Variations in the Methanesulfonate to Sulfate Molar Ratio in Submicrometer Marine Aerosol Particles Over the South Pacific Ocean

TIMOTHY S. BATES

Pacific Marine Environmental Laboratory, NOAA, Seattle, Washington

JULIE A. CALHOUN[1]

Joint Institute for the Study of the Atmosphere and Ocean, University of Washington, Seattle

PATRICIA K. QUINN[2]

Pacific Marine Environmental Laboratory, NOAA, Seattle, Washington

Seawater concentrations of dimethylsulfide (DMS) and atmospheric concentrations of DMS, sulfur dioxide, methanesulfonate (MSA), and non-sea-salt (nss) sulfate were measured over the eastern Pacific Ocean between 105° and 110°W from 20°N to 60°S during February and March 1989. Although the samples collected in the southern hemisphere appear to be of marine origin, no significant correlation was found between the latitudinal distributions of DMS, SO_2, MSA, and nss SO_4^-. However, an inverse correlation ($r^2 = 0.87$) was found between atmospheric temperature and the MSA to nss SO_4^- molar ratio in submicrometer aerosol particles with a decrease in temperature corresponding to an increase in the molar ratio. Although this trend is consistent with laboratory results indicating the favored production of MSA at lower temperatures, it is contrary to southern hemisphere baseline station data. This suggests either a decrease in the supply of DMS relative to nonmarine sources of nss SO_4^- at the baseline stations in winter or additional mechanisms that affect the relative production of MSA and nss SO_4^-.

INTRODUCTION

Oceanic emissions of dimethylsulfide (DMS) are the primary source of sulfur to the atmosphere in the southern hemisphere [*Bates et al.*, 1992; *Spiro et al.*, 1992]. Seawater DMS is derived from the enzymatic cleavage of the biologically produced precursor compound, dimethylsulfoniopropionate or DMSP [*Cantoni and Anderson*, 1956; *Dacey and Blough*, 1987] and is emitted to the atmosphere where it is oxidized by OH or NO_3 radicals to methanesulfonic acid (MSA) or SO_2. SO_2 undergoes gas to particle conversion to form nss SO_4^- submicrometer aerosol particles or is absorbed into cloudwater and oxidized to SO_4^-. The only known source of MSA is oxidation of DMS, whereas SO_2 and hence nss SO_4^- have anthropogenic, volcanic, and biogenic sources. If the ratio of MSA to nss SO_4^- were constant in purely marine air masses, MSA would provide a unique tracer of the amount of nss SO_4^- aerosol attributable to biogenic DMS.

The first reported measurements of the MSA to nss SO_4^- molar ratio were from lower-latitude sites ranging from American Samoa at 14°S to Midway at 8°N [*Saltzman et al.*, 1983; *Saltzman et al.*, 1985]. The ratio averaged around 6.5%. Later measurements from these sites as well as from Fanning (4°N) also revealed a molar ratio of 6.5% [*Saltzman et al.*, 1986; *Savoie and Prospero*, 1989]. The consistency of the ratio led to the suggestion that it could be used as a marker for

the fraction of nss SO_4^- attributable to biogenic DMS [*Savoie and Prospero*, 1989]. The use of the ratio as a marker on a global scale requires that either it is conservative, i.e., it is not affected by factors such as temperature, light intensity, or oxidant concentration, or that the dependence of the ratio on these factors is well understood. Unfortunately, recent laboratory and field data demonstrate that it is not conservative and that the factors controlling it are not well defined.

The MSA to nss SO_4^- molar ratio has been found to vary from 6.5% at low latitudes to up to 100% at high latitudes [*Berresheim*, 1987]. Laboratory studies have demonstrated that the OH-initiated photochemical oxidation of DMS can proceed via an abstraction or addition mechanism [*Hynes and Wine*, 1989] yielding MSA and SO_2 in both pathways [*Yin et al.*, 1990a]. Greater yields of SO_2 are predicted at higher temperatures [*Hynes et al.*, 1986; *Yin et al.*, 1990b] and stronger light intensities [*Yin et al.*, 1990b]. This temperature dependence has been used to explain the larger MSA to nss SO_4^- ratios at higher latitudes and altitudes [*Berresheim*, 1987; *Pszenny et al.*, 1989; *Berresheim et al.*, 1990; *Koga et al.*, 1991]. However, baseline station data from Tasmania show the opposite relationship with higher MSA to nss SO_4^- molar ratios in the warmer summer months [*Ayers et al.*, 1991]. Data from Mawson, Antarctica, show the highest MSA to nss SO_4^- molar ratios at about the March/April equinox period [*Prospero et al.*, 1991]. Thus it may not be possible to explain the variation in the ratio solely on the basis of temperature.

Defining the processes controlling the relative concentrations of MSA and nss SO_4^- is important in understanding the influence of the marine sulfur cycle on global climate. Submicrometer sulfate aerosol particles can affect the Earth's radiation budget either directly or indirectly: directly by backscattering solar radiation to space and indirectly through their role as cloud condensation nuclei [*Charlson et al.*, 1991;

---

[1]Now at Laboratoire de Glaciologie et Geophysique de l'Environnement, Saint-Martin-d'Heres, France.

