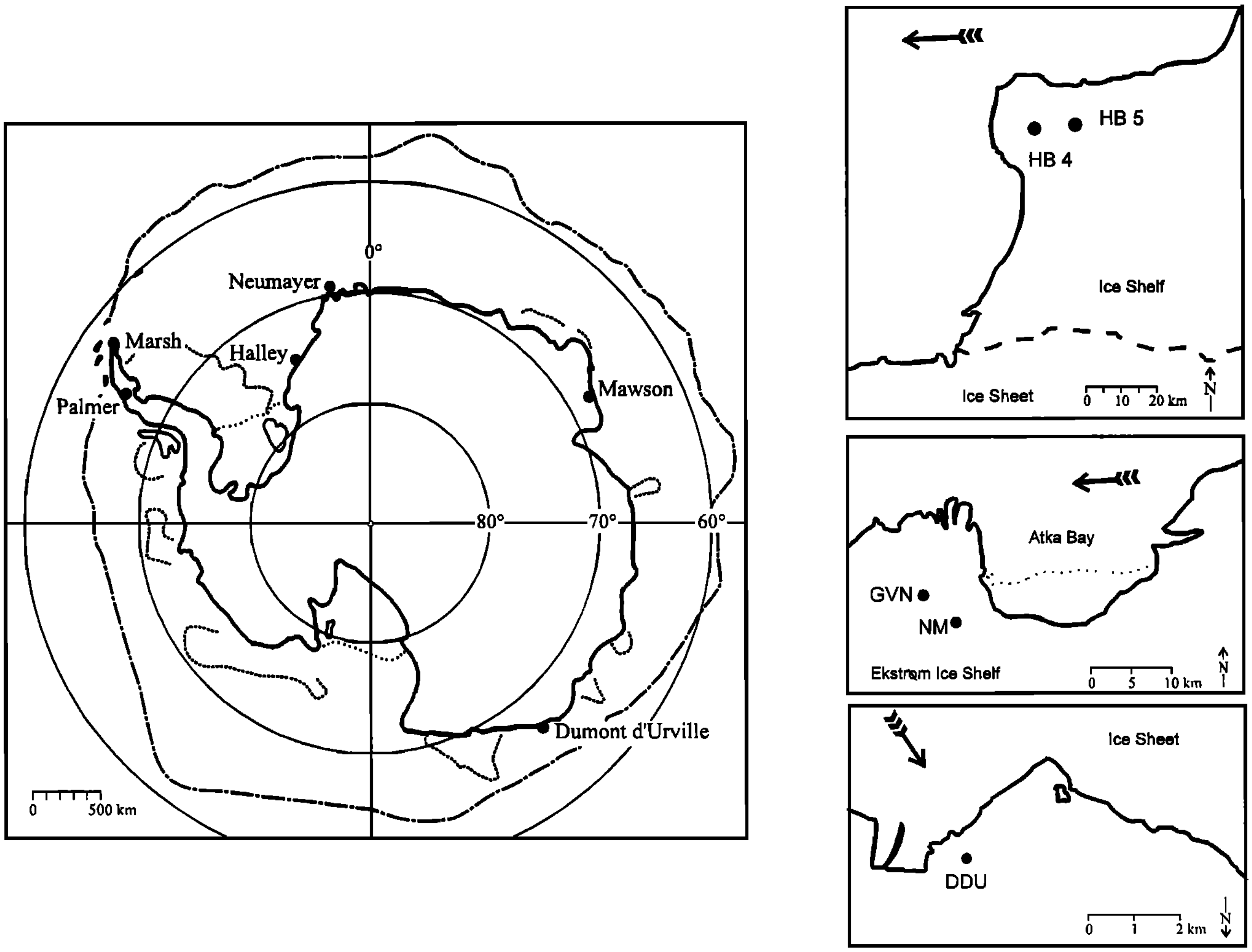

Figure 1. Position of sampling sites in coastal Antarctica with year-round chemical aerosol records. Lines over ocean areas indicate the 50% sea ice coverage during winter (dash-dotted lines) and during summer (dotted lines), respectively (adopted from *Giovinetto and Waters* [1990]. Sites referring to this work are shown in detail with respect to their coastline topography and main wind direction (arrow). GVN denotes the former Georg von Neumayer station, HB4 is the 1991 and HB5 is the 1992 sampling sites at Halley Bay, and DDU is the Dumont D'Urville station.

l'Environnement for DDU, and the Institut für Umweltphysik for NM. The precision of the sea-salt determination calculated via ionic seawater species Na^+ or Cl^- are mainly controlled at DDU and NM by the analytical uncertainty of the ion chromatography procedure (typically less than ± 5% at all sites) since the filter blank contribution could be neglected here. Although local K^+ and Ca^{2+} contamination by soil particles from penguin droppings occur at DDU, sea-salt concentrations

Table 1. Sampling and Analyses Methods of Atmospheric Sea-Salt Species at the Coastal Antarctic Stations Dumont d'Urville, Halley, and Neumayer

	Dumont d'Urville 66°S, 140°E	Halley Bay 75°S, 26°W	Neumayer 70°S, 8°W
Observational period	Jan. 1991 to Dec. 1995	Feb. 1991 to Feb. 1993	March 1983 to Jan. 1996
Collection interval	1–7 days	1–2 days	3–20 days (typical 2 weeks)
Sampling system			
Air intake height	1.8 m above snow level	2 m above snow level	7 m above snow level
Aerosol filter	47 mm ∅, 0.4 μm teflon open face	37 mm ∅, 0.8 μm cellulose membrane open face	240 mm ∅, double cellulose filters in line
Filter face velocity	0.6 $m\ s^{-1}$	0.4 $m\ s^{-1}$	1.1 $m\ s^{-1}$ [a]
Analyzed sea-salt species and methods	Na^+, K^+, Mg^{2+}, Ca^{2+}, SO_4^{2-}, Cl^-, Br^-: ion chromatography	Na^+, Mg^{2+} [b]: flame atomic absorption, Cl^-, SO_4^{2-}: ion chromatography	Na^+, K^+, Mg^{2+}, Ca^{2+}, SO_4^{2-}, Cl^-, Br^-: ion chromatography

[a] Corresponds to 13% of air intake velocity.
[b] Cations available for 1991 only.

derived via Na^+ or Cl^- are shown to be unaffected by such events [*Ducroz*, 1996]. At HB, due to the relatively low sea-salt level and the short sampling intervals, the filter blank variability was found to be substantial, leading to 15% of samples falling below the mean Cl^- detection limit of about 8 ng m^{-3} Cl^- (defined as twice the standard deviation of Cl^- blanks). For all sites the extraction efficiency of the filters for seawater ions is very close to 100%; hence no corrections were applied. Again, a 100% collection efficiency was assumed for HB and DDU membrane filters. At NM the double Whatman filters arranged face to face were individually analyzed to correct for particle penetrations (of the first filter) which were found to be around 10% except for filters occasionally wetted by snow or rime.

3. Atmospheric Sea-Salt Records

In view of the very different sampling intervals ranging from 1 day at HB, up to 7 days at DDU, to typically 2 weeks at NM, the continuous raw data of each site were formally collapsed into continuous series of 10 day means making their temporal variability more comparable. At HB, Cl^- was used to infer the sea-salt concentrations since cation analyses were available for 1991 only. At DDU and NM the commonly more conservative Na^+ (see section 2) was used instead. The Na^+ and Cl^- data, respectively, are then expressed as sea-salt concentration via the bulk seawater (BSW) content given by *Wilson* [1975]. Where possible, all references made to other Antarctic sea-salt data are based on Na^+, or alternatively on Cl^-. To make the atmospheric observations as comparable as possible to ice core results, mean concentration values are given in the text generally as arithmetic means.

