OCEANIC DIMETHYLSULFIDE AND MARINE AEROSOL: DIFFICULTIES ASSOCIATED WITH ASSESSING THEIR COVARIANCE

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Abstract. Simultaneous measurements of oceanic dimethylsulfide (DMS), atmospheric aerosol sulfate and the size-resolved physical properties of the aerosol were made aboard a ship in the equatorial Pacific during July 1987. Under light and variable winds, in an area essentially free of continental and anthropogenic air masses, an observed increase in oceanic DMS concentrations preceded simultaneous increases in non-sea salt sulfate aerosol, the fraction of volatile submicrometer (sub-μm) aerosol, the condensation nuclei population, and the mean particle diameter of the sub-μm aerosol. Although the increase in oceanic DMS can qualitatively account for the corresponding changes in the atmospheric aerosol particles, there are numerous difficulties in quantifying the relationship between the sea-to-air flux of DMS and the formation and growth of atmospheric aerosol particles.

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INTRODUCTION

Dimethylsulfide (DMS) emissions from the ocean vary both seasonally and regionally [Turner and Liss, 1985; Bates and Cline, 1985; Andreae, 1986; Bates et al., 1987a] and have been correlated by latitude and season with atmospheric aerosol particle populations (CN) [Bates et al., 1987b]. Marked increases in atmospheric submicrometer (sub-μm) sulfate particle mass concentrations have also been observed in regions of oceanic upwelling and high primary productivity [Saltzman et al., 1986; Parungo et al., 1986; Clarke et al., 1987], where DMS emissions are generally high. However, simultaneous measurements of oceanic DMS concentrations and the size-resolved, physical properties of aerosol particles necessary to quantitatively relate local DMS emissions to particle formation and growth have not been reported. Establishing such a relationship is not only important with regard to interest in the ocean/atmosphere flux of sulfur [Andreae, 1986] but also for effects such particles may have on cloud reflectivity [Twomey, 1977; Coakly et al., 1987] and climate [Shaw, 1983; Rodhe, 1986; Charlson et al., 1987; Shaw, 1987].

During the summer of 1987 the second joint Soviet American Gas and Aerosol experiment (SAGA II) was conducted in the Pacific and Indian Oceans aboard the R/V *Akademic Korolev* as part of the U.S./USSR Environmental Bilateral Accord. One goal of this expedition was to investigate the relationship between oceanic DMS emissions and the formation, growth, and concentration of atmospheric non-sea-salt (NSS) sulfate aerosol particles. The hypothesis was that if DMS emissions are the major source of NSS sulfate aerosol particles in the remote marine troposphere, then an increase in DMS emissions should lead to the formation and growth of these particles with a resultant increase in the total mass concentration of NSS sulfate. We report here an observed increase in surface seawater DMS

concentration that preceded subsequent increases in CN population, the median particle diameter of the accumulation mode, and the NSS sulfate aerosol concentration. We use this case study to assess the difficulties in quantifying the relationship between oceanic DMS emissions and marine aerosol particle concentrations and to suggest the suite of measurements necessary to define the relevant processes.

METHODS

Seawater samples were collected aboard the ship from a continually flowing (>50 L/min), dedicated sampling line. The inlet was located at approximately 5 m depth amidships. Five milliliters of seawater were purged and analyzed by flame photometric gas chromatography for DMS [Bates et al., 1987a]. Precision of the analysis is typically within 10%.