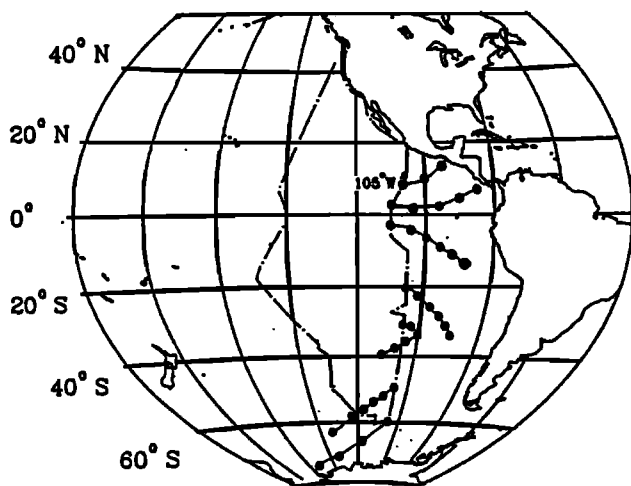[2]Also at Joint Institute for the Study of the Atmosphere and Ocean, University of Washington, Seattle.

Fig. 1. Study area showing the cruise track between 105° and 110°W from 20°N to 60°S. Also shown are calculated isobaric back trajectories at the 1000-mbar level. The symbols show the location of the air mass at 24-hour intervals. The calculated trajectories at 850 and 700 mbar were similar to those at 1000 mbar.

Charlson et al., 1987]. Knowing the factors affecting the production and growth of these particles is important in assessing their climatic significance. Laboratory studies indicate that nss SO_4^- is more effective at nucleating new particles while MSA is more likely to condense onto existing particles [*Hoppel*, 1987]. Hence factors controlling the relative concentration of these two species must be known to understand the link between DMS, particle production, and climate.

Described here are the first-reported measurements over the southeast Pacific Ocean of the concentrations of seawater DMS, atmospheric gaseous DMS and SO_2, and atmospheric particulate nss SO_4^- and MSA. Measurements were made aboard the NOAA ship *Discoverer* in February and March of 1989 along 105° to 110°W between 20°N and 60°S (Figure 1). Unlike baseline station data these samples cover a wide temperature range over a 2-month period in the austral summer and hence offer another perspective on the relative distribution of the various sulfur species.

METHODS

Atmospheric DMS samples were collected through a Teflon line which ran 70 m from the oceanographic laboratory to the end of a boom extending 5 m forward of the ship's flying bridge and 20 m above the sea surface. The DMS analysis, which has been described in detail elsewhere [*Quinn et al.*, 1990b], included a KOH-coated glass fiber filter to eliminate oxidant interferences, cryogenic preconcentration, gas chromatographic separation, and flame photometric detection. Seawater DMS samples were taken from a depth of 5 m using the ship's seawater pumping system. The samples were purged with ultrapure hydrogen and analyzed on the same system as was used for the atmospheric samples. The overall precision of the DMS measurements was approximately ± 10% [*Bates et al.*, 1990].

Atmospheric aerosol particles and gaseous SO_2 were collected at the end of the same boom as DMS using a tandem filter system [*Quinn and Bates*, 1989; *Quinn et al.*, 1990b]. The system consisted of a cyclone separator or 8.0-μm pore size Nuclepore filter followed by a 47-mm Millipore Teflon particle filter (1.0-μm pore size) and two 47-mm Whatman 41 filters coated with 0.1 M K_2CO_3. Only the first coated filter was used for determination of the SO_2 concentration. The cyclone and Nuclepore filter had a 50% collection efficiency of approximately 0.6 μm at the sample flow rate of 80 standard liters per minute (slpm) based on the calibrations of *Quinn and Bates* [1989]. Breakthrough tests using four coated filters in series have shown that about 75% of the SO_2 is collected on the first filter [*Quinn and Bates*, 1989]. Samples were collected in duplicate alongside a blank (flow rate is 0 slpm) for 8 to 48 hours. Duplicate samples for all species agreed within ±10%. To prevent contamination of the filters by stack gases, samples were collected only when the wind direction was forward of the ship's beam and the wind speed was greater than 3 m s^{-1}.

Filters were extracted with distilled deionized water and analyzed immediately by ion chromatography onboard the ship. Details of the ion chromatographic analyses have been reported previously [*Quinn et al.*, 1990b]. The amount of sea-salt SO_4^- on the Millipore filter was calculated from the measured Na$^+$ concentration and a mass ratio of sulfate to sodium in seawater. This value and the concentration of total measured SO_4^- were used to determine the amount of nss SO_4^-. The sea-salt SO_4^- was always less than 10% of the total SO_4^-. Concentrations are reported in units of nmol m^{-3} at standard temperature (25°C) and pressure (101.3 kPa) such that 1 nmol m^{-3} equals 24.5 pptv.

RESULTS AND DISCUSSION

DMS Emissions to the Atmosphere

DMS concentrations in surface seawater ranged between 2 and 11 nmol L^{-1} with three distinct regions of elevated concentrations at 3°N, 15°S, and 35°S (Figure 2a). Most of this DMS is recycled within the water column as the turnover times for biological DMS removal are estimated to be about 10 times faster than removal by ventilation to the atmosphere [*Kiene and Bates*, 1990]. However, there still is a considerable net flux from the ocean to the atmosphere. This flux, *F*, can be estimated from measured surface seawater DMS ([DMS]$_s$) concentrations, and a liquid phase mass transport velocity, k_L, such that

$$F = k_L[\text{DMS}]_s.$$

k_L was calculated from the local wind speed using *Liss and Merlivat* [1986]. It was corrected for the Schmidt number of DMS, as described by *Bates et al.* [1987].