3.1. Intersite Variability

Atmospheric sea-salt records over the years 1990–1995 are displayed at 10 day means for all three stations in Figure 2. Common to all sites is the relatively high sample interval to sample interval variability occurring throughout the year (for details, see descriptive statistics of 10 day means given in section 3.2). This behavior of the atmospheric sea-salt signal is seen also at other Antarctic stations [*Savoie et al.*, 1993] including South Pole [*Bodhaine et al.*, 1986]. It is expected therefore that the episodic properties of this signal may be driven both by rapidly changing production rates and by varying atmospheric transport situations. The obvious differences in the coastal records are the much lower mean level at HB in comparison to the more similar ones of NM and DDU, and the outstanding summer maximum only seen at DDU. The latter finding may be explained by the unique island position of this sampling site, generally not more than some 100 m downwind from open water during December to March. The missing 1994/1995 summer peak supports this view since during that season exceptionally severe sea ice conditions prevailed at DDU until midsummer.

The relatively low sea-salt level at HB of 200 ng m^{-3}, falling below the respective means at NM and DDU by a factor 4.4 and 7, respectively (see Table 2), is more difficult to explain, however. In contrast to the other sites, no vast open water areas exist offshore from HB during summer suggesting that the difference to NM and especially to DDU during that season is due to a reduced local sea-salt source. However, similar intersite sea-salt gradients between HB and NM or DDU prevail during the whole winter season when no such large differences in the local open water fraction are expected. Referring to the site climatologies given by *König-Langlo et al.* [this issue], NM is subject to a 20% frequency of blowing snow days (i.e., heavy snow drift above eye level), whereas only 6% are reported for HB, respectively. This might explain part of the discrepancy compared to the NM sea-salt level as connected to a difference in cyclonic activity. On the other hand, the sea-salt observations at 1–2 day intervals at HB are not significantly correlated with the local wind speed and show, instead, that the very highest sea-salt concentrations occur even during moderate winds. As addressed in section 2, the much longer ice shelf fetch during onshore winds at HB (confined here to westerly ones which are relatively weak and less frequent) may be one important reason for the much lower sea-salt concentrations if compared to NM. However, since at both stations virtually the same sea-salt levels in fresh (surface) snow are observed, also differences in the aerosol sampling systems (described in section 2) may be responsible for the intersite discrepancy.

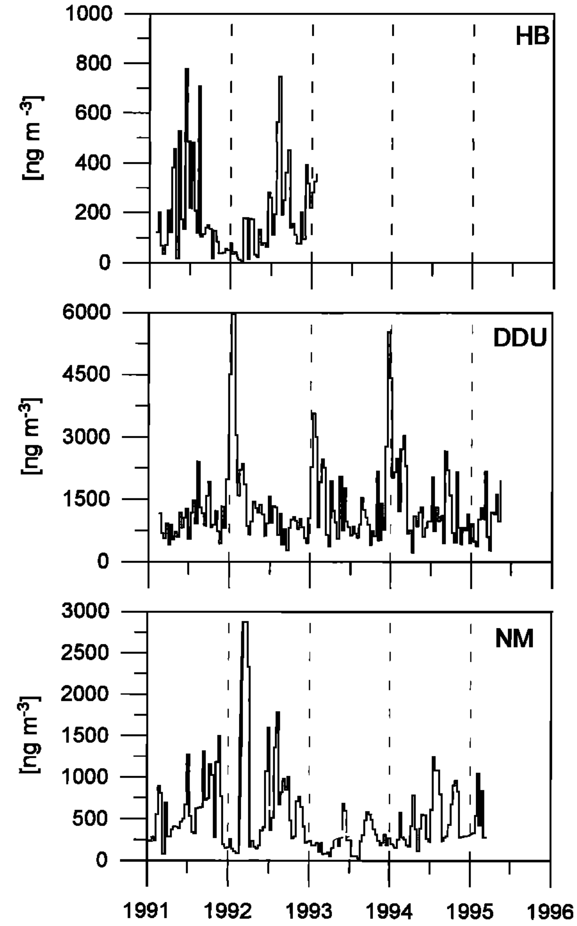

Figure 2. Atmospheric sea-salt records displayed as 10 day means for the overlapping sampling periods at Halley Bay (HB), Dumont D'Urville (DDU), and Neumayer (NM).

Inspection of the geographical distribution of the mean atmospheric sea-salt level in Antarctica summarized in Table 2 (in comparison with relevant ice core data) reveals a rather large spatial variability among coastal sites covering a range of 200 ng m^{-3} at HB to 10,000 ng m^{-3} at Marsh Station. The latter value is difficult to assess, however, since no details on the sampling site and collection procedure are given by *Savoie et al.* [1993]. It would be hard to predict a typical atmospheric

Table 2. Geographical Distribution of Mean Sea-Salt Concentrations in Coastal Antarctic Air and Snow

Site, °S	Elevation, m asl	Distance to Coast, km	Air, ngm^{-3}	Snow, μg g^{-1} Surface Snow	Firn Cores
Weddell Sea sector					
Halley (75°)	10	15	200	1.4[a]	1.7[a]
Ronne Ice Shelve (77°–81°)	~80	50–200	···	···	1.6–0.7[b]
Berkner Island (79°)	700–900	50–150	···	···	1.9–1.0[c]
Atlantic sector					
Neumayer (70°)	<42	10	850[d]	1.7	40[e]
Ekstrøm Ice Shelve (~71°)	<100	30–100	···	···	2.0[e]
Ritscher Hochland (~79°)	~1,000	200–300	···	···	0.5–0.2[e]
Pacific sector					
Dumont d'Urville (66°)	5	<1	1,400	90[f]	···
D10 (66°)	270	4	···	···	0.8[g]
Other stations					
Mawson (68°)		<1	330[h]	···	···
Palmer (65°)	coastal site		3,900[h]	···	···
Marsh (62°)	coastal site		10,000[h]	···	···
South Pole (90°)	2,800	>1,500	62[g]	···	0.03[i]

Surface snow denotes fresh snow sampled concurrently to atmospheric observation.

[a] *Wolff et al.* [this issue (b)].

[b] *Minikin et al.* [1994].

[c] *Wagenbach et al.* [1994].

[d] Refers to 1983–1995.

[e] *Moser* [1991].

[f] *Ducroz* [1996] (sampled during winter seasons only).

[g] *Legrand et al.* [this issue].

[h] *Savoie et al.* [1993].

