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https://escholarship.org/uc/item/73g5058q

Journal

Journal of Atmospheric Chemistry, 14(1-4)

ISSN

0167-7764

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Publication Date

1992-04-01

DOI

10.1007/bf00115233

Copyright Information

Peer reviewed

Nitrogen and Sulfur Species in Aerosols at Mawson, Antarctica, and Their Relationship to Natural Radionuclides

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ABSTRACT. High volume aerosol samples were collected continuously at Mawson, Antarctica (67°36'S, 62°30'E), from February 1987 through October 1989. All samples were analyzed for Na^+, Cl^-, $SO_4^=$, NO_3^-, methanesulfonate (MSA), NH_4^+, [7]Be, and [210]Pb. The annual mean concentrations of many of the species are very low, substantially lower than even those over the relatively pristine regions of the tropical and subtropical South Pacific. The concentrations at Mawson are comparable both in magnitude and in seasonality to those which have been measured in long term studies at the South Pole and at the coastal German Antarctic research station, Georg von Neumayer (GvN). This comparability suggests that the aerosol composition may be relatively uniform over a broad sector of the Antarctic. The concentrations of most of the species exhibit very strong and sharply-defined seasonal cycles. MSA, non-sea-salt (nss) $SO_4^=$ and NH_4^+ all exhibit similar cycles, with maxima during the austral summer (December through February) being more than an order of magnitude higher than the winter minima. The limited [7]Be data appears to exhibit a similar cycle. Although nitrate and ^{210}Pb also exhibit relatively high concentrations during the austral summer, their cycles are far more complex than those of the previous species with indications of multiple peaks. As expected, the concentration of sea-salt (as indicated by Na^+ and Cl^-) peaks during the winter. The results from multiple variable regression analyses indicate that the dominant source of nss $SO_4^=$ is the oxidation of dimethylsulfide (DMS) which produces MSA and nss $SO_4^=$ in a ratio of about 0.31 (about five times higher than that over the tropical and subtropical oceans). However, a very significant fraction (about 25%) of the nss $SO_4^=$ is associated with NO_3^-. The seasonal cycle of NO_3^- is similar to that of ^{210}Pb and distinctly different from that of [7]Be and MSA. These results indicate that the major source of NO_3^- over Antarctica is probably continental as opposed to stratospheric or marine biogenic.

Key words. Antarctica, aerosol particles, ice, biogeochemical cycles, sulfate, nitrate, methanesulfonate, lead-210, beryllium-7, sea-salt.

1. Introduction

Despite the importance of nitrogen and sulfur species to numerous areas of the atmospheric sciences, many aspects of the atmospheric sulfur and nitrogen cycles are still poorly understood. The spatial distributions and temporal variations in the strengths of the natural sources are still not well quantified. Our knowledge of some of the important inter-species transformations in the unpolluted atmosphere is also inadequate. This lack of understanding of the natural cycles stems in part from the relatively few measurements which have been made in the pristine regions of the earth. Over most of the northern hemisphere, where 90 to 95% of the anthropogenic sulfur and nitrogen oxides are emitted (Hameed and Dignon, 1988), it is frequently difficult, if not impossible, to determine whether or not anthropogenic emissions have had a significant impact in a given region during a particular study period.

In contrast, the relatively unpolluted areas in the southern hemisphere, such as the

Antarctic, provide an opportunity to study the natural cycles with minimal complications from anthropogenic materials. For more than a decade, studies of the vertical profiles of dissolved and particulate species in Antarctic snow and ice have been conducted to glean information about the past history of atmospheric composition and climate. However, the interpretation of this extensive data set is ambiguous because of a lack of understanding of the complex processes involved in (1) the atmospheric transport and deposition of the various constituents to the Antarctic ice sheet and (2) the changes in the chemistry of the ice and snow after it has been deposited. Without a clear understanding of the relationships between snow composition and atmospheric chemistry, the interpretation of these trends will continue to be questionable. Because no concurrent atmospheric samples were collected and analyzed over the course of the past tens of thousands of years, it is clearly impossible to verify the interpretation of the long-term ice core records. However, if recent seasonal and multi-year cycles (or trends) in the atmosphere are reflected in the recent ice and snow strata, then one would certainly have more confidence in the interpretation of the deeper profiles.

The objective of the current study was to further our understanding of the seasonal cycles and probable sources of the major sulfur and nitrogen species in aerosols over Antarctica. Toward that objective, we have been collecting bulk aerosol samples at Mawson, Antarctica, since February 1987. These samples are analyzed to determine the atmospheric concentrations of:

1) sodium from which the sea-salt concentrations are calculated;
2) non-sea-salt (nss) $SO_4^=$ which is produced from the oxidation of SO_2 that is derived primarily from anthropogenic combustion sources, from volcanoes and from the oxidation of reduced organic sulfur gases emitted from the ocean;
3) MSA (methanesulfonate), an atmospheric oxidation product of DMS (dimethyl sulfide) which is produced by biological sources in the ocean;
4) NO_3^-, derived from the oxidation of NO and related species that are produced by anthropogenic combustion sources (including biomass burning) and also from natural sources - principally soil emissions, lightning, and stratospheric processes;
5) NH_4^+, derived from continental and oceanic sources;
6) ^7Be, (half-life = 53.6 d) a tracer for transport from the stratosphere and upper troposphere where it is produced from the spallation of nitrogen by cosmic rays;
7) ^{210}Pb, a tracer for air masses that have recently been in convective contact with continental land masses since it is a decay product of ^{222}Rn (half-life = 3.8 d) for which the overwhelmingly dominant source is emission from soils.

2.   Experimental Procedures

The high volume bulk aerosol sampler was installed at Mawson (Fig. 1) with the assistance of the Australian National Antarctic Research Expeditions (ANARE). Ambient air is pumped through a short duct into the building where all of the sampling apparatus is located. The filter holder is mounted in a "clam shell" housing.

For sample collection, air is continuously drawn through 20x25 cm Microdon (Freudenberg, West Germany) filters at a nominal flow rate of 50 m^3h^{-1}. The actual flow rates are determined by measuring the pressure drops across a calibrated orifice system attached to the pump outlet. Nominal weekly sampling periods yield sampled air volumes of about 8500 m^3. Microdon filters consist of polycarbonate microfibers covered on both sides

with mats of PVA/PVC or polypropylene non-woven fleece. Results from tests run at the Department of Energy indicate that these filters have a collection efficiency of essentially 100% for test particles larger than about 0.2 μm diameter. Their minimum efficiency is 87% for particles between 0.07 and 0.10 μm diameter. A blank is taken after every third sample; a blank is handled in the same way as a sample filter except that it has had no air drawn through it. Periodically, batches of samples and blanks are returned to the United States for chemical and radionuclide analyses.
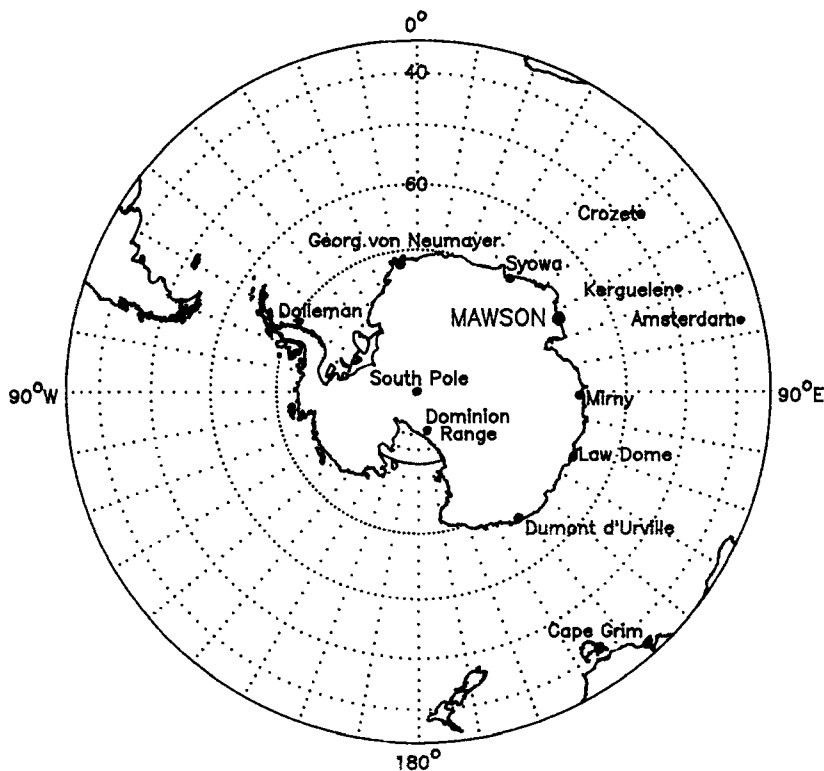

Figure 1. Map of Antarctica showing the locations of some of the major stations.

