Nitrogen and Sulfur Species in Antarctic Aerosols at Mawson, Palmer Station, and Marsh (King George Island)

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Abstract. High volume bulk aerosol samples were collected continuously at three Antarctic sites: Mawson (67.60° S, 62.50° E) from 20 February 1987 to 6 January 1992; Palmer Station (64.77° S, 64.06° W) from 3 April 1990 to 15 June 1991; and Marsh (62.18° S, 58.30° W) from 28 March 1990, to 1 May 1991. All samples were analyzed for Na⁺, SO₄²⁻, NO₃, methanesulfonate (MSA), NH₄⁺, ²¹⁰Pb, and ⁷Be. At Mawson for which we have a multiple year data set, the annual mean concentration of each species sometimes vary significantly from one year to the next: Na⁺, 68-151 ng m⁻³; NO₃, 25-30 ng m⁻³; nss SO₄²⁻, 81-97 ng m⁻³; MSA, 19-28 ng m⁻³; NH₄⁺, 16-21 ng m⁻³; ²¹⁰Pb, 0.75-0.86 fCi m⁻³. Results from multiple variable regression of non-sea-salt (nss) SO₄²⁻ with MSA and NO₃ as the independent variables indicates that, at Mawson, the nss SO₄²⁻/MSA ratio resulting from the oxidation of dimethylsulfide (DMS) is 2.80 ± 0.13, about 13% lower than our earlier estimate (3.22) that was based on 2.5 years of data. A similar analysis indicates that at Palmer, the nss SO₄²⁻/MSA ratio is about 40% lower, 1.71 ± 0.10, and more comparable to previous results over the southern oceans. These results when combined with previously published data suggest that the differences in the ratio may reflect a more rapid loss of MSA relative to nss SO₄²⁻ during transport over Antarctica from the oceanic source region. The mean ²¹⁰Pb concentrations at Palmer and Marsh and the mean NO₃ concentration at Palmer are about a factor of two lower than those at Mawson. The ²¹⁰Pb distributions are consistent with a ²¹⁰Pb minimum in the marine boundary layer in the region of 40°-60° S. These features and the similar seasonalities of NO₃ and ²¹⁰Pb at Mawson support the conclusion that the primary source regions for NO₃ are continental. In contrast, the mean concentrations of MSA, nss SO₄²⁻, and NH₄⁺ at Palmer are all higher than those at Mawson: MSA by a factor of 2; nss SO₄²⁻ by 10%; and NH₄⁺ by more than 50%. However, the factor differences exhibit substantial seasonal variability; the largest differences generally occur during the austral summer when the concentrations of most of the species are highest. NH₄⁺/(nss SO₄²⁻ + MSA) equivalent ratios indicate that NH₄⁺ neutralizes about 60% of the sulfur acids during December at both Mawson and Palmer, but only about 30% at Mawson during February and March.

Key words. Antarctica, Palmer, Marsh, Mawson, aerosol particles, biogeochemical cycles, sulfate, nitrate, methanesulfonate, lead-210, beryllium-7, sea-salt, ammonium.

1. Introduction

Understanding the atmospheric chemistry of the Antarctic is crucial for several reasons. Because this region is far removed from major pollution sources, the
atmospheric cycles of most major components are minimally impacted by products of man's activities. Long-term measurements at numerous locations in the region are required along with analyses of recent snow chemistry to substantiate the assumption that the vertical profiles of species in snow and ice cores provide a reasonably unambiguous record of the atmosphere's historical composition and climate.

The objective of our ongoing study is to further our understanding of the temporal variations and the probable sources of the major sulfur and nitrogen species in aerosols over Antarctica and the southern oceans. To aid in the assessment of the sources, we also measure the concentrations of two natural radioactive tracers, $^{210}$Pb and $^7$Be. Beryllium-7 ($t_{1/2} = 53.6$ d) is a tracer for transport from the lower stratosphere and upper troposphere where it is produced by the cosmic ray-induced spallation of nitrogen and oxygen. Lead-210 is a decay product of $^{222}$Rn ($t_{1/2} = 3.8$ d) for which the overwhelmingly dominant source is emission from soils. Consequently, $^{210}$Pb serves as a tracer for air masses that have recently been in convective contact with continental land masses.

In two recent reports (Prospero et al., 1991; Savoie et al., 1992), we presented and discussed the results that we had obtained from the analyses of aerosol samples collected at Mawson, Antarctica (67.60° S, 62.50° E; Figure 1) from February 1987 through October 1989. In this report, we build on the results from our previous study by examining the additional nss $SO_4^{2-}$, MSA, $NO_3^-$, $NH_4^+$, $^{210}$Pb, and $^7$Be data that were acquired at Mawson through December 1991. This larger data set provides an opportunity to assess the interannual variations in the mean concentrations as well as in the seasonal cycles. The larger number of samples also significantly reduces the statistical uncertainties in the regression coefficients for estimating the nss $SO_4^{2-}$ concentrations from those of MSA and $NO_3^-$ and in the mean $NH_4^+$: nss $SO_4^{2-}$ ratio. To enhance our understanding of the spatial distributions of the concentrations, the Mawson data are compared to those that we have recently obtained at two stations in the vicinity of the Antarctic peninsula: Palmer Station (64.77° S, 64.05° W); and Marsh, King George Island (62.18° S, 58.30° W). Substantial local pollution at the Marsh site was evidenced by frequently extremely high concentrations and erratic variations in $NO_3^-$ and nss $SO_4^{2-}$ and by intense blackening of nearly all of the samples by soot carbon. This feature limits the usefulness of the Marsh data and, consequently, discussion of data from that station is confined to $Na^+$, MSA, $^{210}$Pb, and $^7$Be.

2. Experimental Procedures

For sample collection, air was continuously drawn through 20 × 25 cm Microdon filters at a nominal flow rate of 50 m$^3$ h$^{-1}$. The actual flow rates were determined from the pressure drops across a calibrated orifice system attached to the pump outlets. Weekly sampling periods yield sampled air volumes of about 8500 m$^3$. Results from tests performed for the U.S. Department of Energy (New York) by the Centre in Aerosol and Technology, Laurentian University (Sudbury, Ontario,