Aerosol samples were collected from in front of the ship's flying bridge on 47-mm Millipore Fluoropore-FA, PTFE Membrane, 1.0-μm pore size filters at a flow rate of 50 standard liters per meter (SLPM). These filters have a >99% collection efficiency for particles with diameters >0.035 μm [Liu and Lee, 1976]. A cyclone separator upstream of the filter eliminated most of the coarser, predominantly sea-salt particles (50% cut efficiency at 0.9 μm). Each filter sample was accompanied by a blank filter mounted beside the sample filter. Filter samples were collected for approximately 4 hours, only when the ship was underway, and were changed in a glove box to minimize contamination. The filters were then extracted with 0.5 mL of methanol and 9.5 mL of distilled water and analyzed on board by ion chromatography (Dionex model 2010i) for sulfate and chloride (AS4A column with 2.2 mmol sodium carbonate and 0.75 mmol sodium bicarbonate eluent). The concentration of sea-salt sulfate, as determined by the chloride ion, was subtracted from the total sulfate concentration to obtain NSS sulfate. Although several investigators [Keene et al., 1986, and references therein] have suggested a potential loss of chloride from marine aerosol particles, the correction would be insignificant since the sea-salt sulfate concentration was generally <10% and the filter blank <20% of the total sulfate in this study.

The same marine aerosol was sampled for continuous in situ measurements from the top of a forward mast (18 m above the ocean surface and 3 m forward of and 4 m above the filter sample collections). Air was drawn through a sample line at 200 LPM to a condensation nucleus (CN) counter (General Electric Company) and a modified laser optical particle counter (LOPC) (Particle Measurement Systems, Boulder, Colorado) [Clarke et al., 1987]. The LOPC counted and sized particles in 256 channels for the 0.15- to 7-μm diameter range. A microcomputer calculated and stored 1- to 3-hour averages of the particle size distribution. The LOPC also sequentially sampled ambient aerosol, ambient aerosol heated to 140°C, and ambient aerosol heated to 300°C to discriminate between total aerosol, total aerosol minus the volatile fractions, and finally refractory aerosol such as sea salt, soot, or crustal material [Larson et al., 1982; Clarke et al., 1987]. When only a portion of the fine particle volume mode was visible (i.e., >0.15 μm), the total aerosol was estimated by extending the mode as a log-normal distribution. The accuracy of the LOPC data reported here is estimated at approximately 25%, while the precision is approximately 5%.

RESULTS

Air masses encountered during the first half of the voyage (Singapore to Hawaii) were influenced by the islands in the western tropical Pacific. On Julian day 202 (J.D. 202, July 21, 1987) the wind shifted to the NW bringing air with low background NSS sulfate concentrations (<0.3 nmol/m^3). The next day (J.D. 203) the wind shifted to the southeast and the speed decreased to 1–4 m s^{-1} (mean 2.2 ± .9 m s^{-1}). These light and variable winds existed until midday on J.D. 205 when the wind shifted to the northwest and increased in speed. Five-day isobaric back-trajectories calculated for the 1000 mbar level (J. Harris, personal communication, 1988) suggest that the air masses sampled from J.D. 202 to J.D. 205 were of similar origin and were advected from the equatorial South Pacific (Figure 1).

During the first half of the voyage (Singapore to Hawaii), surface seawater DMS concentrations averaged 1.1 ± 0.17 nmol/L (nanomoles per liter, n = 23 from J.D. 196 to J.D. 201). Seawater DMS concentrations began rising on J.D. 203 and peaked at 2.2 nmol/L on J.D. 204 (Figure 2a). Atmospheric NSS-sulfate concentrations began rising toward the end of J.D. 203 and continued increasing to 1.6 nmol/m^3 on J.D. 205 (Figure 2b).

Between J.D. 202 and J.D. 205, the increase in sub-μm particle volume from the LOPC (0.15 < Dp < 0.5 μm) paralleled the increase in NSS sulfate concentration from the filters (Figures 2b and 2c). By the morning of J.D. 204, the sub-μm particle volume consisted almost completely of aerosols volatile at 140°C (Figures 2d). It has been previously shown in this region that these sub-μm volatile particles consist almost entirely of NSS sulfate aerosols that are more acidic than ammonium bisulfate [Clarke et al., 1987].