The calculated flux of DMS from the ocean to the atmosphere ranged between 0 and 36 μmol m^{-2} d^{-1} (Figure 2b). Low wind speeds of less than 5 m s^{-1} near the equator and between 20° and 30°S resulted in the lowest calculated DMS fluxes. Throughout the rest of the cruise track, higher seawater DMS concentrations of 4 to 11 nmol L^{-1} and wind speeds of 5 to 12 m s^{-1} led to DMS fluxes between 5 and 36 μmol m^{-2} d^{-1}. Previously reported fluxes of DMS in the tropical North Pacific (5° to 20°N) and the equatorial Pacific averaged around 4.7 and 4.3 μmol m^{-2} d^{-1}, respectively [*Bates et al.*, 1987]. Austral summer DMS fluxes from the southern Indian Ocean (Amsterdam Island, 38°S) averaged around 3.0 μmol m^{-2} d^{-1} [*Nguyen et al.*, 1990]. DMS fluxes have also been reported from the Drake Passage during the austral fall and ranged from 3.9 to 5.0 μmol m^{-2} d^{-1} [*Berresheim*, 1987].
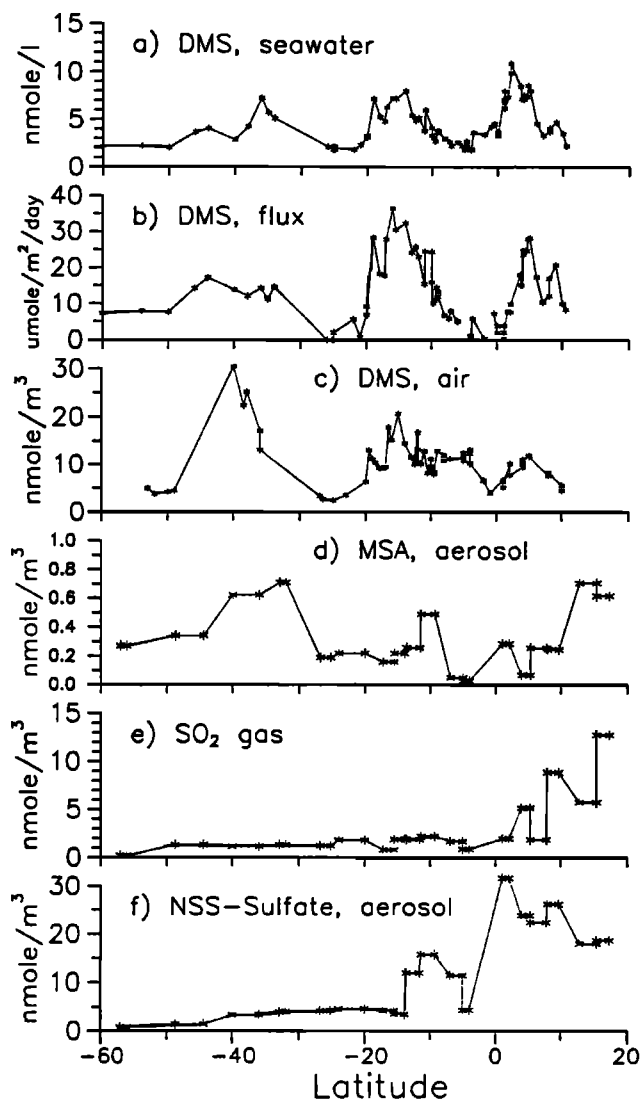
Fig. 2. Latitudinal distributions from 20°N to 60°S of (a) surface seawater DMS concentrations in nmol L^{-1}, (b) the calculated flux of DMS from the ocean to the atmosphere in μmol $m^{-2}\,d^{-1}$, (c) atmospheric DMS concentrations in nmol m^{-3}, (d) atmospheric particulate MSA concentrations in nmol m^{-3}, (e) atmospheric SO_2 concentrations in nmol m^{-3}, and (f) atmospheric particulate nss SO_4^- concentrations in nmol m^{-3}. Horizontal lines in (d), (e), and (f) indicate the latitudinal range over which samples were collected.

Atmospheric Sulfur Species

Correlating simultaneously measured concentrations of seawater DMS and atmospheric DMS and its oxidation products is difficult for several reasons [Bates et al., 1989]. Depending on the time scales of the prevailing oceanic and atmospheric transport processes, the sampled air mass may not correspond to the sampled water mass. The most relevant measurement is of an air mass and the water mass upwind of it. Additional factors making such correlations difficult include the meteorologically dependent and varying lifetimes of the atmospheric gas and particle phase species and the multiple nonmarine sources of SO_2 and nss SO_4^-. An analytical constraint in this set of measurements is the long sampling times of 8 to 48 hours for SO_2, nss SO_4^-, and MSA. These sampling times can be longer than the time scales of the processes controlling the concentrations of the chemical

species. Hence we make no attempt here to correlate the seawater and atmospheric gas and particle phase species on a point by point basis but instead look at regional features in the data.