The chemical analyses are performed at the University of Miami. For analysis of the water soluble species, a one-eighth section of each filter is first wetted with 1 mL of ethanol and then extracted with 30 mL of Milli-Q water (18 Mohm cm) in three separate aliquots of 10 mL each. Nitrate, sulfate, chloride and MSA concentrations in the extract are determined to within ±5% by ion chromatography. Sodium is measured to within ±2% by flame atomic absorption and NH_4^+ to within ±5% by automated colorimetry. Non-sea-salt (nss) sulfate is the difference between total sulfate and sea-salt sulfate, the latter being calculated as total sodium times 0.2517 (the sulfate:sodium ratio in bulk seawater). As discussed elsewhere (Savoie et al., 1989a), the nitrate values reported here are for total inorganic nitrate, i.e. particulate nitrate plus gaseous HNO_3.

Although ^7Be and ^{210}Pb are produced in the gas phase, they are rapidly scavenged by particulate material in the atmosphere and, as a consequence, are efficiently collected on the filters used in this study. The radionuclides are measured at the Department of Energy using a well-type GeLi detector. Because of the long storage period forced by the winter-over, there is often a large decrease in the concentration of ^7Be. In many samples the activity is so low as to be unmeasurable.

Our constant concern about the possibility of contamination from local sources of pollution is especially great at this site because the samplers are continuously active (i.e., there is no gating of the system on the basis of wind direction, CN counts or any other condition). However, contamination does not appear to be a problem for the species that we study. Samples collected during periods of calm, when filters sometimes would have a light grey tint, yielded concentrations that were essentially identical to those obtained from pristine filters. This was true even for filters collected during the Austral winter, when the ambient concentrations are normally extremely low. This result is consistent with the fact that the clear-air (homogeneous) conversion rates for SO_2 and NO to $SO_4^=$ and NO_3^- are relatively slow, especially during winter when photochemical processes will be reduced due to low insolation. Hence, emissions from local sources would not be converted to aerosols rapidly enough to have a significant impact at the sampling site.

We regard our NH_4^+ data to be preliminary until we can establish more stringent procedures to control possible contamination (for example, by the absorption of NH_3 that is emitted by the human body). Nonetheless, our data suggest that contamination is not a major problem. The best evidence is the fact that the values that we measure are very consistent from sample-to-sample and blank-to-blank even during the periods when concentrations are very low.

3.   Meteorology and Sea-Ice

Because the meteorology and the extent of sea-ice in the proximity of Mawson are vital to our understanding of the potential sources and atmospheric transport of the particulate species, we begin with brief descriptions of their pertinent features. For more detail, an excellent review of the surface meteorology over Antarctica is presented by Parish (1988).

The single most dominant meteorological feature over Antarctica is the air flow resulting from the gravity-forced drainage of radiatively cooled air. This phenomena results in a fairly consistent pattern of air flow. Surface cooling creates a low level inversion from the surface up to several hundred meters altitude which persists over nearly the entire continent. The surface winds, i.e. the winds below the inversion, tend to be from the elevated interior plateau and down the marginal ice slopes (Parish, 1988). Even at the coast, the dominant winds tend to be from the interior of the continent rather than from the ocean. At Mawson, for example, the surface winds exhibit a remarkable directional stability, being from inland Antarctica more than 80 percent of the time (Gras and Adriaansen, 1985; Ito, 1989; Streten, 1963). As a consequence, the nature of the aerosol chemistry in the coastal regions of Antarctica tends to be more continental than marine.

Clearly, the persistent surface-level outflow from Antarctica must be balanced by inflow at higher altitudes. This inflow is believed to be responsible for the transport of most of the aerosol particles and/or their precursors to the Antarctic continent (Shaw, 1988). Results from simple models (Egger, 1985; James, 1989) indicate that the low-level outflow induces a cyclonic vortex in the upper troposphere. If there were no meteorological perturbations,

this vortex would be much stronger than observed and the surface drainage flow would die out within a few days. James (1989) concluded that the polar vortex is most likely disrupted by strong interactions with decaying mid-latitude depression systems which spiral toward the pole. The spread of mid-latitude air into the polar region yields a net reduction in the cyclonic vorticity of the circumpolar vortex and allows the low-level outflow to persist.

The extent of ice coverage off the coast of Mawson effectively determines the site's proximity to the open ocean. Hence, one might expect that it would play a major role in determining the concentrations of some of the major aerosol components and/or their precursors, particularly those of marine origin. Ice coverage near Mawson exhibits a strong seasonal cycle. Satellite imagery for this period shows ice at a minimum in February. At this time, there is little to no sea-ice in the vicinity and Mawson is within a few kilometers of the open ocean (W. Betts, ANARE, personal communication). At its maximum in October, the ice extends to about 60°S, placing Mawson about 700 km from open water.

4.   Mean Concentrations and Seasonal Cycles

Because of the large seasonal variations exhibited by most species, we present the mean results for only the first two complete years: February 20, 1987, to February 20, 1989. These means are shown in Table 1 along with comparative data from several other locations.

Table 1. Mean concentrations of the constituents measured at Mawson and comparative data from several other locations.

CONSTITUENT	UNITS	MAWSON	NEUMAYER[a]	SOUTH POLE	CAPE GRIM	AMERICAN SAMOA
Sodium	ng m^{-3}	85.	370.	19.[b]	3300.[f]	5100.[d]
Chloride	ng m^{-3}	113.	.	24.[b]	.	.
Nitrate	ng m^{-3}	27.	36.	.	.	110.[d]
Nss Sulfate	ng m^{-3}	90.	71.[**]	83.[b]	280.[f]	360.[d]
MSA	ng m^{-3}	20.	.	.	18.[f]	26.[d]
Ammonium	ng m^{-3}	21.	.	.	.	25.[i]
^{210}Pb	fCi m^{-3}	0.85	0.84	1.13[e]	3.7[c]	1.5[h]
^{7}Be	fCi m^{-3}	162.[*]	100-150	114.[e]	96.[c]	71.[c,g]

[*] The mean for ^{7}Be is biased because of the very few data available for the austral summer period (a consequence of the previously noted long winter-over sample storage). Judging from the available data, the actual mean may be slightly lower; [**] This value is based on the annual mean total sulfate concentration (164 ng m^{-3}) calculated from the means given for November to March (278 ng m^{-3}) and April to October (82 ng m^{-3}) and the mean sodium concentration (369 ng m^{-3}) estimated from the reported mean sea-salt concentration of 1.2 μg m^{-3}; [a]Wagenbach et al. (1988); [b]Tuncel et al. (1989); [c]Feeley et al. (1988); [d]Savoie et al. (1989b); [e]Larsen (1990, private communication); [f]Ayers et al. (1986); [g]Savoie et al. (1989c); [h]Turekian et al. (1989); [i]Savoie et al. (unpublished data, 1990).

4.1.   SODIUM AND CHLORIDE

The "continentality" of the surface air at Mawson is most dramatically indicated by the extremely low sodium concentrations which average only 85 ng m^{-3} (Table 1). This mean is only about four times higher than that at the South Pole. Although the mean sodium concentration at GvN is a factor of four higher than that at Mawson, it is still well below the level that one might expect at a coastal location. Normally, sodium concentrations over the open ocean are about an order of magnitude higher, 3000-5000 ng m^{-3}. The seasonal cycles of sodium and chloride are quite different from those of the other species in that the concentrations are highest during the winter (Figure 2). However, even at their peak, the concentrations of sodium (about 300 ng m^{-3} or less) are far less than those expected of a coastal site. A similar sea-salt seasonality occurs at the South Pole (Tuncel et al., 1989) and at GvN (Wagenbach et al., 1988).
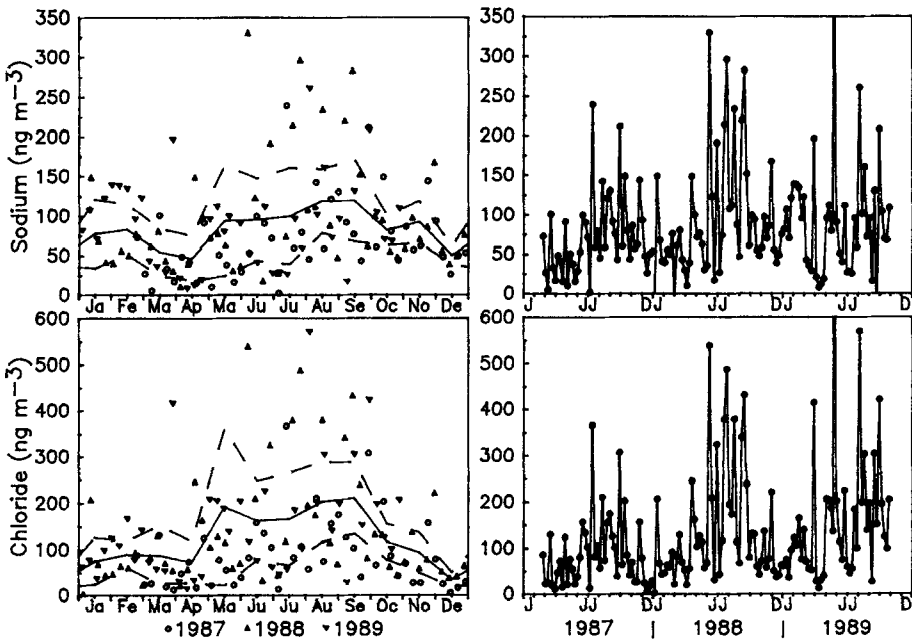

Figure 2. The graphs on the left illustrate the composited seasonal cycles of sodium and chloride showing the monthly mean concentrations (solid line) and their 95% confidence limits (dashed lines). The graphs on the right show the actual time series of the weekly-average concentrations.