The integrated LOPC volume distribution can be used to infer a particle sulfate volume concentration. The latter is less than the LOPC measured volume due to both the chemical form of the aerosol and the relative humidity (RH). When the ammonium to sulfate molar ratio is less than one, the aerosol remains as a droplet and retains bound water even at very low RH [Tang et al., 1978]. Since these data are consistent with a primarily sulfuric acid aerosol volatile at <140°C [Tang et al., 1978; Clarke et al., 1987], the water uptake can be established for the LOPC measurement RH (35–40% RH). The results of our laboratory calibrations are in accordance with theory [Tang et al., 1978] and were used to calculate the corrected sulfate volume in Figure 2c. Using the density of sulfuric acid (1.8 g/cm^3) to convert this LOPC "dry" sub-μm volume to a mass [Clarke et al., 1987], the LOPC mass concentration measured between J.D. 202 and J.D. 205 was within 15% of the NSS sulfate mass on the filters.

In addition to the increase in aerosol volume and mass on J.D. 204, the mass median particle diameter in the sub-μm mode increased from about 0.15 to 0.23 μm (Figure 2e). The total particle number concentration, as measured with the CN counter during this period, increased from a low of 50 particles/cm^3 on J.D. 203 to a high of 160 cm^{-3} on J.D. 205 (Figure 2f). The CN counter, which measures the total number concentration of particles with diameters >0.01 μm, includes not only the sub-μm volume mode (as measured by the LOPC) but also the smaller nucleation mode. Although
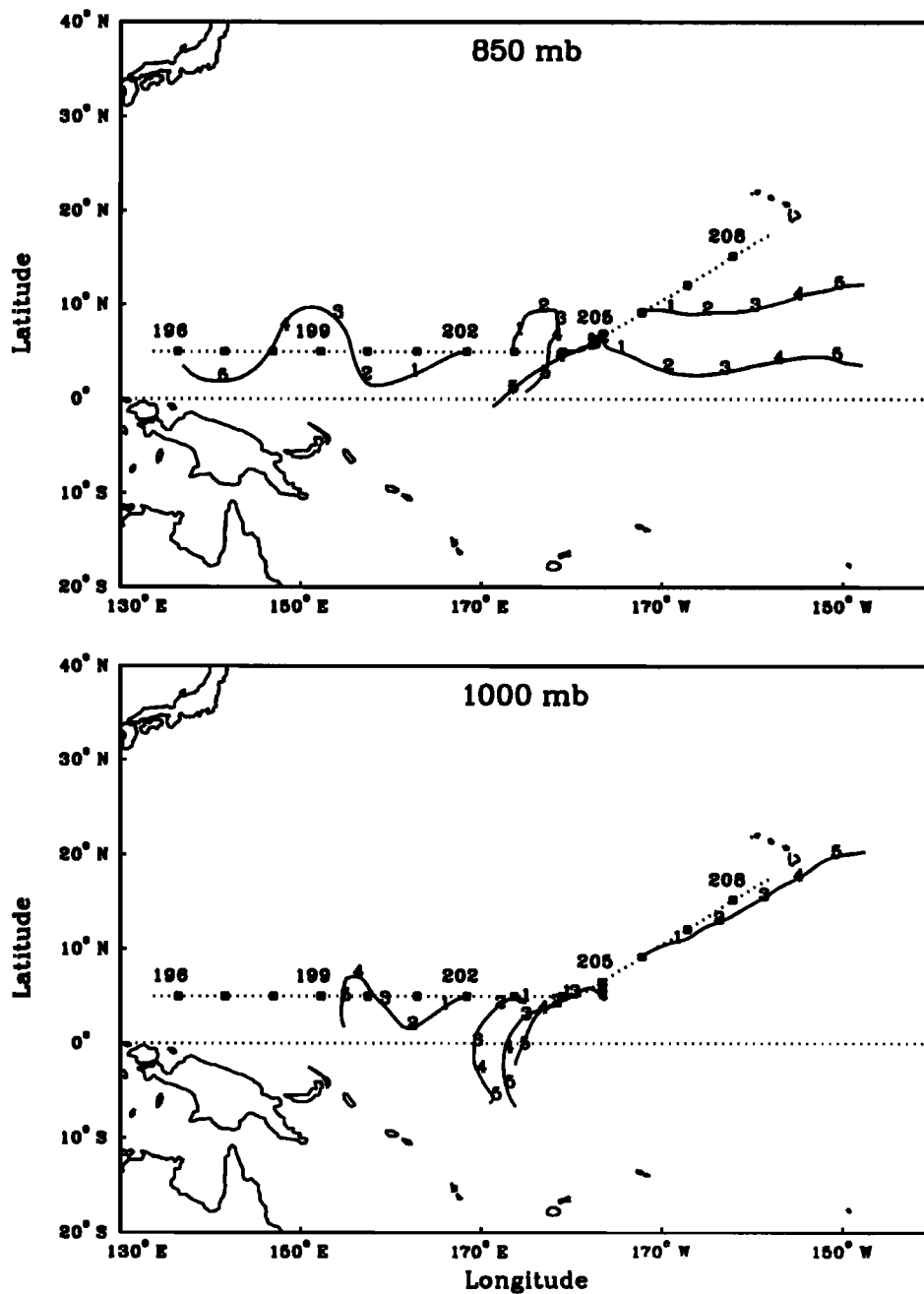
Fig. 1. The cruise track of the *Akademic Korolev*, with the position of the ship at the start of each Julian day (square symbols, J.D. 196–J.D. 208, July 15–27, 1987) and the 5-day isobaric back trajectories at 850 and 1000 mbar (J. Harris, private communication). During this period, light and variable winds existed in the region 10° north and south of the equator, while the strongest trade winds were between 10° and 25°N.