Along the cruise track, atmospheric DMS concentrations ranged from 2 to 30 nmol m^{-3} (Figure 2c) with the highest concentrations occurring between 10° and 20°S and also near 40°S. Vertical soundings of pressure, temperature, and dew point indicate that these changes in concentration are not a result of a changing boundary layer height [Johnson and Mitchell, 1991] where the boundary layer height is defined as the distance from the Earth's surface to the bottom of the lowest cloud layer. The high concentrations at 40°S correspond to the large flux of DMS in this region (Figure 2b). The concentrations at the lower latitudes (10°N to 20°S) were fairly uniform averaging around 10 nmol m^{-3}. In this area the atmospheric DMS concentrations did not correlate significantly with the calculated DMS flux. This could be the result of a more uniform air/sea flux upwind or atmospheric mixing. The average equatorial atmospheric DMS concentrations reported here are similar to those reported by Andreae et al. [1985] in the eastern equatorial Pacific (2 to 12 nmol m^{-3}).

The residence time of atmospheric DMS was calculated from estimated DMS fluxes, measured concentrations, and boundary layer heights [Johnson and Mitchell, 1991]. The average residence time over the equatorial Pacific was about 1 day and between 40° and 60°S it was of the order of 2 to 3 days. As the main sink for DMS in the remote marine atmosphere is oxidation by the OH radical, this difference in residence times can be explained by the OH concentrations in these two latitudinal belts. Model calculations indicate that the OH concentration in marine low latitudes is about 2 times higher than in the mid-latitudes of the southern hemisphere [Thompson et al., 1990].

MSA concentrations ranged from 0.03 to 0.7 nmol m^{-3} (Figure 2d) with the highest concentrations at 15°N and from 30° to 40°S. The southern region of high MSA concentrations corresponds to the region of high DMS flux. Concentrations in the equatorial region were variable, ranging from 0.03 to 0.5 nmol m^{-3}. Again, the variation in the latitudinal distribution of MSA concentrations cannot be attributed to changes in the boundary layer height.

The interpretation of SO_2 and nss SO_4^- data often is complicated as these species have volcanic, anthropogenic, and marine sources. Isobaric back trajectories calculated at 1000, 750, and 500 mbar were used to determine the origin of the sampled air masses (Figure 1). Air masses in the southern hemisphere appear to have not contacted land for at least 5 days prior to sampling. North of the equator, the air masses appear to have crossed North America 3 to 4 days prior to sampling.

The chemical data were consistent with the trajectory analysis. SO_2 and nss SO_4^- concentrations (Figures 2e and 2f) in the northern hemisphere ranged from 1.9 to 13 nmol m^{-3} and 18 to 32 nmol m^{-3}, respectively. These are high compared to previously reported remote marine values [Quinn et al., 1990b]. The lower concentrations found in the southern hemisphere of 0.16 to 2.1 nmol m^{-3} and 0.8 to 16 nmol m^{-3} for SO_2 and nss SO_4^-, respectively, are more typical of remote marine concentrations. One curious feature of the southern hemisphere nss SO_4^- data is an area of relatively high concentration at 10°S. The concentration peak is shifted

slightly from and extends over a narrower latitude band than the elevated DMS concentrations. MSA concentrations also are elevated in this region but SO_2 concentrations are not. Although the isotope data [*Calhoun et al.*, 1991] and trajectory analysis suggest that this nss SO_4^- is of marine biogenic origin, long-range transport from the Peruvian coast cannot be ruled out as a possible explanation for the high nss SO_4^- concentrations at 10°S.

Molar Ratio of MSA to nss SO_4^-

Although there are difficulties associated with direct comparisons of seawater and atmospheric gas and particle phase species, comparisons of particulate nss SO_4^- and MSA concentrations are simplified as they have similar lifetimes. The measured MSA and nss SO_4^- both occurred on submicrometer aerosol particles and therefore should be removed from the atmosphere on the same time scales. Nevertheless, the MSA to nss SO_4^- molar ratio ranged from less than 0.2% near the equator to 32% at 55°S (Figure 3). Based on trajectory analysis, the low concentrations of SO_2 and nss SO_4^-, and stable sulfur isotope ratios [*Calhoun et al.*, 1991], the nss SO_4^- measured in the southern hemisphere appears to have originated from the oxidation of DMS. Therefore the variation in the ratio of MSA to nss SO_4^- with latitude does not appear to be related to sink mechanisms or input of anthropogenic sulfate. Instead, it must be a function of variations in the factors controlling the pathways and/or rates of DMS oxidation.