The generally low sodium concentration and its seasonal cycle suggest that the katabatic flow at this site prevents a strong transport of sea-salt directly to Mawson by on-shore winds. This flow is apparently strong enough to completely negate any seasonal cycle that one might have expected based on the seasonal fluctuation in the distance to the open ocean. Indeed, the seasonality of sea-salt at Mawson is probably a consequence of the same phenomenon that yields the comparable cycle over the interior. This seasonality has been attributed to the

generally enhanced storm activity over the oceanic regions surrounding Antarctica during the winter. On occasion, these storms penetrate to the inland plateau and the sea-salt concentrations increase dramatically (Shaw, 1988) to produce the "sodium storms" discussed by, among others, Bodhaine et al. (1987). Although the impact of katabatic flow on reducing the direct transport of marine aerosols to Mawson is most dramatic for relatively large sea-salt particles, one might expect a similar, but smaller, effect for other ocean-derived constituents, e.g. MSA and nss $SO_4^=$ (and their precursors).

4.2. METHANESULFONATE

Overall, the results from our studies and other recent work suggest that the MSA concentrations at Mawson may be representative of those over a broad area of the Southern Ocean, both in absolute magnitude and in seasonal variation. The mean MSA concentration at Mawson is 20 ng m^{-3}. MSA exhibits a very strong annual cycle that peaks in the Austral summer (Fig. 3). The highest monthly mean concentrations, typically in the range 30-60 ng m^{-3} occur from December through March. During the winter, the concentrations are about 15 times lower with means of 2-3 ng m^{-3} from June through August.

Minikin and Wagenbach (1990) present the results from quasi-continuous measurements made at GvN since 1984. These are the only other long-term MSA measurements made over Antarctica. The concentrations and seasonal cycle at GvN are similar to those at Mawson with mean MSA concentrations decreasing from about 60 ng m^{-3} during the summer to baseline concentrations of 3 ng m^{-3} during the winter.

The only comparable multi-year record in the high-latitude southern hemisphere is that from Cape Grim, Tasmania (40°41'S, 144°41'E, Ayers et al., 1986, 1991). Both the mean MSA concentration and the seasonal variations at Cape Grim are nearly identical to those at Mawson: annual mean, 18 ng m^{-3}; summer mean, 40-50 ng m^{-3}; winter mean, 3 ng m^{-3} (Ayers et al., 1986). The MSA data reported for Cape Grim by Ayers et al. (1991) was for the submicron fraction only. While those concentrations were lower by about a factor of two than the total concentrations reported by Ayers et al. (1986), they exhibited a similar seasonal cycle.

Comparable MSA concentrations and a similar amplitude in the seasonal cycle have also been reported for Norfolk Island (29°05'S, 167°59'E) which is located much farther north (east of Australia and northwest of New Zealand) (Savoie et al., 1989b). Here, the annual mean MSA concentration is 24 ng m^{-3}; this value is about 20%-30% higher than, but not significantly (95% confidence level) different from, those at Mawson and Cape Grim. The monthly mean concentrations at Norfolk range from 40-75 ng m^{-3} from November through January to 5-6 ng m^{-3} during June and July (Savoie et al., 1989b). However, the peak in the MSA cycle occurs about a month earlier than those at the higher latitude sites, in December rather than January.

Short term measurements made in the Antarctic region are consistent with the cycles present in the long term data sets. A few shipboard measurements were made in the Antarctic region (the Drake Passage and Gerlache Straits) during March and April, 1986 (Berresheim, 1987; Pszenny et al., 1989). The resultant data yield mean MSA concentrations of 32 and 18-22 ng m^{-3}, respectively, compared to the March and April means of 36 and 19 ng m^{-3} at Mawson. Samples collected aboard aircraft in the marine boundary layer west of Tasmania during December 1986 (Berresheim et al., 1990) yielded typical MSA concentrations of 44 ng m^{-3} (about midway between the December and January means of 30 and 62 ng m^{-3} at Mawson).
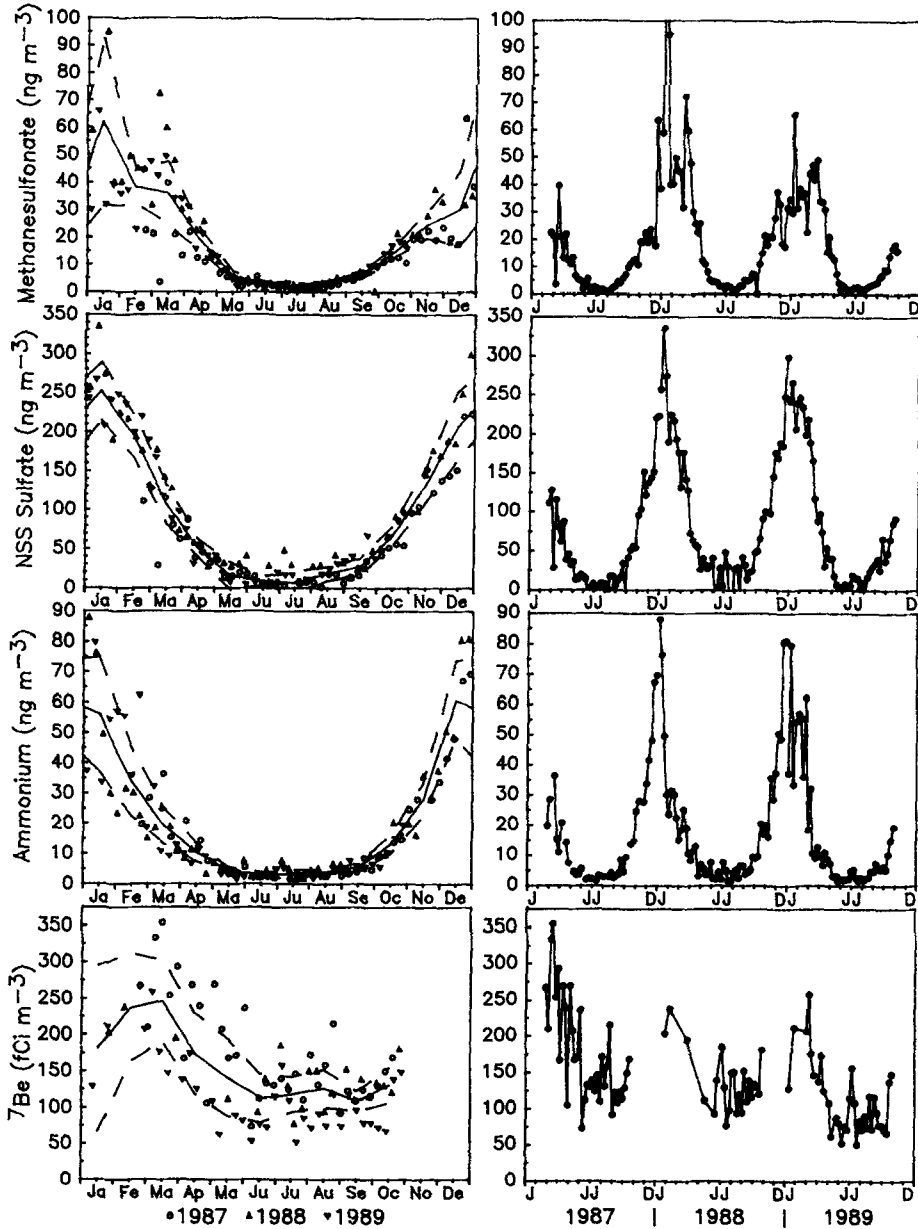
Figure 3. The graphs on the left illustrate the composited seasonal cycles of methanesulfonate, non-sea-salt (nss) sulfate, ammonium, and beryllium-7 showing the monthly mean concentrations (solid line) and their 95% confidence limits (dashed lines). The graphs on the right show the actual time series of the weekly-average concentrations.