particles in the nucleation mode generally contribute little to the total particle mass or volume, they often dominate the number distribution. On J.D. 203 (1400 UT) only 15–20% of the total CN were found in the sub-μm volume mode, but by J.D. 204 and J.D. 205, the number had increased to 60%.

DISCUSSION

The biogeochemical sulfur cycle has been studied in several remote marine environments [Berresheim, 1987; Andreae et al., 1988; Pszenny et al., 1989; Bates et al., 1989; Berresheim
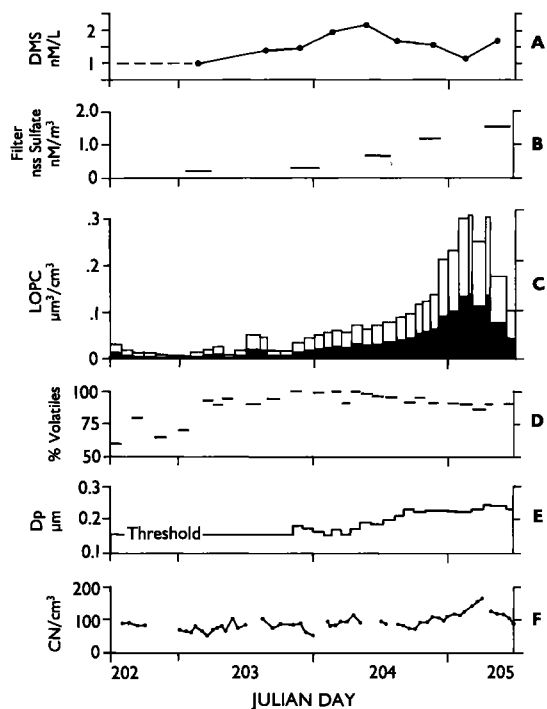
Fig. 2. (a) Surface seawater DMS concentrations in nanomoles per liter, (b) atmospheric NSS sulfate concentrations from filter/ion chromatography measurements in nanomoles per cubic meter, (c) sub-μm total aerosol volume from the LOPC (open bars) and the equivalent sulfate aerosol volume (shaded bars-see text) in cubic microns per cubic meter, (d) the percent volatile (140°C) aerosol to the total volatile (300°C) aerosol for particle diameters <0.5 μm as measured by the LOPC, (e) the volume median particle diameter in the sub-μm mass mode expressed in microns, and (f) the total particle population as measured with a CN counter in number per cubic meter. The DMS data are averaged over 6-hour time intervals, while the atmospheric LOPC data are averaged over 1- to 3-hour time periods and the CN data are averaged over 1-hour time intervals. The sampling time periods for the filter sulfate measurements are shown by the length of the line.