[i] *Tuncel et al.* [1989].

sea-salt concentration for each specific site from their position relative to the relevant large scale phenomena alone (such as sea ice edge, main storm tracks, or regional wind systems) if the very local situation has the major control on the occurrence of high sea-salt events. There are several examples for such local impacts: DDU and Mawson, although experiencing similar downslope winds, differ by a factor of 4 in their mean winter sea-salt level (see also the discrepancy between NM and HB addressed above). Similarly, concurrent samplings performed on the DDU archipelago 3 km apart by *Ducroz* [1996] show systematic sea-salt concentration differences in the range of a factor 2 over a 6 week period in January. There are also doubts on the spatial and temporal representativeness of the atmospheric observations given the extremely high sea-salt concentrations in the snow pack at NM (reflecting salty drift snow advection from the upwind Atka Bay) and in surface snow at DDU as well as the high temporal variability indicated in Table 3 by the arithmetic mean to median ratio. The geometric standard deviation of the raw sea-salt data are 2.5 at NM and DDU and 3.5 at HB which translates to a rather high episodicity, showing that roughly 10% of the highest concentrations explain as much as 30% of the total sampled sea-salt at NM and DDU and even 50% at HB. There is no surprise therefore that general circulation models failed to simulate the present mean sea-salt concentration and its seasonal cycle within the coastal Antarctic boundary layer [*Genthon*, 1992]. At least, where sea-salt records are available in daily resolution, local and large scale effects might be disentangled through synoptic analyses. The comparability between sites will remain weak, however, until the sampling procedures are

Table 3. Descriptive Statistics of 10 Day Mean Atmospheric Sea-Salt Concentrations

	Dumont d'Urville[a] Jan. 1991 to Dec. 1995 Annual Mean	Summer	Winter	Halley Bay[b] Feb. 1991 to Feb. 1993 Annual Mean	Summer	Winter	Neumayer[a] March 1983 to Jan. 1996 Annual Mean	Summer	Winter
n	146	36	33	71	16	18	431	100	112
Arithmetic mean	1360	2100	1060	200	160	330	860	580	910
s.d.	1000	1570	440	180	140	240	780	570	660
25% quartile	790	900	810	70	40	150	340	230	470
Median	1060	1750	990	140	70	240	630	350	690
75% quartile	1600	2730	1300	260	290	490	1100	700	720
Mean/Median	1.28	1.20	1.07	1.43	2.29	1.38	1.37	1.66	1.32

Sea-salt concentrations are in ng m^{-3}. Summer refers to November–April, winter refers to May–October, *n* denotes number of data values, and s.d. is arithmetic standard deviation.

[a] Calculated from Na^+.

[b] Calculated from Cl^-.

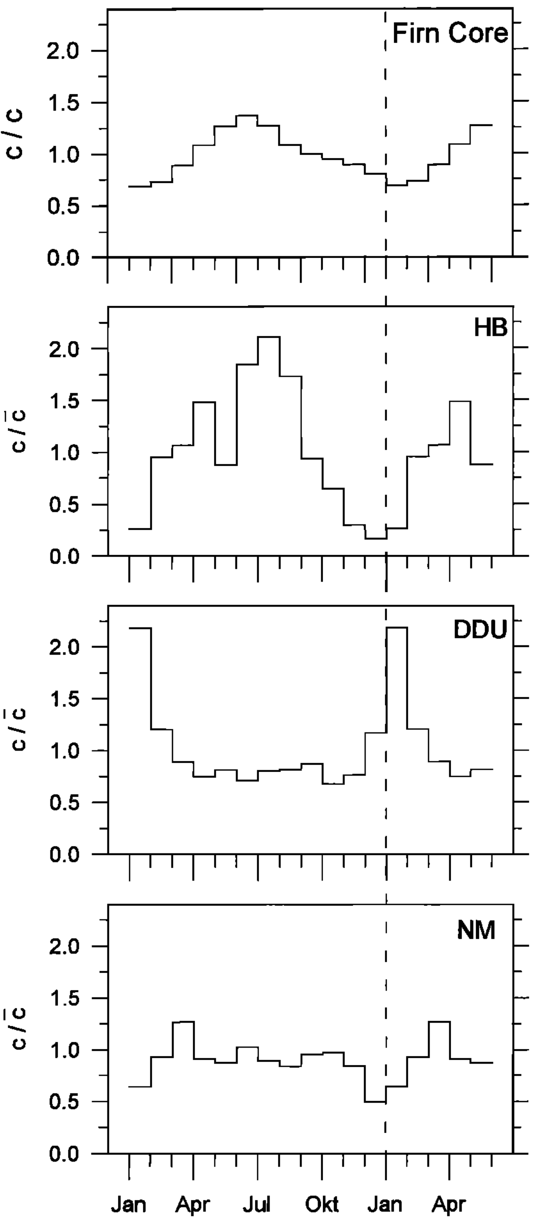

Figure 3. Mean annual sea-salt cycle at Halley Bay (HB), Dumont D'Urville (DDU), and Neumayer (NM) displayed as monthly means and normalized to grand average concentrations over the observational periods shown in Figure 2 (except for Neumayer representing the period 1983–1995). In the top panel the normalized mean sea-salt cycle observed over the last 25 years in the firn core D 235 of the eastern Ronne Ice Shelf [*Minikin*, 1994] is shown for comparison.

clearly characterized and homogenized. In this context, a well-defined dissection into a large and small sea-salt particle fraction by cyclon or (virtual) impactor stages may be recommended in future campaigns. Quantification of the large sea-salt fraction during snow drift episodes will remain troublesome, however, due to its size distribution partly overlapping with the size of blowing snow crystals.

3.2. Seasonal Cycle

As shown in Figure 3, the mean annual sea-salt cycle seen at all three stations is relatively weak, if the distinct summer peak at DDU arising from local sea spray is disregarded. The annual sea-salt maximum at HB and NM occurs during the winter half year which is also observed in the atmospheric records at Mawson [*Prospero et al.*, 1991] and South Pole [*Bodhaine et al.*, 1986], as well as in almost all seasonally resolved firn cores [*Mulvaney and Peel*, 1988; *Mosley-Thompson et al.*, 1991; *Minikin et al.*, 1994; *Wagenbach et al.*, 1994]. No seasonal cycles were reported, however, for Palmer and Marsh [*Savoie et al.*, 1993] lying far north close to the tip of the Antarctic Peninsula. For the mid to high latitude southern hemisphere, *Erickson et al.*, [1986] predict from analyses of wind speed distributions also a rather low winter to summer ratio in the sea-salt production rate (less than two between the midwinter and midsummer periods). The seasonal pattern at HB and NM is mainly driven by the low concentration levels during the summer months which may be underestimated in the HB data by roughly a factor of 1.4 since sea salt was calculated via Cl^- (see Cl^- losses discussed in section 4). Comparing the mean arithmetic sea-salt concentration of the midsummer (D, J, F) with the midwinter months (J, J, A) given in Table 3, winter to summer ratios of 1.6 at NM and up to 2 at HB are obtained. A further difference between the midsummer and midwinter sea-salt situation is clearly seen at all three stations in the higher variability of the 10 day means (expressed as the mean to median ratio in Table 3) during summer. This seasonal difference may reflect the proximity of open water during summer making it easier to produce extreme sea-salt peaks during favorable high wind speed episodes. On the basis of the station climatologies described by *König-Langlo et al.* [this issue] there is no substantial change in the surface wind regime over the year at all three stations and only a slight tendency for lower mean wind speeds to occur at HB and NM between December and February. Such a weak decrease in the storm activity during these months may not explain, however, the relative sea-salt minimum in the annual cycle regularly appearing during the open water season at NM, HB, and Mawson. Hence, except for the peculiar situation of DDU, the proximity of open seawater areas during summer is not seen in the atmospheric sea-salt records nor in firn cores of coastal regions. This poses questions about the sea-salt source, responsible during the winter seasons for short term (1–2 day) peaks regularly seen at HB and DDU in the range of some $\mu g\ m^{-3}$ although the sea ice coverage is well developed. These sources, finally leading to winter sea-salt maximum concentrations, would have to overcompensate the reduced offshore open water area, as well as particle removal during long range transport over the sea ice. The following potential sources for the winter sea salt may be considered:

1. Coastal polynyas transiently opened by strong winds and ocean currents may provide a local source, which, however, cannot explain the huge peaks seen in winter snow layers even 500 km south or at elevations around 1000 m asl (see Table 2 and references therein).