Dimethylsulfide measurements provide additional evidence for the large-scale spatial consistency of the marine biogenic sulfur source. Based on samples collected over a 20-month period at Cape Grim, the MSA and atmospheric DMS seasonal cycles appear to be tightly coupled (Ayers et al., 1991), exhibiting very similar amplitude, phase and shape. The DMS concentrations ranged from 0.5-1 nmole m^{-3} in the winter to 6-10 nmole m^{-3} during the summer. This seasonal cycle is essentially identical to that measured at Amsterdam Island (37°50'S, 77°31'E) about 5600 km to the west (Nguyen et al., 1990). Samples collected from January through August 1984 and from March 1987 through February 1988 yield monthly mean DMS concentrations ranging from 1.5-3 nmole m^{-3} from June through October to 5.6-11.3 nmole m^{-3} from November through March. The few shipboard measurements made in the Drake Passage and Gerlache Straits during March and April, 1986, yield a mean of 4.4 nmole m^{-3} (Berresheim, 1987) compared to the March and April means of 7.2 and 4.8 nmol m^{-3} at Amsterdam Island. However, boundary layer aircraft measurements west of Tasmania during December 1986 are rather low by comparison, typically 0.6 to 2.5 nmol m^{-3} (Berresheim et al., 1990). The timing and magnitude of the seasonal cycles of DMS in the atmosphere are in general accord with those in the water column (Berresheim, 1987; Deprez et al., 1986; Gibson et al., 1990; Nguyen et al., 1990); measurements of the latter, however, are much more limited both in number and in spatial and temporal coverage.

The annual mean MSA concentration at Mawson and perhaps over a vast area of the southern ocean is 25-30% lower than that at American Samoa in the tropical South Pacific and 50% lower than that at Fanning Island (44 ng m^{-3}) in the equatorial Pacific (Saltzman et al., 1985, 1986a). However, these differences may not reflect the actual differences in the DMS fluxes from the ocean. First, the removal processes and rates may be substantially different in the two regions. Second, the percentage of the DMS that is oxidized to MSA may be substantially higher at the high latitude sites. Our assessment of the MSA/nss $SO_4^=$ ratio resulting from the oxidation of DMS in the Antarctic region is discussed later.

4.3.   NON-SEA-SALT SULFATE

Over the Antarctic continent itself, the nss $SO_4^=$ concentrations appear to be reasonably consistent from one location to another. The two-year mean nss $SO_4^=$ concentration at Mawson is 90 ng m^{-3} (Table 1). This value is only 27% higher than the 3-year mean (1984-1987) at GvN, 71 ng m^{-3} (Wagenbach et al., 1988). Since the time period of the GvN data does not significantly overlap that at Mawson, the difference may reflect a significant temporal variation. However, at least part of the difference may be attributable to the fact that Wagenbach et al. reported long periods of negative nss $SO_4^=$ values that were usually associated with very high sea-salt concentrations during the winter. Tuncel et al. (1989) have recently reported the results from eight years of study at the South Pole. The mean nss $SO_4^=$ calculated from their data (83 ng m^{-3}) is only about 10% lower than that at Mawson.

The extremely strong seasonal cycle at Mawson (Fig. 3) is also consistent with that at the other sites. At Mawson, the nss $SO_4^=$ concentrations during the summer are 30-40 times higher than those during the winter, 210 and 250 ng m^{-3} during December and January versus 8.2 and 6.5 ng m^{-3} during June and July. Judging from the plots presented by Wagenbach et al. (1988), the peak nss $SO_4^=$ values at GvN are comparable. We cannot easily compare our winter data with GvN because of their numerous negative nss $SO_4^=$ values. Nonetheless, the GvN nss $SO_4^=$ concentrations were certainly extremely low during the winter. Tuncel et al. (1989) present the South Pole data only as "summer" and "winter"

averages without stating explicitly the months which were included in each season. The summer mean nss $SO_4^=$ concentration at the South Pole was 133 ng m^{-3} versus a winter mean of 22 ng m^{-3}. Taking "summer" to extend from October through March, the "summer" mean at Mawson (160 ng m^{-3}) is only about 20% higher than that at the South Pole and the "winter" mean (21 ng m^{-3}) is nearly identical. Measurements of nss $SO_4^=$ at Gipps Ice Rise on the east coast of the Antarctic peninsula (Dick, 1990) during the 1984/85 summer season yield a comparable mean of 172 ng m^{-3}; again, however, the specific sampling period was not explicitly stated.

Comparisons with the nss $SO_4^=$ concentrations measured at and near the coastal site at Cape Grim and aboard a ship near the coast of Antarctica are more problematical. It is difficult to assess the nss $SO_4^=$ concentrations at Cape Grim because of the high atmospheric concentrations of sea-salt sulfate (Ayers et al, 1991). The annual mean nss $SO_4^=$ concentration (280 ng m^{-3}) measured by Ayers et al. (1986) from bulk filter samples is about 3 times higher than that at Mawson. In a later study, Ayers et al. (1991) collected size segregated samples and reported only the concentration in the submicron fraction in which sea-salt $SO_4^=$ has far less of an impact. The concentration in this fraction ranged from about 30 ng m^{-3} during the winter to 150-300 ng m^{-3} in mid-summer. If the submicron fraction contains a large majority of the total nss $SO_4^=$ at Cape Grim (as has generally been found elsewhere), then these concentrations are reasonably consistent with those measured over Antarctica. They are also more consistent with those measured aboard aircraft in the marine boundary layer near Cape Grim during December 1986, 64-210 ng m^{-3} (Berresheim et al., 1990). The few concentrations measured in the Drake Passage and Gerlache Straits during March and April, 1986 (Berresheim, 1987; Pszenny et al., 1989), average 29 and 34 ng m^{-3}, much lower than the Mawson March and April means of 110 and 50 ng m^{-3}.

The mean nss $SO_4^=$ concentration at Mawson is relatively low compared to other ocean regions. For example, in the equatorial and central South Pacific (where continental sources are not important), annual nss $SO_4^=$ concentrations are in the range of 200 to 700 ng m^{-3} (Savoie and Prospero, 1989; Savoie et al., 1989b) and are relatively uniform all year long. At Mawson, the concentrations reach comparable levels only from December through February.

4.4. AMMONIUM

The two-year mean NH_4^+ concentration at Mawson is 21 ng m^{-3}. The strong seasonal cycle in NH_4^+ is similar to that for nss $SO_4^=$. The monthly mean concentrations vary by a factor of 20 from 3-4 ng m^{-3} during June through August to 50-60 ng m^{-3} during December and January. Our ammonium measurements are unique for the Antarctic except for four measurements reported by Gras (1983). Gras measured NH_4^+ concentrations of 37 and 47 ng m^{-3} near the New Zealand station Vanda during November and December 1980 and concentrations of 58 and 43 ng m^{-3} at the South Pole during December. These values are clearly within the range of our November and December means of 28 and 61 ng m^{-3} at Mawson.

The mean NH_4^+ concentration at Mawson is similar to that which we measured at American Samoa during November 1990 (Table 1). For comparison, the NH_4^+ concentrations near the coast of Washington average about 110 ng m^{-3} (Quinn et al., 1988) which is comparable to those from our preliminary results at Midway (96 ng m^{-3}), Norfolk Island (129 ng m^{-3}) and Barbados (92 ng m^{-3}). An intermediate average (46 ng m^{-3}) was measured at Rarotonga in the central South Pacific during the same November 1990 period

that the American Samoa data were obtained.

4.5. NITRATE

The mean nitrate concentration at Mawson is 27 ng m^{-3} (Table 1). The only other long term measurements of this constituent in the Antarctic region were made at GvN where the 1984-1987 mean concentration, 36 ng m^{-3}, is about 33% higher (Wagenbach et al., 1988). As with nss $SO_4^=$, the difference may reflect a significant temporal variation. Although Tuncel et al. (1989) indicated that nitrate analyses were performed on their South Pole samples, no nitrate data were presented.