In the remote marine troposphere, oxidation of DMS occurs primarily by reaction with the OH radical. The details of the oxidation mechanism are not known, but it is thought to be initiated either by the addition of OH to the S atom or abstraction of a proton [*Hynes et al.*, 1986]. The reaction rates for these two pathways have been shown to depend on temperature such that addition is favored at lower temperatures and abstraction at higher temperatures [*Hynes et al.*, 1986]. Although the products from the two pathways are somewhat ambiguous [*Yin et al.*, 1990a], it appears that DMSO, $DMSO_2$, and MSA are major products of the addition mechanism, while SO_2 is a major product of the abstraction mechanism [*Plane*, 1989]. The rate of decomposition of reaction intermediate, CH_3SO_2, to form SO_2 also is slower at lower temperatures, presumably further reducing the yield of SO_2 [*Yin et al.*,
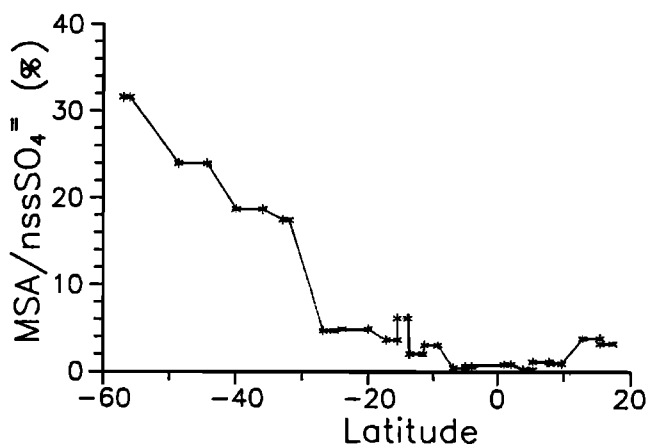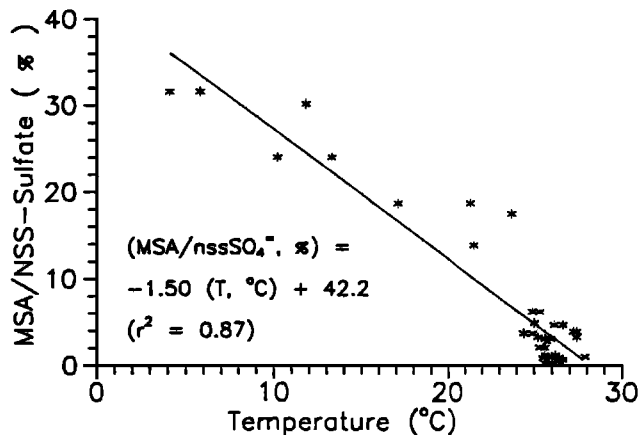

Fig. 4. MSA to nss SO_4^- molar ratios as a function of average daily air temperature. The data are from the southern hemisphere samples only.

1990b]. Hence relatively higher concentrations of MSA and lower concentrations of SO_2 are expected at colder temperatures.

In this study, a strong inverse relationship was observed between MSA to nss SO_4^- molar ratios and atmospheric temperature (r^2 = 0.87), with higher MSA to nss SO_4^- molar ratios occurring at lower temperatures (Figure 4). This increase in the measured MSA to nss SO_4^- molar ratio can be compared to the change in the relative rates of addition and abstraction that is expected over the same temperature range. According to the rates of *Hynes et al.* [1986] a temperature decrease from 25°C to 5°C should result in a factor of 3.8 increase in the branching ratio of addition to abstraction. The observed MSA to nss SO_4^- molar ratios over this same temperature range increased by a factor of 7.3.

There are difficulties in comparing laboratory and field measurements of the relative distribution of DMS oxidation products. Laboratory experiments yield poor mass balances of sulfur and carbon which are indicative of significant wall losses [*Yin et al.*, 1990b]. In addition, they have been unable to mimic the chemical composition of the remote marine atmosphere. Further work is needed in which conditions of the marine troposphere are better approximated, including chemical composition and solar intensity. Although many of the primary reactions have been characterized, products of the intermediate and final reactions also need to be identified.

In addition to laboratory experiments there have been several field studies investigating the cycling of sulfur through the remote marine atmosphere. These studies reveal the same general trend of increasing MSA to nss SO_4^- molar ratio with decreasing temperature (Figure 5). At Fanning (4°N) and American Samoa (14°S) the average MSA to nss SO_4^- molar ratio was 6.5% at temperatures ranging from 25°C to 27°C [*Saltzman et al.*, 1986; *Savoie and Prospero*, 1989). At Cape Grim, Tasmania (41°S), the MSA to nss SO_4^- ratio during the summer months was approximately 18% at an average temperature of 16°C [*Ayers et al.*, 1991]. In maritime air, west of Tasmania (42°S), the MSA to nss SO_4^- ratio was about 45% with temperatures near 12°C [*Berresheim et al.*, 1990]. MSA to nss SO_4^- molar ratios in the Drake Passage and Gerlache Strait (54° to 66°S) averaged 64% for temperatures ranging from -3°C to 3°C [*Berresheim*, 1987; *Pszenny et al.*, 1989]. This temperature dependence at high latitudes is about 50%