2. Leads responsible for an open water fraction in the winter sea ice cover in the range of up to some 10% should show a much weaker specific particle production rate due to the reduced wind fetch over water. On the other hand, an increased production of spume drops may be expected from the surf zones prevailing at the rim of leads and ice floes already under moderate wind speeds.

3. Putting the major sea-salt source during winter north of the sea ice edge would require a much more efficient meridional transport in the surface layer or an unrealistically increased production rate by bubble bursting. The scale length

for sea-salt particle removal determined by *Minikin et al.* [1994] over 600 km on the Ronne ice shelf is around 30% per 100 km (same for winter and summer) which can be regarded as a lower limit, due to much lower precipitation there. Accordingly, the depletion in the atmospheric sea-salt load during a 1000 km transport over (source free) sea ice would be larger than a factor of 20.

In any case, a dominating sea-salt source north of the actual sea ice edge would suggest that the observed sea-salt level should vary broadly in antiphase with the sea ice extent which is clearly in contradiction to what is observed in aerosol samples and ice core records. In conclusion, it appears that none of the open water sea-salt sources addressed here may explain the magnitude and seasonal variability in the winter sea-salt load seen at the higher latitudes of coastal Antarctica.

4. Chemical Sea-Salt Fractionation

Enrichments of SO$_4^{2-}$ or depletions of halogens with respect to seawater in marine bulk aerosol are common phenomena arising at remote marine sites from additional biogenic non-sea-salt (NSS) SO$_4^{2-}$ contributions and from reaction of other acidic species (MSA, HNO$_3$, N$_2$O$_5$) with the alkaline sea-salt particles, respectively [*Parungo et al.*, 1986]. During summer months a huge SO$_4^{2-}$ surplus and a clear Cl$^-$ deficit was indeed observed at all three stations due to the relatively high atmospheric load of biogenic sulphur [*Minikin et al.*, this issue] and NO$_3^-$ [*Wagenbach et al.*, this issue] during that season. However, during winter a significant SO$_4^{2-}$ deficit (as previously reported from NM [*Wagenbach et al.*, 1988] and a slight Cl$^-$ surplus (relative to Na$^+$) was evident at all three stations. No such systematic depletion of SO$_4^{2-}$ in bulk aerosol samples was reported from remote marine sites outside the Antarctic region. In the following section, the emphasis will be on the SO$_4^{2-}$ depletion phenomenon and its underlying processes.

4.1. Chloride Depletion

Acid-induced Cl$^-$ mobilization may occur from airborne sea-salt particles or (as a sampling artifact) from sea-salt already accumulated on the filter surface. During the major Cl$^-$ depletion period December to February the typical depletion of the Cl$^-$ to Na$^+$ ratios with respect to BSW are a factor of 2.3 at NM, 1.1–1.5 at DDU and ~1.4 at HB. The relatively high NM value possibly arises from the much longer collection time (1–2 weeks), whereas at DDU, Cl$^-$ mobilization is much less likely (although teflon filters are used) due to the high summer sea-salt level and the occurrence of summer NH$_3$ concentrations of up to 5 μg m^{-3} observed by *Legrand et al.* [this issue] via (double) mist chamber samplings. The Cl$^-$ depletion at HB is highly uncertain due to the lack of sufficient Na$^+$ data. Since generally no major problem arises in calculating the sea-salt contribution in coastal areas via Na$^+$, Cl$^-$ depletions are not further discussed here.

4.2. Sulphate Depletion

A significant SO$_4^{2-}$ depletion, recognized from negative NSS-SO$_4^{2-}$ concentrations, was first reported by *Gjessing* [1984] for firn samples from near the ice edge and by *Wagenbach et al.* [1988] at NM for winter bulk aerosol. As illustrated in Figure 4, the negative NSS-SO$_4^{2-}$ values found in winter aerosol at NM, HB, and DDU cannot be explained by the overall analytical uncertainty in the calculation of NSS-SO$_4^{2-}$: the sea-salt SO$_4^{2-}$ fraction is not so high as to preclude the calculation of a meaningful difference between total and sea-salt SO$_4^{2-}$ if a realistic lower limit of the background NSS-SO$_4^{2-}$ level around 20 ng m^{-3} [*Minikin et al.*, this issue] is assumed. Such analytical limitations are commonly encountered, however, during winter at island positions in the southern midlatitudes [*Ayers and Ramsdale*, 1988], but possibly also at Marsh Station where sea salt may be higher than 20 μg m^{-3} [*Savoie et al.*, 1993].

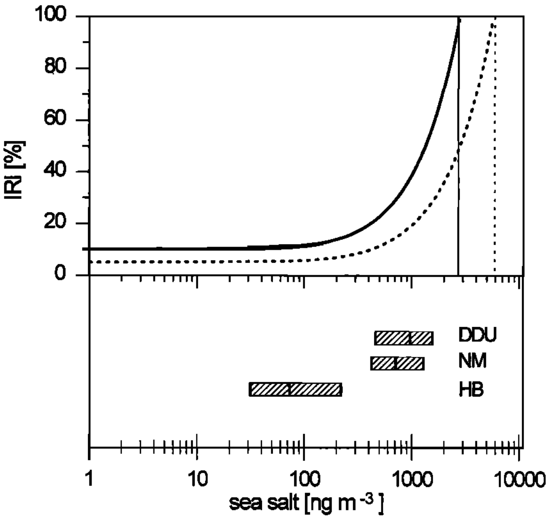

Figure 4. Expected relationship between the relative uncertainty R (1σ) in the NSS-SO$_4^{2-}$ calculation of Antarctic winter aerosol samples as a function of sea-salt concentration. Pure analytical uncertainties of 10% (solid line) and 5% (dashed line) are assumed which are taken independent of the concentration levels and identical for SO$_4^{2-}$ and Na$^+$ (Cl$^-$) analyses. The real NSS-SO$_4^{2-}$ winter background level was fixed at 20 ng m^{-3}. The observed raw winter sea-salt data at Dumont d'Urville (DDU), Neumayer (NM), and Halley (HB) are displayed in the lower panel by bars: 25% quartile (left margin), median (central mark), and 75% quartile (right margin). Almost all data are well below the 100% uncertainty limit in quantifying NSS-SO$_4^{2-}$ winter aerosol concentrations.

As illustrated in Figure 5, depending on the individual sea-salt contribution, the negative NSS-SO$_4^{2-}$ may reach values up to 200 ng m^{-3} in NM aerosol and up to some 100 ng g^{-1} in a firn core from the Ronne Ice Shelf. Similar figures are obtained from DDU and HB aerosol samples as well as from fresh snow at HB and NM. This "apparent fractionation" of sea-salt SO$_4^{2-}$ between seawater and airborne particles leads to a systematic underestimation of the mean annual atmospheric NSS-SO$_4^{2-}$ generally not much larger than 10%. It may lead, however, even to negative grand average NSS-SO$_4^{2-}$ values in ice cores drilled relatively near the coast (e.g., Berkner Island, North Dome [*Wagenbach et al.*, 1994]). Furthermore, serious misinterpretation of the MSA to NSS-SO$_4^{2-}$ ratio [*Wagenbach*, 1996; *Legrand and Pasteur*, this issue] as well as of an eventual anticorrelation between NSS-SO$_4^{2-}$ and sea salt in coastal ice core records [*Wagenbach et al.*, 1994] may be expected by this phenomenon. For example, SO$_4^{2-}$ depletion was not considered by *Savoie et al.* [1993] in evaluating their aerosol data, which led to erroneously high MSA to NSS-SO$_4^{2-}$ ratios during winter. *Peel and Mulvaney* [1992] interpreted the clear negative correlation they found between NSS-SO$_4^{2-}$ and Cl$^-$ in the Dolleman ice core in terms of climatic changes although SO$_4^{2-}$ depletion might have contributed substantially to the observed