Although there is a well-defined seasonal cycle in the NO_3^- concentration (Fig. 4), the cycle is more complex than that of most of the other constituents and it varies significantly from year to year. The lowest monthly means (8.5-9.5 ng m^{-3}) occur during April and May, but the concentrations are consistently around or below 10 ng m^{-3} from mid-March through June. This seasonal range is the lowest that we have measured anywhere. In sharp contrast to those of the other ionic species, the concentrations of nitrate begin to increase during July and exhibit a peak during August. The concentrations then remain at relatively high levels until they begin to decrease in March. Although the seasonal cycle is well-delineated and consistent, the concentrations during a given period can vary from year to year. Note, for example, that the concentrations during January and February, 1988 (mean=27 ng m^{-3}), are substantially lower than those during the same period of 1989 (mean=44 ng m^{-3}).
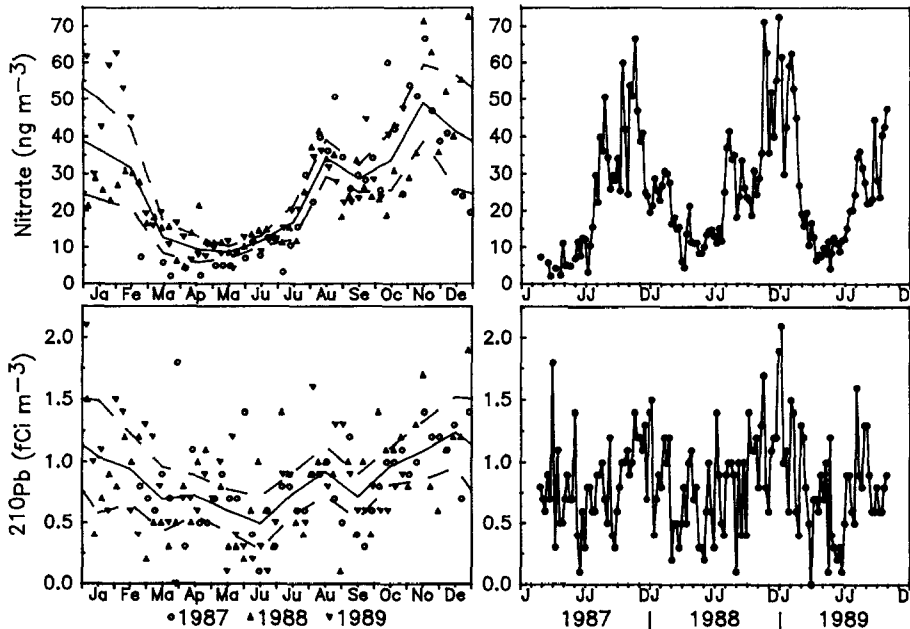

Figure 4. The graphs on the left illustrate the composited seasonal cycles of nitrate and lead-210 showing the monthly mean concentrations (solid line) and their 95% confidence limits (dashed lines). The graphs on the right show the actual time series of the weekly-average concentrations.

A similar seasonal cycle and marked year-to-year variations in the peak concentrations are also evident at GvN (Wagenbach et al., 1988). Their somewhat higher mean nitrate concentration may well be a consequence of these interannual variations. However, judging from their plot, the period of low concentrations at GvN coincides with that at Mawson and the concentrations during that period are all less than about 15 ng m^{-3}. In contrast, Pszenny et al. (1989) reported a mean concentration of 37 ng m^{-3} from several shipboard measurements during April, 1986, in the Drake Passage and Gerlache Strait.

The mean concentrations at Mawson and GvN are factors of three to four lower than those which we have measured at stations in the tropical and subtropical region of the central South Pacific, where continental impacts are expected to be quite low. The annual means at Rarotonga and Funafuti are nearly identical to that given in Table 1 for American Samoa, 110 ng m^{-3} (Savoie et al., 1989b,c; Prospero and Savoie, 1989). Clearly then, the "background" nitrate concentration in the Antarctic is substantially lower than the "background" values previously reported for the lower latitude South Pacific. Even the peak concentrations in the annual cycle, with higher values mostly in the range 30-70 ng m^{-3}, are well below the central South Pacific mean.

4.6.   BERYLLIUM-7

^{7}Be is a tracer of input from the stratosphere and upper troposphere where it is produced by the cosmic-ray induced spallation of nitrogen. The data for ^{7}Be at Mawson are somewhat limited because of the large gap in the summers of 1987-1988 and 1988-1989. These samples were delayed a very long time and the activity was too low to count in most samples. Nonetheless, the data suggest that there is a very significant seasonal cycle with the maximum in the late summer, February-March (Fig. 3). The monthly means during these months (240-250 fCi m^{-3}) are about double those from May through October (110-140 fCi m^{-3}). If these low concentrations continue into November and December, then the annual mean concentration at Mawson would be about 150 fCi m^{-3} which is only 6% lower than the mean which we present in Table 1.

The seasonal cycle at Mawson and our preliminary extension of low values into November and December are consistent with the data presented for GvN. Recently, Lambert et al. (1990) have presented the results from long-term monitoring at Dumont d'Urville (66°40'S, 140°01'E). At that site, the monthly-averaged ^{7}Be concentrations from 1977 through 1981 exhibited much less seasonal variation, ranging from about 150 fCi m^{-3} in July to 200 fCi m^{-3} from December through March. Although the seasonal cycle appears to be considerably less than that at Mawson, the general levels at the two coastal sites do not differ substantially. The summer level at Dumont d'Urville is about 20% lower and the July mean is about 10%-35% higher than those at Mawson.

Another stratospheric/upper tropospheric tracer ^{32}P exhibited a much stronger seasonal cycle at Dumont d'Urville, being a factor of about two higher during the summer (2.7-3 fCi m^{-3} from October to April) than during the winter (1.6 fCi m^{-3} during June and July). The concentration of ^{32}P with a half-life of only 14.3 days (a factor of about 4 smaller than that of ^{7}Be) should be more strongly dependent on the recency of the injection of stratospheric and/or upper tropospheric air. That the cycle of ^{32}P is consistent with but stronger than that of ^{7}Be indicates that the transport from these high altitude sources occurs rather rapidly and/or over a reasonably short distance.

At the South Pole, the peak concentrations of ^{7}Be occur during December-January and, as at Mawson, with concentrations that are about double those from April through

September (based on data from 1970 through 1989, R. Larsen, personal communication, 1990).

Our data also indicate that there is a substantial year-to-year variation in the mean levels of ^{7}Be. Note that there has been a fairly substantial and consistent decrease at Mawson from 1987 through 1989. Hence, caution must be used in directly comparing the mean concentrations at Mawson with those at other locations where the measurements were made during different periods. At the South Pole, for example, the mean for 1987-1989 (81 fCi m^{-3}) is 30% lower than the full 20-year average (114 fCi m^{-3}) presented in Table 1. Clearly, this variability would markedly affect any inter-station comparison. However, the 1987-1989 results do suggest that the mean concentration at the South Pole is significantly lower than that at Mawson.

4.7. LEAD-210

^{210}Pb is important as a tracer of the transport of material from continental sources. The record for ^{210}Pb at Mawson (Fig. 4) is much noisier than that for ^{7}Be, primarily due to the poor counting statistics. However, the two year mean at Mawson (0.85 fCi m^{-3}) is nearly identical to that reported for GvN (0.84 fCi m^{-3}, Wagenbach et al., 1988). The mean concentration at the South Pole is also similar. The South Pole mean given in Table 1 is for data collected from 1974 through most of 1989. While that mean is about 30% higher than those at Mawson and GvN, the 1987-1989 mean (0.73 fCi m^{-3}) is 13% lower. The long-term ^{210}Pb record at Dumont d'Urville, Terre Adelie coast, shows a general decrease in concentration from 1.1 fCi m^{-3} in 1969 to 0.68 fCi m^{-3} in 1986 (Lambert et al., 1990). However, there is too much scatter in the trend to predict what the levels are likely to be during the same time period as our data. The 1986 mean at Dumont d'Urville was actually higher than those from 1983 through 1985. For the moment, we can only suggest that the levels are comparable. The general levels over Antarctica are a factor of about 3-4 lower than those at Cape Grim where there is often direct transport from Australia and/or Tasmania itself.

Wagenbach et al. (1988) suggest that there is no clear annual cycle at GvN. However, our data, when averaged on a monthly basis over several years, suggest that there is a significant seasonal cycle (Fig. 4) which is similar to that of nitrate. The same type of averaging yields a similar seasonal cycle of ^{210}Pb at the South Pole. Given the noisy records, the ^{210}Pb cycles at these stations must be viewed with some caution. However, they are generally consistent with that obtained by similar averaging at Dumont d'Urville (Lambert et al., 1990) where about 400 values were averaged for each monthly mean. The lowest mean at that site occurred during March-April, with a maximum from November through February and, as at Mawson, a secondary maximum in August.

Latitudinal profiles of sea level ^{210}Pb and its precursor ^{222}Rn both exhibit minima between 40°S and 60°S (Polian et al., 1986; Lambert et al., 1990) during the summer. Yet, both exhibit similar cycles at Dumont d'Urville with summer maxima. These authors argue that, since ^{222}Rn has too short a half-life (3.8 days) to be transported through the stratosphere, the major transport path for these nuclides must be through the mid-to-upper troposphere. In addition, the short lifetime of ^{222}Rn requires that the transport from the continental sources be fairly rapid.