et al., 1989]. These studies have all used a steady state box model approach to show that oceanic DMS emissions are sufficient to account for the natural atmospheric NSS sulfate. Although these models are useful for summarizing the various sulfur reservoirs, the uncertainties and variabilities associated with the fluxes between these reservoirs obscure any quantitative relationship between DMS flux and particle formation and growth. Hence a different approach is needed to determine if an increase in the sea-to-air exchange of DMS leads to the formation and growth of NSS sulfate aerosol particles.

The ideal conditions under which to observe the formation and growth of NSS sulfate aerosol particles are when the number and mass concentrations are small so that any change

is a significant fraction of the total signal. These meteorological and environmental conditions were encountered during July 21–24, 1987 (5–9°N, 170°E–170°W), over the equatorial Pacific Ocean. The background sub-μm aerosol population was low (<100 particles/cm³), indicating air masses free of continental influence. Winds were light (1–4 m/s) and the relative wind (6–10 m/s) was within 30° of the ship's bow, providing air that was free of ship contamination. These light and variable winds minimized advective transport and facilitated comparisons of the chemical composition of seawater and the overlying atmosphere. Furthermore, the near homogeneity of the surface trajectories for J.D. 202–205 suggests a homogeneity of the sampled air masses.

As the ship steamed downwind into a region of higher seawater DMS concentrations (Figure 2a), marked changes were observed in the chemistry and physics of the atmospheric aerosol particles. The averaged total number population increased by roughly a factor of 2 (Figure 2f). The mass mean particle diameter of the sub-μm mass mode increased from slightly less than 0.15 to 0.23 μm (Figures 2e) resulting in an average particle volume increase of a factor of 3.5. The product of the increase in number and increase in volume or mass is a factor of 7, in close agreement with the factor of 8 increase in NSS sulfate during this episode (Figures 2b and 2c). The increase in sulfate aerosol mass appears to result from both multiphase (heterogeneous condensation, i.e., deposition of gases on to existing particles) and homogeneous processes (gas phase nucleation of new particles) since both particle volume and total number increased. The presence of scattered clouds (both precipitating and nonprecipitating) likely promoted the rapid particle growth, since the lifetime of these particles with respect to coagulation in the absence of clouds is weeks or more. From a Lagranian perspective, we hoped to demonstrate that the increase in DMS was associated with both the formation and growth of NSS sulfate aerosol particles.

This Lagranian analysis of the data, however, contains several inconsistencies. The increase in seawater DMS was probably a spatial phenomenon resulting from algal patchiness. Why is there a 1-day lag between the increase in seawater DMS and the increase in atmospheric sulfate aerosol? If the increase in seawater DMS was a temporal phenomenon, the 1 day could perhaps be explained by the atmospheric lifetimes of DMS and SO_2. Unfortunately, there are far too many uncertainties in oceanic DMS cycling to resolve the spatial/temporal question [Taylor and Kiene, 1989]. A further question concerns the DMS flux rate. Since there was no significant change in wind speed, the oceanic emission of DMS should have been proportional to its seawater concentration [Liss and Merlivat, 1986]. Why, then, does the seawater DMS concentration increase by a factor of 2, while the atmospheric NSS sulfate concentration increases by a factor of 8?

There are several other explanations for these data. Although this period of low wind speed minimized advection, horizontal transport of atmospheric DMS from regions of higher seawater DMS cannot be excluded. Consequently, the analysis of these data in a Lagranian context is perhaps inappropriate. A better way to assess the flux or source of sulfur to the atmosphere is through a coordinated

investigation that includes a thorough survey of seawater DMS concentrations upwind of the atmospheric measurements.