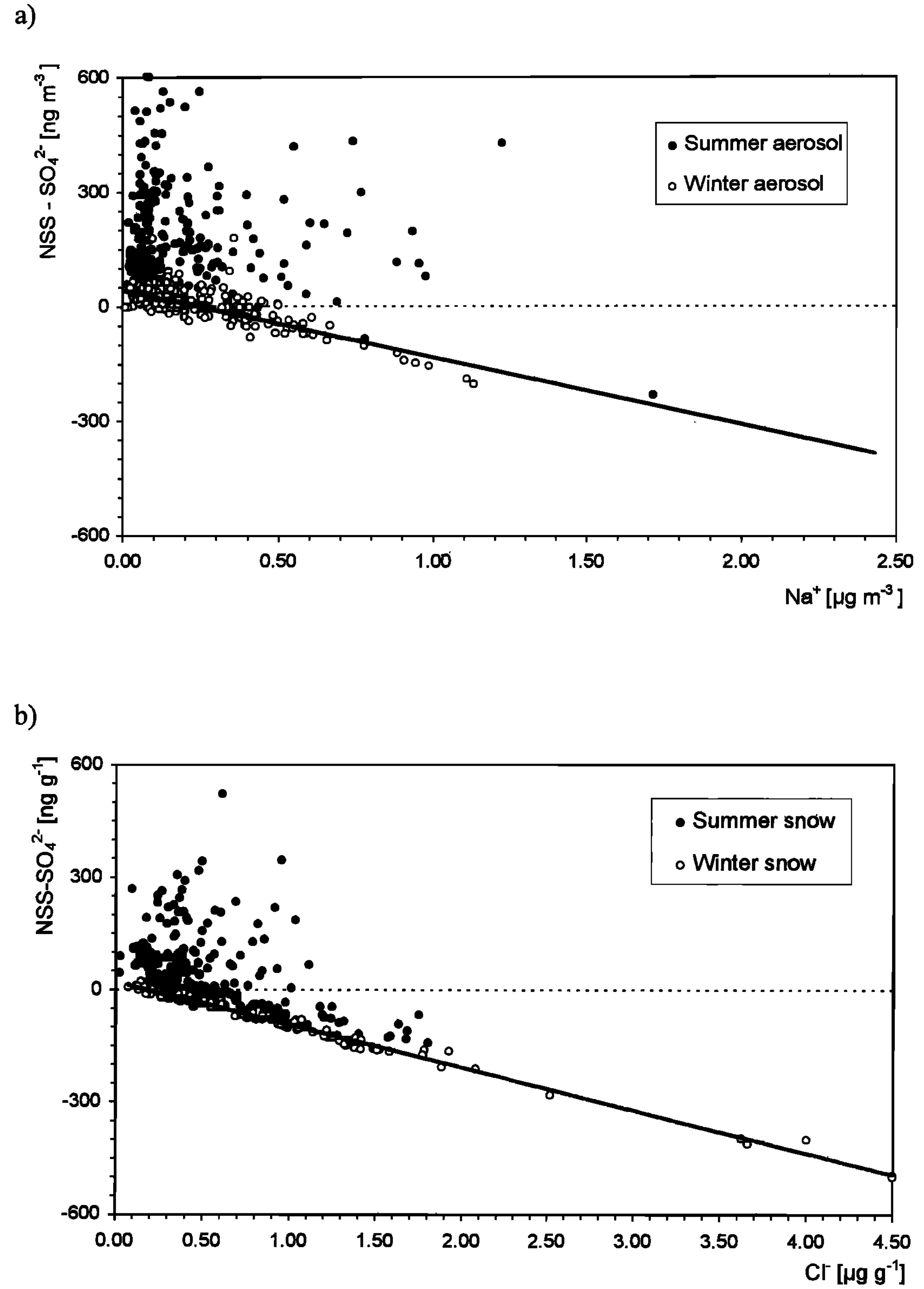

Figure 5. (a) Scatterplot of NSS-SO_4^{2-} (calculated via the BSW ratio) versus Na^+ for the complete, raw aerosol data set at Neumayer. (b) Same as Figure 5a, but for shallow firn core data used in Figure 3 and Cl^- as BSW reference species. Linear regression lines refer to winter data (associated with the May–September period for the aerosol date and with approximately the midwinter season for the firn core date).

coupling. An attempt is needed therefore to get at least a first-order correction for NSS-SO_4^{2-} which is normally calculated via:

$$[NSS - SO_4^{2-}] = [SO_4^{2-}]_{total} - k[x]$$

with x denoting the ionic seawater reference species (e.g., Na^+) and $k = [SO_4^{2-}]/[x]$ denoting the respective bulk seawater (BSW) ratio. As already applied for firn cores of the Weddell Sea region by *Minikin et al.* [1994] and for NM aerosol data by *Wagenbach* [1996], a formal downward correction of k may be achieved by linear regression of the winter NSS-SO_4^{2-} data versus Na^+ (alternatively Cl^-) or, less simple and giving the maximum correction, by determining the lower envelope of the whole data set. Adding the obtained (negative) slope to the conventional k value (i.e., 0.25 in the case $x = Na^+$) gives the corrected mean k value k' ($k' \leq k$) associated with airborne sea-salt particles. For the NM aerosol example shown in Figure 5 the slope is −0.175, and the mass ratio k' becomes 0.075 (instead of 0.25) which corresponds to a dramatic SO_4^{2-} depletion factor f (defined as $f = k/k'$) between sea-salt particles and bulk seawater of 3.3. In the case of the firn core example (based on Cl^-) of Figure 5, f is found to be 5.5.

Alternatively, k' may be obtained by requiring that the correlation between winter NSS-SO_4 and Na^+ (or Cl^-) becomes a minimum which is a reasonable assumption at coastal sites at least for high sea-salt concentrations. This procedure (clearly illustrating the artificial coupling between NSS-SO_4^{2-} and sea-salt species) can be applied even to more scattered data sets and may be used to check the regression results. In the case of the aerosol and firn core data already processed above, f becomes 4.1 and 5.3, respectively (see Figure 6). Regarding the relatively large scatter for low concentration values, both methods are very sensitive to the most negative NSS-SO_4^{2-} data points generally associated with high sea-salt concentrations and tend to give an overestimated fractionation factor. Also, further shortcomings (de-emphasizing the need for a formally high accuracy of k') are that the procedures still rely on a more or less subjective data dissection into summer and winter values and that it is a priori unknown for what seasons the derived k' are truly representative. Some hints on the seasonal occurrence of artificially reduced NSS-SO_4^{2-} values (conservatively defined as being lower than 10 ng m^{-3}) at each station may be drawn from Figure 7, however. At all stations, maximum frequencies in the occurrence of underestimated NSS-SO_4^{2-} consistently emerge during midwinter. As illustrated in Figure 7, the leveling off of depletion frequency toward the equinox is ambiguous due to a steady increase of biogenic NSS-SO_4^{2-} during that period.

To provide a common base in calculating NSS-SO_4^{2-} concentration within this special JGR section, the most simple regression method was individually applied for each year's aerosol data sets, defining the winter subsamples as June to August or, instead, June to September. Surface snow samples taken at HB and DDU in high temporal resolution are processed identically. Excluding the September 1991 data already affected by volcanic SO_4^{2-} from Mount Cerro Hudson (M. Legrand, personal communication, 1997) and 2 years with correlation coefficients below 0.5, the grand average k' (referring to Na^+) for aerosol and fresh snow becomes close to 0.07. No attempts were made at this stage to define seasonally adjusted k' values, hence $k' = 0.07$ corresponding to the sea-salt SO_4^{2-} to Na^+ mass ratio in bulk reference sea-salt particles was normally applied in the respective papers for aerosol as well as for snow samples throughout all seasons.