There has been substantial discussion recently of the so-called "radonic" storms which transport high concentrations of ^{222}Rn from South Africa to the subantarctic Indian Ocean (Polian et al., 1986; Balkanski and Jacob, 1990; Heimann et al., 1990). These storms are

most frequent during the winter, and the ^{222}Rn transport occurs primarily in the marine boundary layer. As a consequence, the surface level ^{222}Rn concentrations at Crozet, Amsterdam and Kerguelen Islands exhibit winter maxima which are clearly out of phase with those over Antarctica.

5.   Sources of Sulfur and Nitrogen

5.1.   NITRATE

The seasonal cycle of nitrate at Mawson is most similar to that of ^{210}Pb. This similarity suggests that a substantial fraction of the nitrate is associated with air masses that are transported from continental regions. In contrast, the nitrate cycle is distinctly out of phase with that of ^{7}Be. This divergence is most clearly seen in the data for early 1987. This feature argues against the hypothesis that the stratosphere or upper troposphere is a major source of nitrate or its precursors. The seasonal nitrate cycle is also quite different from that for MSA which suggests that biological sources in the ocean are not significant in this regard.

A continental source is consistent with recent studies that show that nitrate over the relatively pristine regions of the tropical South Pacific is most likely derived from sources in South America (Savoie et al., 1989c). The mean ^{210}Pb concentration at Mawson is only a factor of two lower than that at American Samoa whereas the mean nitrate concentration at Mawson is a factor of 3-4 lower. Hence, if a continental region is indeed the source of the nitrate over the tropical South Pacific, then it is not unlikely that one is also the major source of nitrate over Antarctica where the nitrate:^{210}Pb ratio is considerably lower.

Additional data further support the conclusion that a major continental source for nitrate is not unreasonable. The reasonably rapid transport of continental material to Antarctica is unequivocally documented by the levels of ^{222}Rn and ^{210}Pb which have already been discussed. Trace metal data and the inferred crustal dust concentrations from the South Pole (Tuncel et al., 1989, and references therein) indicate that particulate material is also transported from continental sources. Pollutant transport to Antarctica has frequently been discounted on the basis of the low levels of trace metals in the South Polar atmosphere. However, Boutron and Patterson (1987) reported that Pb has increased five-fold in the Antarctic atmosphere compared to the pre-industrial period and concluded that 80% of the total lead over the continent today is anthropogenic. "Black" carbon has also been measured in significant quantities at the South Pole (Hansen et al., 1988) even after the infrequent local contamination events were deleted. Notably, the seasonal cycle of "black" carbon at the South Pole is very similar to those of nitrate and ^{210}Pb at Mawson.

Australia could be the most important continental source. The distributions of mica, illite, and kaolinite in the sediments of the southwest Pacific have been attributed to the wind-borne transport of minerals from Australian deserts (Arrhenius, 1966; Griffin et al., 1968; Windom, 1975). Eolian transport of dust from Australia southeastward across the Tasman Sea to New Zealand is particularly well documented (Glasby, 1971 and references therein). Although the greatest potential for long-range transport from central Australia occurs during the austral summer (Theide, 1979), documented cases of substantial dust transport from Australia to southern New Zealand have occurred as early as November (Collyer et al., 1984). The trajectories and weather charts presented in the latter report indicate that the dust-containing air parcels would subsequently be transported to even higher latitudes. Loewe (1943) had previously reported that the highest incidence of dust

storms in New South Wales also occurs during the late austral spring and summer which coincides with the period of high nitrate concentrations at Mawson. Seasonally higher concentrations of nitrate and nss sulfate at Norfolk Island during the summer have also been attributed to the transport of material from Australia (Savoie et al., 1989b). Although it is likely that a significant portion of the current continental nitrate is anthropogenic, the major sources may well be natural, e.g. the oxidation of NO from soil emissions, from lightning, and from lightning-induced fires.

The conclusion that little, if any, of the nitrate is derived from the stratosphere is supported by the results from numerous past studies as well as by the differences in the seasonal cycles of nitrate and [7]Be at Mawson. Aircraft measurements by Hogan (1986) from October through December of three years indicated that ozone and aerosol concentrations over a wide geographic area of Antarctica are stratified into separate altitude layers. The author concluded that ozone exchange is vigorous above about 400 mb and that frequent aerosol exchange occurs at lower altitudes; however, stability in the mid-troposphere prevents mixing among these two levels. Furthermore, the maximum in the seasonal cycle of surface-level ozone at the South Pole occurs during the winter, June through August (Robinson et al., 1988), which corresponds to the minimum in the nitrate concentration. Additional evidence is provided in two recent review papers (Ito, 1989; Shaw, 1988). Legrand and Kirchner (1988) recently speculated that large nitrate-containing particles associated with polar stratospheric clouds may sediment into the troposphere. Since no downmixing is required, this process would result in an increase in nitrate in the lower troposphere without a concurrent increase in ozone. However, Iwasaka and Hayashi (1990) report that stratospheric aerosol enhancement, as revealed by lidar measurements at Syowa, occurs from June to September which is again during the period of the nitrate minimum.

Our conclusion that the primary source of nitrate at Mawson is continental clearly conflicts with that of Zeller et al. (1986) and others who suggest that nitrate in ice cores is related to solar activity. Instead, it tends to support the conclusions of Legrand and Kirchner (1990) and others who hold that the major nitrate sources are located in the troposphere.

5.2.   METHANESULFONATE AND NON-SEA-SALT SULFATE

Here, our major interest is the origin of the nss $SO_4^=$. Based on the MSA data, we would expect that a large fraction of the nss $SO_4^=$ is derived from oceanic sources of reduced sulfur, principally DMS. However, a more detailed analysis of our data indicates that a significant portion of the nss sulfate is associated with nitrate, suggesting that other sources are also important.

A plot of the MSA/nss $SO_4^=$ ratio and the nss $SO_4^=$ concentrations at Mawson as a function of time is shown in Figure 5 using 8-week running averages for smoothing. Note the apparent increase in the ratio as the summer progresses: ranging from roughly 0.15 at the beginning of the sulfate peaks to nearly 0.40 at the end. Interestingly, Ayers et al. (1991) noted a similar trend in submicron aerosols collected at Cape Grim, but with ratios that were lower by factors of about two. The discrepancy in the magnitude of the ratios found in the two studies is most likely a consequence of the differences in the size distributions of MSA and nss $SO_4^=$. Numerous studies (e.g. Saltzman et al., 1983, 1986b; Zhu et al., 1989; Pszenny et al., 1989; Pszenny, 1990; Howell and Huebert, 1990) have shown that the MSA particle size distribution extends over a larger particle size range than does that of nss $SO_4^=$. Consequently, the exclusion of the supramicron fraction (as done by Ayers et al.) will remove a much larger percentage of the MSA than the nss $SO_4^=$ and the MSA/nss $SO_4^=$ ratio

measured in the sample will be reduced accordingly. In fact, Ayers et al. indicated that their submicron MSA concentrations were a factor of about two lower than those from their bulk aerosol samples. The results from the cited studies further demonstrate that the size distributions of MSA and nss $SO_4^=$ frequently do not vary in concert with one another. Some of the short term fluctuations in the ratios reported by Ayers et al. may well be a consequence of these incongruous variations.
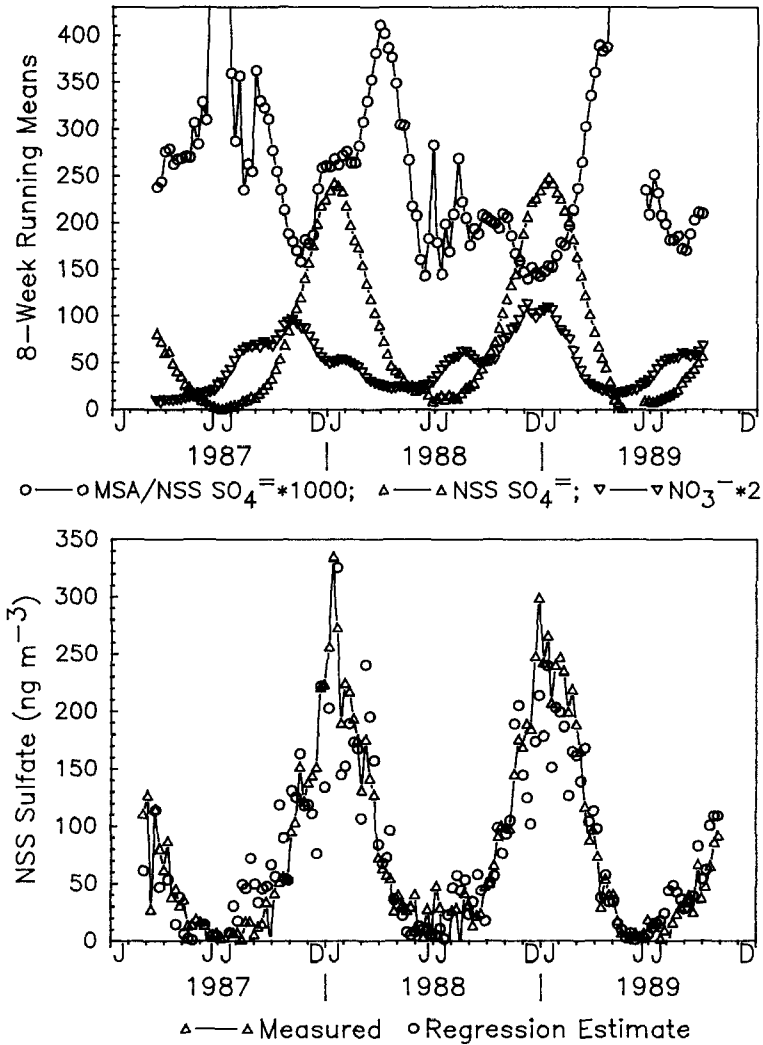

Figure 5. Plots of (a) the 8-week running means of the MSA/nss sulfate mass ratio and of the nss sulfate and nitrate concentrations and (b) a comparison of the measured weekly nss sulfate concentrations and those calculated from the regression equation with methanesulfonate and nitrate as the independent variables (see text for a discussion of the equation).