Fig. 3. Latitudinal distribution of the molar ratio of MSA to nss SO_4^- from 20°N to 60°S. Horizontal lines indicate the latitudinal range over which samples were collected.
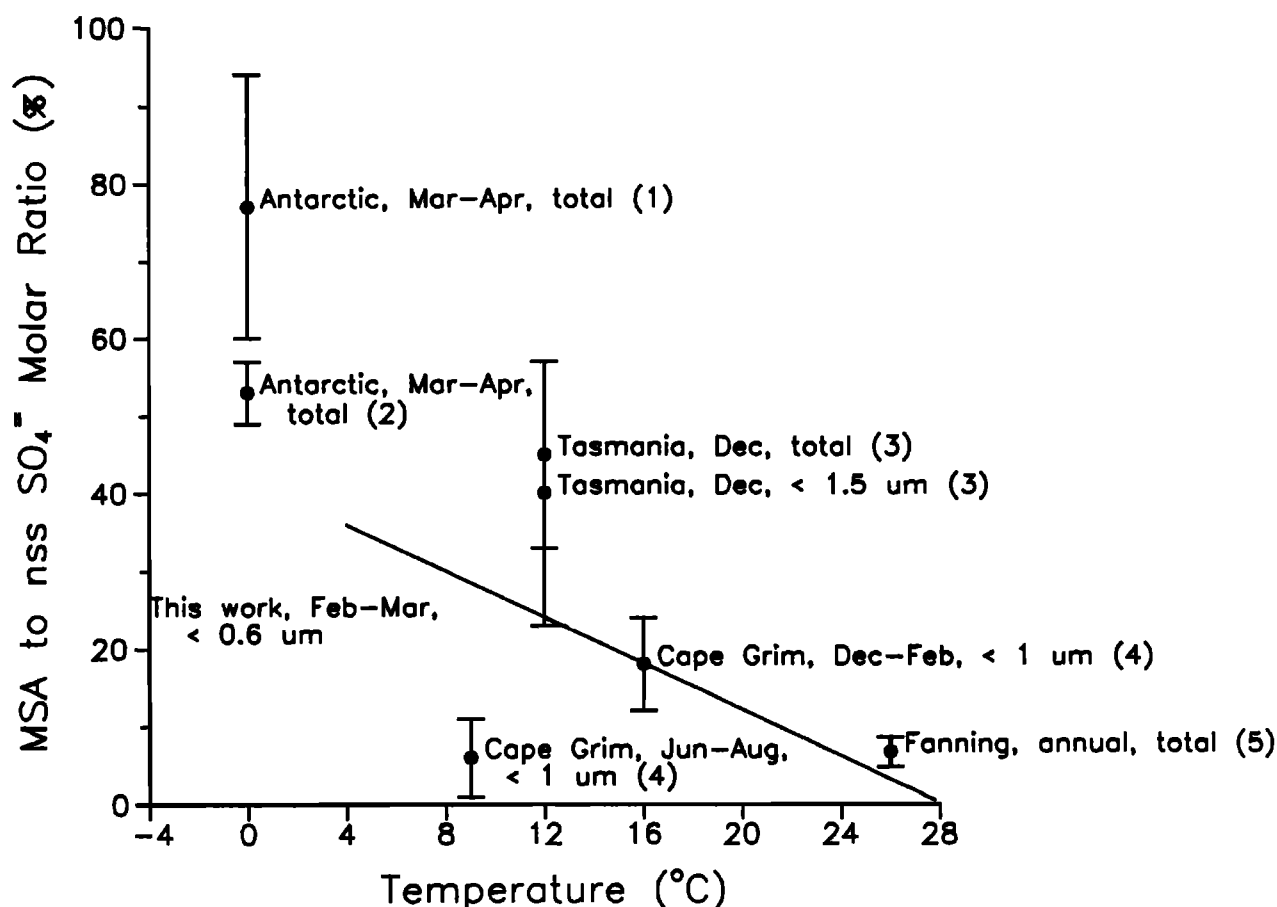
Fig. 5. MSA to nss SO_4^- molar ratios as a function of average daily air temperature. The figure includes data both from this study (Figure 4) and from the recent literature [*Berresheim*, 1987 (1); *Pszenny et al.*, 1989 (2); *Berresheim et al.*, 1990 (3); *Ayers et al.*, 1991 (4); *Saltzman et al.*, 1986 (5)]. The symbols and vertical lines represent the reported mean concentrations and standard deviation or range of reported values, respectively. Concentrations are defined as "total" referring to collection of the entire particle size range or <1.0 or <1.5 μm referring to only the smaller-size range.

greater than the others described here and could be due, in part, to the sampling technique used.

MSA and nss SO_4^- have been found to occur on particles with diameters ranging from a fraction of a micron to several microns [*Saltzman et al.*, 1983; *Saltzman et al.*, 1986; *Pszenny et al.*, 1989; *Quinn et al.*, 1990a; *Pszenny*, 1992]. Although nss SO_4^- is associated primarily with submicrometer particles, MSA can be distributed on larger particles, presumably as a function of aerosol surface area [*Pszenny*, 1992]. *Berresheim et al.* [1990] and *Ayers et al.* [1991] have found as much as 50% of the MSA mass on supermicron particles. Hence the size range of the sampled particles can have a large effect on the measured MSA to nss SO_4^- molar ratio. Of the measurements discussed here, samplers were used which collected submicrometer aerosol particles (this study; *Ayers et al.* [1991]), the entire size range of particles [*Saltzman et al.*, 1986; *Savoie and Prospero*, 1989; *Pszenny et al.*, 1989], and both a submicron and a supermicron fraction [*Berresheim*, 1987; *Berresheim et al.*, 1990]. The larger MSA to nss SO_4^- molar ratios measured at high latitudes could be, in part, a result of sampling both the submicron and the supermicron fraction.

Measurements taken during this study and from *Berresheim et al.* [1990] allow us to estimate the effect of different sampling techniques on the magnitude of the measured ratio.

During both of these field experiments, size-segregated samples were collected with an 8.0-μm pore size Nuclepore filter followed by a 1.0-μm pore size Teflon filter. The size cut from this study is estimated to be at a particle diameter of 0.6 μm and that from the work of *Berresheim et al.* [1990] to be about 1.5 μm. Size-segregated samples were collected during this study from 20°N to 25°S. The MSA to nss SO_4^- molar ratio over the total particle size range was 2.7 to 22% larger than that of the size range less than 0.6 μm. Data from *Berresheim et al.* [1990] indicate that the molar ratio over the total size distribution ranged from being 11% lower to 43% higher than that of the size range less than 1.5 μm. Clearly, the size cut of the sampling method controls the magnitude of the measured MSA to nss SO_4^- molar ratio. To understand the role of the DMS oxidation products in particle formation and growth as well as the biogeochemical cycling of marine sulfur, the sampling method used should allow for size-segregated sampling with several well-defined size cuts over the entire particle size range.