The SO_4^{2-} depletion factor f derived by the above procedure appears to be almost independent of the site specific sea-salt level. The value of f is virtually the same for NM and HB aerosol samples (4.1 and 3.6, respectively) but is significantly lower at DDU (2.6): there is also no obvious difference in f between aerosol and fresh snow at each site which suggests that f is not very sensitive to the particle size fraction considered. Available f values from 11 high resolution firn cores from the Weddell Sea sector range between 6.7 and 3.8 (mean 5 ± 0.9) in the region up to 600 km inland on the eastern Ronne Ice Shelf [*Minikin*, 1994] with no obvious relation to the ice edge distances and with similar f values also at higher elevations of Berkner Island. Interestingly, firn cores analyzed south of NM show a decreasing trend with f close to 3 and 2.5 at 70 and 160 km distance from NM, respectively, down to 1.4 at the Ritscher Hochland (1000 m asl, distance 300 km) [*Moser*, 1991; *Trefzer*, 1992]. The reason for this pattern is not clear yet, but might be connected to the difference in the sea ice cycle at this sector if compared to the Weddell Sea region (see following section).

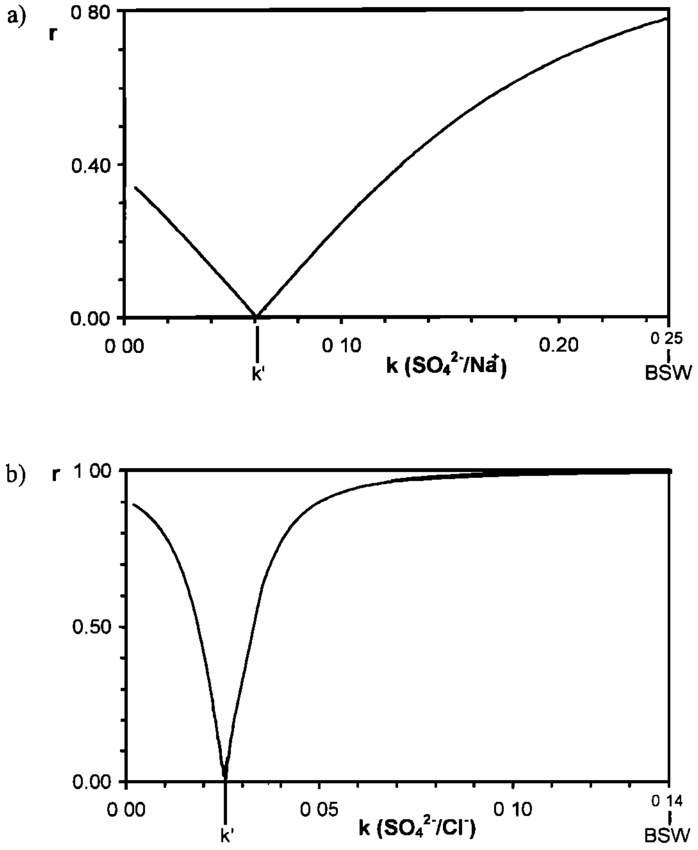

Figure 6. Correlation coefficient r between NSS-SO_4^{2-} and the seawater reference species concentration versus the seawater reference ratio k used to calculate the NSS-SO_4^{2-} values with k' indicating the absolute minimum of r: (a) for Neumayer winter aerosol data shown in Figure 5 with Na^+ as seawater reference species and (b) for firn core winter data shown in Figure 5 with Cl^- as reference species.

4.3. Sulphate Fractionation Process

Gjessing [1989] suggested reemission of $(NH_4)_2SO_4$, fractionation during fog formation, as well as fractionation during freezing of airborne seawater droplets as possible reasons for the extremely negative NSS-SO_4^{2-} concentrations he found in coastal firn. The clear evidence that bulk aerosol is also depleted in seawater SO_4^{2-} makes only his latter suggestion likely. Indeed, SO_4^{2-} fractionation during freezing of seawater (ice) is a well known process [*Richardson*, 1976] which is basically