   Despite the discrepancy with the Cape Grim ratios, the seasonal trend in the ratio is clearly similar to that which we observe at Mawson, and it is the cause of this trend that needs to be evaluated. Even at their lowest, the ratios at Mawson are substantially higher than those of about 0.06-0.07 found in the warmer tropical and subtropical regions. Hynes et al. (1986) found that, in the oxidation of DMS by OH, the addition of OH increases in importance relative to H abstraction as the temperature decreases. Various authors have suggested that this temperature dependence is the cause of the higher MSA/nss $SO_4^=$ ratios found over high latitude regions. However, even beyond the initial OH attack, the reaction sequences are complex, and no studies have been performed to determine the effect of temperature on the relative concentrations of the final products. If the primary cause of the ratio variations were the simple temperature dependency of addition versus abstraction, the ratio should be lowest during the mid-summer (December through February) when the temperatures are highest. This is clearly not what is observed.

   A comparison of the plots in Figure 5a reveals that the low points in the ratio plot are associated with higher nitrate concentrations. Note particularly the depressed ratios associated with the nitrate peaks during October 1987 and December 1988-January 1989. These results indicate that the depressions in the MSA/nss $SO_4^=$ ratio could be a consequence of the input of $SO_4^=$ from an additional source and that the magnitude of this input might be directly related to the concentration of nitrate.

   A multiple variable regression of the nss sulfate data using nitrate and MSA as the independent variables yields the following equation:

$$\text{Nss } SO_4^= = 1.72 \times NO_3^- + 3.22 \times MSA - 23.6; \quad N=136, \quad r^2=0.82 \qquad (1)$$
$$\text{Std Error} \quad (0.19) \qquad (0.15)$$

where all of the concentrations are in ng m^{-3}. This equation indicates that the MSA/nss $SO_4^=$ ratio resulting from the oxidation of DMS is 0.31. The negative intercept is attributed to a "background" nitrate which has no nss sulfate associated with it. The equation is then appropriately rewritten as:

$$\text{Nss } SO_4^= = 1.72 \times (NO_3^- - 14) + 3.22 \times MSA \qquad (2)$$

The 14 ng m^{-3} estimated NO_3^- "background" is reasonably consistent with the mean nitrate concentrations during the winter months. The nss sulfate concentrations based on this equation are compared to the measured values in Figure 5b. In general the estimates agree very well with the measured values. However, the MSA/nss $SO_4^=$ ratio of 0.31 obtained from the regression analysis is primarily a function of the higher concentrations which occur during the summer months. To assess the ratio during the winter, we use the average MSA and nss $SO_4^=$ concentrations from May through August when the nitrate concentrations are lowest, 3.41 and 12.1 ng m^{-3}, respectively. The ratio of these averages 0.28 is clearly consistent with that obtained from the regression analysis. It appears, then, that the MSA/nss $SO_4^=$ ratio resulting from the oxidation of DMS alone does not vary substantially through the year.

   On the basis of these results, we calculate that of the total mean nss sulfate (90 ng m^{-3}) about 65 ng m^{-3} (72%) are associated with MSA and 25 ng m^{-3} (28%) are associated with non-background nitrate. An Australian source for the high nitrate concentrations and their associated concentrations of nss $SO_4^=$ would explain the similarities in the seasonality of the MSA/nss $SO_4^=$ ratios at Cape Grim and Mawson.

Another possible explanation has been proposed for the association of lower MSA/nss $SO_4^=$ ratios with increased nitrate concentrations. That is, that the long-range transport which results in higher nitrate concentrations also leads to the influx of MSA and nss $SO_4^=$ from more temperate latitudes where the MSA/nss $SO_4^=$ ratio produced by the oxidation of DMS is much lower. However, if we assume a MSA/nss $SO_4^=$ ratio of 0.065 from the temperate region and a ratio of 0.31 for the high latitudes, then the temperate region aerosols would have to supply about 65% of the nss $SO_4^=$ and 28% of the MSA to account for the ratio of about 0.15 during December 1988 and January 1989 at Mawson. If the actual MSA/nss $SO_4^=$ ratio from DMS oxidation were higher in either of the two regions, then the estimated percentage input from the temperate region would increase accordingly. During this two month period, MSA concentrations average about 40 ng m^{-3}. Hence, the concentrations in air arriving from the temperate source would need to be about 11 ng m^{-3}.

MSA concentrations of tens of ng m^{-3} have been measured in the free troposphere west of Tasmania (Berresheim et al., 1990). The authors suggested that these high levels were consistent with the fact that some of their isentropic trajectories indicated sporadic vertical motions which may have caused transport from the marine boundary layer to upper levels. Furthermore, the trajectories during these periods were from over the southern oceans (from higher not lower latitudes) and the MSA/nss $SO_4^=$ ratios are similar to those at Mawson (0.12-0.50). Hence, while this free tropospheric material could reasonably contribute to the MSA and nss $SO_4^=$ concentrations at Mawson and over Antarctica in general, they would not account for the much lower MSA/nss $SO_4^=$ ratios that are associated with the influx of high nitrate concentrations.

It is very unlikely that free tropospheric transport of MSA and nss $SO_4^=$ from tropical and subtropical ocean regions would have a significant impact on the concentrations of these species near Antarctica. Especially, during the summer season, these are regions of general atmospheric subsidence except in the vicinity of the intertropical convergence zones. Moreover, MSA concentrations in the free troposphere of these regions are only about 1-5 ng m^{-3} (Talbot et al., 1986; Prospero and Savoie, 1990). These levels are clearly not high enough to substantially affect the concentrations in the high latitude regions, especially when one considers the amount of dilution that is likely to occur during the transport of these air parcels to very high latitudes.

5.3. AMMONIUM

The source of the NH_4^+ over Antarctica is still an open question. The NH_4^+ temporal record is similar (but not identical) to that of the MSA seasonal cycle. Based on equilibrium calculations, Quinn et al. (1988, 1990) have previously concluded that the ocean was a net source for ammonia over many regions. The cycle of NH_4^+ at Mawson appears to follow the solar cycle more closely than does that of MSA; the maxima in solar intensity and length of day both occur on the solstice, December 22. If the NH_4^+ is derived from an ocean source, then it would be as a consequence of a different process than that which produces DMS and, ultimately, MSA. Hence, the differences between the two cycles is hardly surprising and does not preclude a marine biogenic source for NH_4^+.

The NH_4^+ cycle is most similar to that for nss $SO_4^=$. In fact, the NH_4^+/nss $SO_4^=$ molar ratio is reasonably consistent, ranging from about 0.6 to 1.4 throughout most of the record (Fig. 6). The mean NH_4^+/nss $SO_4^=$ molar ratio is 1.2, a value similar to that previously reported for relatively remote marine areas (Quinn et al., 1988, 1990; Covert, 1988). Since the previous data were obtained primarily over the North Pacific with very little in any from

the southern hemisphere, it appears that the oceanic background aerosol is fairly homogeneous with regard to the NH_4^+/nss $SO_4^=$ ratio. A ratio of 1 implies a composition equivalent to that of NH_4HSO_4, i.e. a partially neutralized but still acidic constituent.
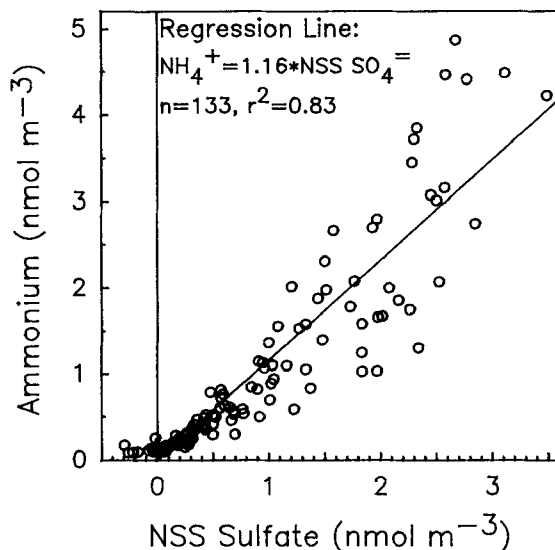

Figure 6. Plot of the particulate ammonium concentrations versus those of nss sulfate at Mawson.