CONCLUSIONS

The data reported here show a strong inverse correlation between the molar ratio of MSA to nss SO_4^- and atmospheric temperature with the ratio increasing with decreasing

temperature. Although this trend is consistent with laboratory results indicating the favored production of MSA at lower temperatures [Hynes et al., 1986; Yin et al., 1990b), it is contrary to southern hemisphere baseline station data. At both Cape Grim, Tasmania [Ayers et al., 1991], and Mawson, Antarctica [Prospero et al., 1991], the highest MSA to nss SO_4^- molar ratios are found in the warmer summer months. Covering a long latitudinal transect in the southern hemisphere during February and March gave us the opportunity to measure MSA to nss SO_4^- molar ratios over a wide temperature range when DMS emissions to the atmosphere were near their peak. These high oceanic emissions would tend to obscure any minor source of nonmarine sulfate aerosol that might dominate in the high-latitude winter season. The strong signals of biogenic MSA and nss SO_4^- allowed for the observation of a striking correlation between the MSA to nss SO_4^- molar ratio and temperature.

In contrast, the colder temperatures at the baseline stations occur during winter when DMS emissions are low resulting in weaker signals of biogenic MSA and nss SO_4^-. Hence the MSA to nss SO_4^- molar ratio is more susceptible to perturbation by nonmarine sources of sulfate [Ayers and Gras, 1991; Ayers et al., 1991; Prospero et al., 1991]. Therefore the decrease in the MSA to nss SO_4^- molar ratio with a decrease in temperature may not be due to the prevailing pathway of DMS oxidation but to a decrease in the supply of DMS relative to nonmarine sources of sulfate in winter.

REFERENCES

Andreae, M. O., R. J. Ferek, F. Bermond, K. P. Byrd, R. T. Engstrom, S. Hardin, P. D. Houmere, F. LeMarrec, H. Raemdonck, and R. B. Chatfield, Dimethylsulfide in the marine atmosphere, *J. Geophys. Res., 90*, 12,891–12,900, 1985.

Ayers, G. P., and J. L. Gras, Seasonal relationship between cloud condensation nuclei and aerosol methanesulphonate in marine air, *Nature, 353*, 834–835, 1991.

Ayers, G. P., J. P. Ivey, and R. W. Gillet, Coherence between seasonal cycles of dimethylsulfide, methanesulfonate, and sulphate in marine air, *Nature, 349*, 404–406, 1991.

Bates, T. S., J. D. Cline, R. H. Gammon, and S. R. Kelly-Hansen, Regional and seasonal variations in the flux of oceanic dimethylsulfide to the atmosphere, *J. Geophys. Res., 92*, 2930–2938, 1987.

Bates, T. S., A. D. Clarke, V. N. Kapustin, J. E. Johnson, and R. J. Charlson, Oceanic dimethylsulfide and marine aerosol: Difficulties associated with assessing their covariance, *Global Biogeochem. Cycles, 3*, 299–304, 1989.

Bates, T. S., J. E. Johnson, P .K. Quinn, P. D. Goldan, W. C. Kuster, D. C. Covert, and C. J. Hahn, The biogeochemical sulfur cycle in the marine boundary layer over the Northeast Pacific Ocean, *J. Atmos. Chem., 10*, 59–81, 1990.

Bates, T. S., B. K. Lamb, A. Guenther, J. Dignon, and R. E. Stoiber, Sulfur emission to the atmosphere from natural sources, *J. Atmos. Chem., 14*, 315–337, 1992.

Berresheim, H., Biogenic sulfur emissions from the Subantarctic and Antarctic oceans, *J. Geophys. Res., 92*, 13,245–13,262, 1987.

Berresheim, H., M. O. Andreae, G. P. Ayers, R. W. Gillett, J. T. Merrill, V. J. Davis, and W. L. Chameides, Airborne measurements of dimethylsulfide, sulfur dioxide, and aerosol ions over the southern ocean south of Australia, *J. Atmos. Chem., 10*, 341–370, 1990.

Calhoun, J. C., T. S. Bates, and R. J. Charlson, Sulfur isotope measurements of submicrometer sulfate aerosol particles over the Pacific Ocean, *Geophys. Res. Lett., 18*, 1877–1880, 1991.

Cantoni, G., and D. G. Anderson, Enzymatic cleavage of dimethyl propiothetin by *Polysiphonia larosa, J. Biol. Chem., 222*, 171–177, 1956.

Charlson, R. J., J. E. Lovelock, M. O. Andreae, and S. G. Warren, Oceanic phytoplankton, atmospheric sulfur, cloud albedo and climate, *Nature, 326*, 655–661, 1987.

Charlson, R. J., J. Langner, H. Rodhe, C. B. Leovy, and S. G. Warren, Perturbation of the northern hemisphere radiative balance by backscattering from anthropogenic sulfate aerosols, *Tellus, 43*, 152–163, 1991.

Dacey, J. W. H., and N. V. Blough, Hydroxide decomposition of dimethylsulfonioproprionate to form dimethylsulfide, *Geophys. Res. Lett., 14*, 1246–1249, 1987.

Hoppel, W. A., Nucleation in the MSA-water vapor system, *Atmos. Environ., 21*, 2703–2709, 1987.

Hynes, A. J., and P. H. Wine, OH-initiated oxidation of biogenic sulfur compounds, in *Biogenic Sulfur in the Environment, ACS Symp. Ser.,* vol. 393, edited by E. Saltzman and W. Cooper, pp. 424–436, American Chemical Society, Washington, D. C., 1989.