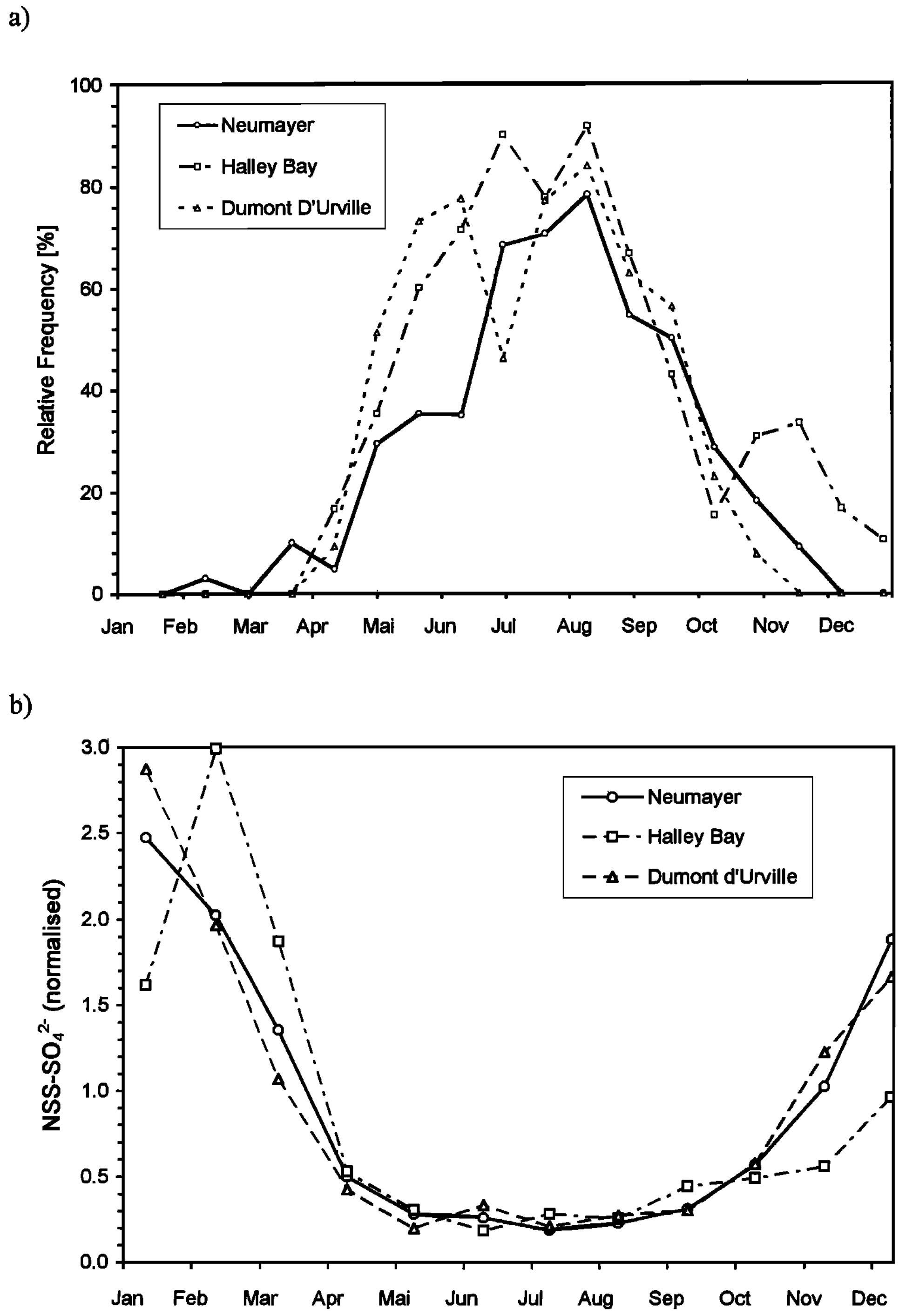

Figure 7. (a) Relative frequency for the monthly occurrence of seawater SO$_4^{2-}$ depletions in aerosol samples versus seasons. For all three stations, NSS-SO$_4^{2-}$ values calculated via the BSW ratio are assumed to be affected by sea-salt SO$_4^{2-}$ depletion if they are lower than 10 ng m^{-3}. (b) Annual cycles of NSS-SO$_4^{2-}$ calculated via the corrected SO$_4^{2-}$ to Na$^+$ mass ratio in bulk reference sea salt of 0.07 and normalized to the respective grand average (shown to indicate the NSS-SO$_4^{2-}$ increase toward equinox).

driven by the crystallization of $Na_2SO_4 \cdot 10H_2O$ (mirabilite) already occurring at temperatures below −8.2°C. Since the salt crystals are associated with the ice lattice, the remaining brine starts to get increasingly depleted in SO$_4^{2-}$ (and to a much lesser extent in Na$^+$) on progressive cooling below this critical temperature. Some connection of the SO$_4^{2-}$ fractionation with cold air temperatures is to be expected from the missing depletion effect at temperate marine sites. Again, in the coastal high Arctic which is subject to huge contamination by anthropogenic SO$_4^{2-}$ during winter [*Barrie*, 1986], sea-salt SO$_4^{2-}$ deficits would not be immediately recognized.

In a series of laboratory experiments, sea-salt particles were produced, therefore (from clean, deep Atlantic) seawater samples, under air temperature conditions down to −28°C attempting to simulate the observed SO_4^{2-} fractionation. The main results of these experiments performed at the Institut für Umweltphysik by *Keck* [1994] are summarized below:

In experiment 1, spume droplets were investigated at low temperatures. Seawater droplets sprayed into a sedimentation chamber at temperatures down to −24°C show no significant fractionation in the deposited large particles nor in the remaining airborne fraction. In contrast to freshwater droplets which may burst upon freezing [*Hobbs and Alkezweeny*, 1968] due to volume expansion of its still liquid core, no such fragmentation for seawater droplets was observed in experiment 1.

In experiment 2 the chemical composition of jet and film droplets generated at various ambient temperatures was analysed. Sea-salt droplets produced by bubble bursting at air temperatures in the range of +20 to −28°C and analyzed in six size classes (0.4–11 μm diameter sampled by an Anderson impactor) are also found to be not significantly fractionated. In particular, no systematic SO_4^{2-} depletion effects were observed as a function of particle size.

Experiment 3 focused on the freezing of the skin of air bubbles at the water surface. A slight SO_4^{2-} depletion of the order of 10% was found in the skin of seawater bubbles which are forced to freeze before bursting by increasing their lifetime artificially (adding of surfactants made up by detergent).

In experiment 4, seawater spray icing was studied. SO_4^{2-} was found to be depleted by up to a factor of 4 if seawater droplets are sprayed at a low rate onto a cold surface and the water film was continuously removed for analyses.

Experiment 5 simulated the freezing of seawater superimposed on sea ice. Depletion factors in the range of those observed in aerosol and snow were easily achieved if seawater was partly frozen at temperatures well below −8°C to the surface of artificial sea ice and the remaining liquid was removed for analyses.

The results of experiments 1, 2, and 3 gave no evidence for a freezing induced fractionation process operating during the airborne state of the droplets or at the air water interface which may explain the enormous SO_4^{2-} depletion observed in nature. Indeed, the complementary sea salt fraction enriched in SO_4^{2-} was never observed in surface snow even close to the ice edge [*Gjessing*, 1989] and has to remain somewhere offshore. From experiments 4 and 5, one may infer that liquid brine contained in or superimposed on ice floes constitutes the main source of the depleted sea-salt particles. Transport of the material onto the sea ice surface may be achieved by (1) deposition of spume drops (produced over leads) on bare ice floes or on the overlying snow pack (followed by percolation) or (2) squeezing of interstitial brine out of young sea ice by thermal ice volume contraction and expansion of the interstitial brine during progressive cooling [*Doronin and Kheisin*, 1977; *Reeburgh and Springer-Young*, 1983].

A major complication arises, however, in getting the brine airborne (i.e., fragmented into particles small enough to become readily transported by wind) and in overcoming the damping effect of an overlying snowpack. Newly formed sea ice (e.g., as occurring in leads) would be less affected by a snow cover, whereas dry surface snow may be easily removed by strong winds and may finally be dumped in leads. Again, strong winds may mobilize the liquid brine from bare sea ice surfaces by spraying it over the ice floe edges or by driving the impaction of large spume droplets (see experiment 4). Alternatively, wind-induced abrasion of salt crystals formed at the ice/air interface from progressively concentrated brine may be considered as well. Admittedly, none of the proposed processes are presently known to be as effective as needed to explain the observed SO_4^{2-} depleted sea-salt load and to produce the (small) particle mode typically encountered in the long range transport of sea-salt aerosols.

4.4. Fractionation of Cation Species

Assuming that the partitioning of crystallized mirabilite ($Na_2SO_4 \cdot 10H_2O$) between the brine and the ice matrix is the only dominating SO_4^{2-} fractionation process, then Na^+ should be depleted as well in the brine. Taking Cl^- as the reference species for BSW (halite precipitates only below −23°C), a simple mass balance calculation shows that the Cl^- to Na^+ mass ratio would then be linearly related to the SO_4^{2-} to Na^+ ratio with a slope of −0.98 and an intercept of 2.045. Accordingly, from the average SO_4^{2-} depletion factor $f = 3.57$ with respect to Na^+ found in aerosol and fresh snow during the winter half year, a Na^+ depletion factor with respect to Cl^- of 1.1 is predicted. Indeed, inspection of the winter aerosol data revealed mean Na^+ depletion factors of 1.14 ± 0.09 at DDU, 1.11 ± 0.10 at NM, and 1.30 ± 0.18 at HB among samples showing negative NSS-SO_4^{2-} values. As shown in Figure 8, the respective raw winter aerosol data roughly follow the theoretical relationship between the Na^+ and SO_4^{2-} depletion factors but indicate a systematically higher Na^+ depletion than would be predicted from mirabilite precipitation alone. The significance of this deviation is hard to assess in view of the relatively high scatter in the measured ratios and since any NSS-SO_4^{2-} contribution was neglected here.

This finding suggests that precipitation of mirabilite is the controlling process of the observed SO_4^{2-} depletion ın sea-salt particles. Indeed, regression analyses of Ca^{2+}, K^+, and Mg^{2+} versus Na^+ and Cl^-, respectively performed for all winter aerosol data sets, reveal no significant deviation from the respective seawater ratios (if the small Na^+ depletion with respect to Cl^- is taken in account). This is in accordance with the initial precipitation temperatures of the respective cryohydrates reported by *Nelson and Thompson* [1954] and confirms that mirabilite is the missing SO_4^{2-} compound. As a consequence, Cl^- excess concentrations of the winter season calculated via the BSW Cl^-/Na^+ ratio are systematically overestimated by roughly 10% of the sea-salt Cl^- contained in the samples. Cl^- excess (and among others possibly also Br^- excess) concentrations in winter samples with high sea-salt loads are thus too uncertain to provide useful results if Na^+ is used as BSW reference species. Taking instead of Na^+ one of the less abundant cation species would not improve the situation since these ions are analyzed generally at lower accuracy. Furthermore, *Legrand et al.* [this issue] showed that Ca^{2+} and K^+ are sensitive to contamination by Antarctic bird rockeries, whereas Mg^{2+} is suspected by *Wolff* [1996] to migrate out of sea-salt horizons in deeper Antarctic firn core sections.