Changes in number and mass concentration of NSS sulfate aerosols can also result from changes in atmospheric mixing. Although radiosonde data from the ship showed no significant variations in atmospheric temperature and wind structure, this was a region of unstable convection and hence there was no clearly defined boundary layer. Consequently, changes in vertical advection and input of sulfur from higher in the free troposphere cannot be assessed without concurrent measurements of the various sulfur species at these altitudes.

Atmospheric chemistry further complicates the data analysis. The relative amounts of the different DMS oxidation products (SO_2, methanesulfonate, dimethylsulfone, dimethylsulfoxide) vary with latitude [Berresheim, 1987], presumably as a function of temperature and hydroxyl radical (OH) concentration [Hynes et al., 1986]. The atmospheric lifetimes of the numerous atmospheric sulfur compounds also vary as a function of temperature, OH concentration, and sunlight [Berresheim, 1987]. Without measurements of all related major species in all phases (seawater, gas phase, aerosol, cloud water, and precipitation), it is not possible to resolve the chemical processes from the physical processes.

Although we believe we have observed the formation and growth of NSS sulfate aerosol particles that probably resulted from an increase in the sea-to-air DMS flux, we cannot sufficiently define the system to unequivocally relate the two processes. Since the conditions experienced during this period were as close to ideal as one might reasonably expect for a single-ship experiment, we believe that no shipboard study alone will be able to resolve these questions. All ship studies suffer from a lack of definition of the chemistry and physics above the lowest layer of the atmosphere [Berresheim, 1987; Pszenny et al., 1989; Bates et al., 1989]. Studies aboard ships in transit are further hindered by being unable to define the seawater DMS concentrations upwind of the atmospheric measurements. On the other hand, aircraft studies alone provide no data on DMS fluxes from the ocean or sulfur deposition and are limited by the short data sets that can be obtained during a single flight [Berresheim et al., 1989]. The ideal combination would include a ship to provide ocean and lower boundary layer data, an aircraft to define chemical concentrations and aerosol physics as a function of altitude, and a shore-based measurement site that could be occupied for longer periods to put the ship/aircraft measurements in a broader perspective. Such a program has been outlined for the Atlantic Ocean (AEROCE); however, the continental air masses that dominate this region would likely overwhelm the natural processes under study here.

CONCLUSIONS

Although the measurements presented here suggest a link between DMS emissions and sulfate aerosol particle formation and growth, it clearly points out the difficulties in quantifying this relationship. The oceanic and atmospheric processes (e.g., production and consumption of DMS, air-sea exchange of DMS, atmospheric oxidation of DMS, aerosol microphysics, atmospheric mixing, atmospheric sulfur

deposition) involved are complex and do not necessarily occur on the same time/space scales. Short-term measurements from shore, ship, or aircraft alone will not adequately define these competing processes. Future experiments will require an interdisciplinary approach utilizing both ships and aircraft to describe concurrently the biological, chemical, and physical oceanography, the atmospheric gas-phase chemistry, the condensed phase chemistry as a function of particle size, the aerosol size distribution, the cloud water chemistry, and the meteorology. Only after the surface ocean/atmosphere system is thoroughly defined will it be possible to begin quantifying the processes connecting the various sulfur reservoirs.

Establishing a link between DMS emissions and the formation and growth of marine aerosol particles is an essential first step in assessing the climatic role of marine biogenic sulfur. However, to have a significant effect on the Earth's climate, changes in the sea-to-air flux of DMS must affect not only the CN population but also the cloud condensation nuclei (CCN) number concentration (i.e., the number of aerosol particles capable of forming cloud droplets), since it is the CCN number population that is calculated to affect the reflectivity of clouds [Charlson et al., 1987]. The above suite of measurements, therefore, need to be expanded to include CCN number population and cloud albedo to thoroughly define the interaction of the atmospheric marine sulfur cycle with cloud microphysics and climate.