6. Comparison to Condensation Nuclei Measurements

Gras and Adriaansen (1985) measured the CN concentrations at Mawson over nearly three annual cycles from June 1981 to May 1984. These data exhibit a strong seasonal cycle with weekly median concentrations ranging from 300-400 cm^{-3} during the summer to about 30 cm^{-3} during the winter. From the winter minimum, the concentrations increase most rapidly during September and then remain fairly constant from October to March. The concentrations then decrease back to their low winter levels during April and May.

A very important feature of this cycle is that it does not correspond to the cycles that we have just presented for the total mass concentrations of any of the individual chemical constituents. Seasonal variations in the particle size distribution may be a major factor. Gras and Adriaansen note that the typical particle mode radius during the winter is less than about 0.01 μm versus about 0.03-0.04 μm during the summer. A simple calculation reveals that concurrent increases of factors of 3-4 in the mode radius and factors of 30-60 in the total mass concentration would result in little change in the total number concentration. Without more detailed information on the cycles of the chemical constituents, it is not possible to make similar comparisons for the long-term CN and chemistry data at the South Pole. However, the results reviewed by Ito (1989) indicate that marked variations in particle size distributions also occur at the South Pole as well as at the Syowa Station.

These results indicate that the relationship between the CN concentrations and the mass concentrations of the chemical constituents in Antarctica is far from simple. Clearly, there will need to be intensive studies combining measurements of CN, particle size distributions

and mass concentrations to determine if the relationship can be more rigorously defined as a function of season and geographical location.

7. Relevance to Antarctic Snow and Ice Studies

There is an extensive and growing body of data regarding the chemistry of Antarctic ice, which has been collected towards the goal of reconstructing a paleoenvironmental record of climate and atmospheric chemistry. The interpretation of this data suffers from 1) a lack of an equally extensive chemical climatology for the Antarctic atmosphere, 2) an incomplete understanding of the transfer processes involved in deposition of airborne species (both gas phase and particulate) to the ice sheet, and 3) very limited knowledge of the post-depositional processes that may alter the distributions and concentrations in the snow and/or ice. A comparison of the seasonal cycles of the chemical constituents in atmospheric particulates and those inferred from ice/firn core studies indicate that the relationship between the concentrations in the ice and those in the atmosphere may be far from straightforward. In this regard, the currently available data are certainly not consistent; some of the ice-core-derived "seasonal" cycles correspond reasonably well with those from the aerosol studies while others differ dramatically.

For example, Ivey et al. (1986) measured $\Delta^{18}O$, MSA, and nss $SO_4^=$ in 62 samples from an ice core from Law Dome (Fig. 1). These samples spanned two 2.5 year periods near 1920. Their nss $SO_4^=$ concentrations exhibit a strong summer maximum which is consistent with that discussed above for the aerosols. MSA, on the other hand, shows no consistent seasonal variation. In addition, the mean MSA/nss SO4= ratio in the ice core samples, 0.40, is about 30% higher than that which we have estimated for the biogenic component alone, 0.31, and 80% higher than the overall mean MSA/nss $SO_4^=$ ratio at Mawson, 0.22.

In collaboration with the British Antarctic Survey, we have recently analyzed a more extensive set of samples from a 10-year (1884-1894) section of a coastal Antarctic ice core from Dolleman Island in the Weddell Sea (Fig. 1). As at Law Dome, nss $SO_4^=$ exhibits the expected summer maxima (R. Mulvaney and D. Peel, personal communication) and winter minima. Although MSA exhibits systematic seasonal variations in this core, the phase of these variations, winter maxima and summer minima, is exactly opposite to the MSA seasonality in the aerosol data. Because MSA and nss $SO_4^=$ are out of phase, the MSA/nss $SO_4^=$ ratios in individual samples varies widely. The overall mean MSA/nss $SO_4^=$ ratio in this core, 0.55, is nearly 80% greater than our estimate of the biogenic ratio and 150% greater than the overall mean ratio at Mawson.

In both sets of ice core samples, the overall mean MSA/nss $SO_4^=$ ratio is significantly larger than that which we estimate for the biogenic source alone and substantially larger than that observed in atmospheric particles at Mawson. These differences may indicate that the deposition velocity of MSA over Antarctica is significantly greater than that of nss $SO_4^=$. Such a difference would be consistent with the fact that (as discussed earlier) a substantial fraction of the MSA is usually found on supramicron particles. The discrepancies between the seasonal cycles of MSA in the aerosols and those inferred from the ice core data indicate that post-depositional processes may substantially modify the vertical profiles of MSA in the firn. The mechanisms that might be involved in such a redistribution are currently unknown.

In contrast to nss $SO_4^=$ whose atmospheric seasonal cycle appears to be accurately reflected in the snow and to MSA whose seasonal cycles in the air and snow appear to be exactly out of phase, the nitrate cycles inferred from snow and ice studies are sometimes

consistent with those in the atmosphere while, at other times, they are not. For example, Neubauer and Heumann (1988) determined the concentration versus depth profiles of nitrate in seven firn cores near the Weddell Sea. The results revealed no significant seasonal cycle in four of the cores and only a very weak cycle with a summer maximum and a winter minimum in the other three. Although nitrate exhibits a fairly strong and relatively consistent summer maximum in snow layers near the South Pole (Legrand and Delmas, 1984; Legrand and Kirchner, 1988), winter maxima about equal in magnitude to the summer maxima were observed during some years. Yet, these same samples always indicated a winter maximum in the sodium concentration (Legrand and Kirchner, 1988) and a strong summer maximum in the nss $SO_4^=$ concentration (Legrand and Delmas, 1984), both of which are consistent with the atmospheric seasonal cycles.

8. Conclusions

Our results when combined with previously published data indicate that the aerosol composition is very uniform over a broad sector of Antarctica and the southern oceans. The biogenic sulfur component appears to be particularly uniform over a region of the southern ocean that covers perhaps as much as 25-30% of the earth's surface. However, it is clearly premature to conclude that all of the species exhibit similar cycles throughout Antarctica. MSA and nitrate have been measured in atmospheric particles at only two stations, and no measurements of either of these species have been made in the interior of the continent.

The results from multiple variable regression analyses indicate that the dominant source of nss $SO_4^=$ at Mawson is the oxidation of dimethylsulfide (DMS). The MSA/nss $SO_4^=$ ratio from this source does not appear to vary significantly from a value of 0.31. However, a very significant fraction (about 25%) of the nss $SO_4^=$ is associated with NO_3^-. The source of the latter fraction appears to be the transport of continentally-derived material from Australia. While the seasonal cycle of nss $SO_4^=$ at Mawson appears to be primarily controlled by the marine biogenic source, that is not necessarily the case for other regions. The cycle over the interior or at higher altitudes, for example, could well be controlled by variations in the source associated with nitrate. Moreover, the strengths of the two nss $SO_4^=$ sources can and probably do vary independently. Consequently, it would not be surprising if the generally lower MSA/nss $SO_4^=$ ratios and their fluctuations with depth in the interior ice cores were found to be simply related to variations in the relative importance of these sources.

All of our data and that from previous investigators clearly demonstrate that the concentrations of the nitrogen and sulfur species exhibit very strong seasonal cycles in the high latitude regions of the southern hemisphere. This feature has very important implications with regard to the interpretation of historical snow and ice core records. It is not inconceivable that some of the fluctuations in the concentrations of these species are simply related to variations in the seasonality of snowfall. That is, one would expect the concentrations to be much higher during periods when summer snowfall dominates than during those when winter snowfall dominates, assuming of course that other factors remained constant. In view of the fact that, for most of these species, the summer concentrations are more than an order of magnitude higher than those during the winter, it would take little change in the relative importance of winter and summer snowfall to alter the concentrations in the ice by factors of 2-3 or more.

Clearly, more studies are required to resolve the apparent inconsistencies between the cycles of nitrate and, especially, of MSA in the atmosphere and those inferred from ice/snow studies. The fact that the seasonal cycle of MSA as inferred from coastal firn samples is so

far out of phase with that of MSA and its precursors in the atmosphere is very difficult to explain. The processes responsible for this phenomenon must be rigorously investigated for they may well apply to other constituents.

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