4.5. Implications of SO_4^{2-} Fractionation

The clear evidence that SO_4^{2-} depletion in sea-salt particles is governed by precipitation of mirabilite constrains the occurrence of this phenomena to a formation temperature well below −8°C. Adding the hypotheses that the depleted source is brine formed at the sea ice surface implies furthermore that particles directly produced from ice free seawater are not fractionated. Hence fractionation is confined to periods when substantial amounts of sea ice prevail which may be subject to (radiative) surface cooling well below −8.2°C. The role of the

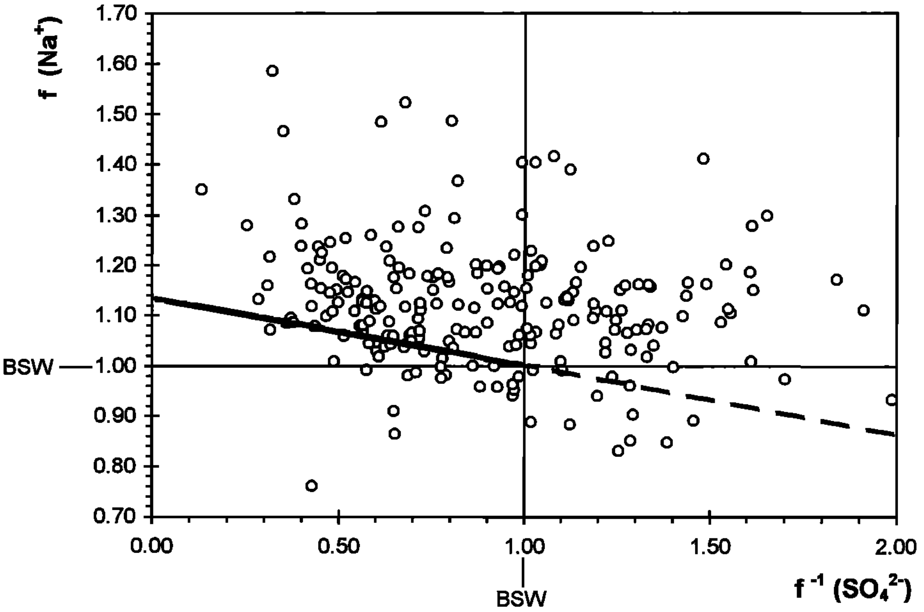

Figure 8. Theoretical linear relationship between the Na^+ depletion factor f (Na^+) (with respect to Cl^-) and the reciprocal SO_4^{2-} depletion factor f^{-1} (SO_4^{2-}) (with respect to Na^+) in seawater if mirabilite ($Na_2SO_4 \cdot 10H_2O$) is progressively precipitated and instantaneously removed (straight line). For definition of depletion factors f see text. Data points refer to raw winter aerosol values from Halley Bay (HB), Dumont D'Urville (DDU), and Neumayer (NM) with $Na^+ > 300$ ng m^{-3} (in order to minimize the effect from unknown NSS-SO_4^{2-} contributions not considered here) and to Cl^- to Na^+ mass ratios between 3 and 0.5 to take account of analytical outlyers.

annual sea ice and air temperature cycles is thus expected to confine the most probable occurrence of surface brine formations to the winter half year (see also Figure 7). It is expected therefore that the SO_4^{2-} depletion factors derived above are not commonly applicable for the open water season (i.e., mid to late summer depending on the position of the station). This may explain the relatively low SO_4^{2-} depletion factor f in aerosol and surface snow at DDU where the open water season is longer and the mean sea ice coverage is smaller if compared to the other stations. Applying the SO_4^{2-} to Na^+ reference ratio of 0.07 also for DDU midsummer samples (generally enhanced in sea salt) was found by *Minikin et al.* [this issue] to lead to a 20% overestimation of NSS-SO_4^{2-}. They assumed therefore that no significant SO_4^{2-} fraction occurs at DDU during that season. As addressed above, also f values in ice cores of the Weddell Sea sector where ice coverage is more persistent appear to be enhanced over their counterparts from the more easterly position in the Atlantic sector. No SO_4^{2-} aerosol data are presented by *Savoie et al.* [1993] from Marsh (62°S), which among the sites in question is least influenced by sea ice and where extremely high sea-salt concentrations prevail year-round. Inspection of the NSS-SO_4^{2-} data points they presented for Palmer (65°S) revealed, however, only relatively few negative values despite a rather high sea-salt level (3900 ng m^{-3}). Accordingly, for a given site at the coast, seasonally adjusted f values need to be established, for example, by considering the site specific temperature and sea ice climatology of the summer half year. The assumption, not confirmed yet, that sea ice brine provides the SO_4^{2-} fractionated particles suggests that sea ice constitutes the major sea-salt source for high latitude coastal Antarctica. This is because in that region almost all aerosol samples or ice core horizons responsible for the regularly occurring annual sea-salt maximum in winter appear to be significantly depleted in sea-salt SO_4^{2-}.

5. Conclusions

Atmospheric sea-salt loads at coastal Antarctic sites are characterized by an extremely large short time variability over all seasons and significantly lower concentrations at the Weddell Sea coast. The mean annual concentrations appear to be strongly influenced by site specific aspects. This includes the sampling site position with respect to the coastline and surface wind pattern, but also nonuniform sampling strategies and techniques. More effort is certainly needed here to achieve a better defined large particle sampling in order to improve the comparability of the results. Consequently, the site specific observations available are generally of questionable validity in giving a representative picture for a general use (e.g., in general circulation model (GCM) validations).

The main features common to all records at higher coastal Antarctic latitudes include, first, no echo of the seasonal sea ice cycle (e.g., of the respective offshore open water fraction). This is shown by the fact that (with one peculiar exception) at all sites the lowest sea-salt level occurs during summer. Consequently, the major source associated with strong winter sea-salt peaks appears to be not simply related to the common bubble bursting process operating at open water areas. A second common feature is a systematic, strong, depletion of sea-salt SO_4^{2-} in aerosol and snow samples of the winter seasons compared to bulk seawater. Here major unknowns still exist with respect to the seasonal as well as to the spatial occurrence of this phenomenon.

The latter finding, persistently ignored in most of the previous glacio-chemical studies in coastal regions, deserves further attention in order to obtain reliable winter NSS-SO_4^{2-} values. Thus evaluations of biogenic SO_4^{2-} ice core records may be significantly improved: in particular concerning their quantitative relationship to MSA as well as their (possible) intimate connection to sea-salt records through the spatio-temporal sea ice variability.

Although first laboratory experiments suggest that brine superimposed on sea ice is depleted in SO_4^{2-} and thus may constitute the hidden source for winter sea-salt aerosol, field experiments are still urgently needed to identify the controlling mobilization process to get the brine airborne. Confirmation of the proposed role of sea ice brine in the observed SO_4^{2-} fractionation would make the sea ice cover the dominating sea-salt source (at least) with respect to coastal Antarctic snow fields with far reaching implications for the interpretation of the respective long term ice core records.

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