REFERENCES

Andreae, M.O., The ocean as a source of atmospheric sulfur compounds, In *The Role of Air-Sea Exchange in Geochemical Cycling,* edited by P. Buat-Menard, pp. 331–362, D. Reidel, Hingham, Mass., 1986.

Andreae, M.O., H. Berresheim, T.W. Andreae, M.A. Kritz, T.S. Bates and J.T. Merrill, Vertical distribution of dimethylsulfide, sulfur dioxide, formic acid, aerosol ions, and radon over the northeast Pacific Ocean, *J. Atmos. Chem., 6,* 149–173, 1988.

Bates, T.S., and J.D. Cline, The role of the ocean in a regional sulfur cycle, *J. Geophys. Res., 90,* 9168–9172, 1985.

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, 1987a.

Bates, T.S., R.J. Charlson, and R.H. Gammon, Evidence for the climatic role of marine biogenic sulphur, *Nature, 329*, 319–321, 1987b.

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.*, in press, 1989.

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. Gillet, J.T. Merrill, V.J. Harris, and W.L. Chameides, Airborne measurements of dimethylsulfide, sulfur dioxide, and aerosol ions over the southern ocean south of Australia, *J. Atmos. Chem.*, in press, 1989.

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

Clarke, A.D., N.C. Alquist, and D.S. Covert, The Pacific marine aerosol and evidence for natural acid sulfates, *J. Geophys. Res., 92*, 4179–4190, 1987.

Coakley, J.A., Jr., R.L. Bernstein, and P.A. Durkee, Effect of ship-stack effluents on cloud reflectivity, *Science, 237*, 1020–1022, 1987.

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.

Keene, W.C., A.A.P. Pszenny, J.N. Galloway, and M.E. Hawley, Sea-salt corrections and interpretation of constituent ratios in marine precipitation, *J. Geophys. Res., 91*, 6647–6658, 1986.

Larson, T.V., N.C. Ahlquist, R.E. Weiss, D.S. Covert, and A.P. Waggoner, Chemical speciation of H_2SO_4–$(NH_4)_2SO_4$ particles using temperature and humidity controlled nephelometry, *Atmos. Environ., 16*, 1587–1590, 1982.

Liss, P.S., and L. Merlivat, Air-sea 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, Hingham, Mass., 1986.

Liu, B.Y.H., and K.W. Lee, Efficiency of membrane and Nuclepore filters for sub-micrometer aerosols, *Environ. Sci. Technol., 10*, 345–350, 1976.

Parungo, F.P., C.T. Nagamoto, J. Rosinski, and P.L. Haagenson, A study of marine aerosols over the Pacific Ocean, *J. Atmos. Chem., 4*, 199–226, 1986.

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

Rodhe, H., Biocontrolled thermostasis involving the sulfur cycle, *Clim. Change, 8*, 91–92, 1986.

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

Shaw, G.E., Bio-controlled thermostasis involving the sulfur cycle, *Clim. Change, 5*, 297–303, 1983.

Shaw, G.E., Aerosols as climate regulators: A climate biosphere linkage, *Atmos. Environ., 21*, 985–986, 1987.

Tang, I.N., H.R. Munkelwitz, and J.G. Davis, Aerosol growth studies-IV. Phase transformation of mixed salt aerosols in a moist atmosphere, *J. Aerosol Sci., 9*, 505–511, 1978.

Taylor, B.F., and R.P. Kiene, Microbial metabolism of dimethyl-sulfide, in *Biogenic Sulfur in the Environment, ACS Symposium*, edited by E. Saltzman and W. Cooper, pp. 202–221, American Chemical Society, Washington, D.C., 1989.

Turner, S.M., and P.S. Liss, Measurements of various sulphur gases in a coastal marine environment, *J. Atmos. Chem., 2*, 223–232, 1985.

Twomey, S., *Atmospheric Aerosols*, Elsevier, New York, 1977.

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