Hynes, A. J., P. H. Wine, and D. H. Semmes, Kinetics and mechanisms of OH reactions with organic sulfides, *J. Phys. Chem., 90*, 4148–4156, 1986.

Johnson, J. E., and W. Mitchell, Structure of the marine boundary layer over the Pacific Ocean during the RITS 88 and RITS 89 cruises, *NOAA Tech. Rep. ERL PMEL-27*, 105 pp., U.S. Government Printing Office, Washington, D. C., 1991.

Kiene, R. P., and T. S. Bates, Biological removal of dimethyl sulphide from sea water, *Nature, 345*, 702–705, 1990.

Koga, S., H. Tanaka, M. Yamato, T. Yamanouchi, F. Nishio, and Y. Iwasaka, Methanesulfonic acid and non-sea-salt sulfate over both hemispheric oceans, *J. Meteorol. Soc. Jpn., 69*, 1–13, 1991.

Liss, P. S., and L. Merlivat, Air-sea gas exchange rates: Introduction and synthesis, in *The Role of Air-Sea Exchange in Geochemical Cycling,* edited by P. Buat-Menard, pp. 113–128, D. Reidel, Norwell, Mass., 1986.

Nguyen, B. C., N. Mihalopoulos, and S. Belviso, Seasonal variation of atmospheric dimethylsulfide at Amsterdam Island in the southern Indian Ocean, *J. Atmos. Chem., 11*, 123–141, 1990.

Plane, J. M. C., Gas-phase atmospheric oxidation of biogenic sulfur compounds: A review, in *Biogenic Sulfur in the Environment, ACS Symp. Ser.,* vol. 393, edited by E. Saltzman and W. Cooper, pp. 404–423, American Chemical Society, Washington, D. C., 1989.

Prospero, J. M., D. L. Savoie, E. S. Saltzman, and R. Larsen, Impact of oceanic sulphur on sulphate aerosol concentrations at Mawson, Antarctica, *Nature, 350*, 221–223, 1991.

Pszenny, A. P., Particle size distributions of methanesulfonate in the tropical Pacific marine boundary layer, *J. Atmos. Chem.,* in press, 1992.

Pszenny, A. P., A. J. Castelle, and J. N. Galloway, A study of the sulfur cycle in the Antarctic marine boundary layer, *J. Geophys. Res., 94*, 9818–9830, 1989.

Quinn, P. K., and T. S. Bates, Collection efficiencies of a tandem sampling system for atmospheric aerosol particles and gaseous ammonia and sulfur dioxide, *Environ. Sci. Technol., 23*, 736–739, 1989.

Quinn, P. K., T. S. Bates, D. S. Covert, and C. Leck, Size dependent concentrations of non-seasalt sulfate and methanesulfonic acid: Implications on the dimethylsulfide-climate connection, *Eos Trans. AGU, 71*, 1225, 1990a.

Quinn, P. K., T. S. Bates, J. E. Johnson, D. S. Covert, and R. J. Charlson, Interactions between the sulfur and reduced nitrogen cycles over the central Pacific Ocean, *J. Geophys. Res., 95*, 16,405–16,416, 1990b.

Saltzman, E. S., D. L. Savoie, R. G. Zika, and J. M. Prospero, Methane sulfonic acid in the marine atmosphere, *J. Geophys. Res., 88*, 10,897–10,902, 1983.

Saltzman, E. S., D. L. Savoie, J. M. Prospero, and R. G. Zika, Atmospheric methanesulfonic acid and non-seasalt sulfate at Fanning and American Samoa, *Geophys. Res. Lett., 12*, 437–440, 1985.

Saltzman, E. S., D. L. Savoie, J. M. Prospero, and R. G. Zika, Methane sulfonic acid and non-sea-salt sulfate in Pacific air: Regional and seasonal variations, *J. Atmos. Chem.*, *4*, 227–240, 1986.

Savoie, D. L., and J. M. Prospero, Comparison of oceanic and continental sources of non-sea-salt sulphate over the Pacific Ocean, *Nature, 339,* 685–689, 1989.

Spiro, P. A., D. J. Jacob, and J. A. Logan, Global inventory of sulfur emissions with a 1° × 1° resolution, *J. Geophys. Res, 97,* 6023–6036, 1992.

Thompson, A. M., M. A. Huntley, and R. W. Stewart, Perturbations to tropospheric oxidants, 1985–2035, 1, Calculations of ozone and OH in chemically coherent regions, *J. Geophys. Res.,* *95,* 9829–9844, 1990.

Yin, F., D. Grosjean, R. C. Flagan, and J. H. Seinfeld, Photooxidation of dimethyl sulfide and dimethyl disulfide, I, Mechanism evaluation, *J. Atmos. Chem., 11,* 365–399, 1990*a*.

Yin, F., D. Grosjean, and J. H. Seinfeld, Photooxidation of dimethyl sulfide and dimethyl disulfide, I, Mechanism development, *J. Atmos. Chem., 11,* 309–364, 1990*b*.

T. S. Bates and P. K. Quinn, Pacific Marine Environmental Laboratory, NOAA, 7600 Sand Point Way NE, Building 3, Seattle, WA 98115.

J. A. Calhoun, Laboratoire de Glaciologie et Geophysique de l'Environnement, BP96, 38402 Saint-Martin-d'Heres Cedex, France.