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Interactions Between the Sulfur and Reduced Nitrogen Cycles Over the Central Pacific Ocean

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In April and May of 1988 along 170°W from 53°N to 14°S, simultaneous concentration measurements were made of the major components of the sulfur and reduced nitrogen cycles. The species measured included seawater dimethylsulfide, DMS (s), and total ammonia, NH_3 (s,tot) = NH_3 (s) + NH_4^+ (s); atmospheric gas phase DMS (g), NH_3 (g), and SO_2 (g); and atmospheric particulate phase NH_4^+ (p), non-seasalt sulfate, nss $SO_4^=$ (p), and methanesulfonate, MSA (p). Based on isentropic calculated back trajectories at 1000, 950, 850, and 700 mbar arrival heights, three apparent air mass regimes were encountered; one from 50°N to 30°N which recently had been in contact with Asia, one from 29°N to 15°N which had passed over Hawaii during a volcanic eruption several days earlier, and one from 14°N to 11°S which was the most representative of remote marine air. Changes in the relative concentrations of the atmospheric S and NH_3 species reflected the origin of the air masses sampled. The NH_3 (g) concentrations were low over the entire region studied, indicating that the lifetime of NH_3 in the marine boundary layer is on the order of hours. These low NH_3 concentrations led to only partially neutralized sulfate aerosol particles. The mean NH_4^+ (p) to nss $SO_4^=$ (p) molar ratio was 1.3 ± 0.71. The highest ratios were found in continentally influenced air masses where the NH_4^+ (p) was most likely of continental origin and in remote marine air masses with an absence of continentally derived nss $SO_4^=$ (p). The lowest ratios found were a result of high nss $SO_4^=$ (p) concentrations in air masses influenced by the Hawaiian volcanic plume. Seawater concentrations of DMS (s) and NH_3 (s,tot) were lowest in the North Pacific central gyre and highest in the northern latitudes and near and south of the equator.

1. INTRODUCTION

Acid-base interactions play a significant role in the heterogeneous chemistry of the remote marine troposphere. Non-seasalt sulfate, nss $SO_4^=$, is the dominant anion in submicron aerosol particles and, therefore, the major contributor to acidity in submicron particles and rainwater in the remote marine troposphere [*Vong et al.*, 1988*a*, *b*; *Galloway et al.*, 1982]. Likewise, ammonia is the dominant base, other than seasalt, in the remote marine troposphere [*Quinn et al.*, 1987]. In many remote marine regions, the particulate NH_4^+ to nss $SO_4^=$ molar ratio has been found to be significantly less than two [*Covert*, 1988; *Quinn et al.*, 1988; *Parungo et al.*, 1986], indicating only partial neutralization of acid sulfates by ammonia. Precipitation scavenging of these unneutralized particles may be responsible for the *p*H values less than 5.6 found in remote marine rain [*Charlson and Rodhe*, 1982; *Vong et al.*, 1988*a*, *b*]. Because of the acid-base significance of $SO_4^=$ and NH_3, a knowledge of the interactions of the sulfur and nitrogen cycles is necessary for a complete understanding of the acid-base stoichiometry and heterogeneous chemistry of the marine atmosphere.

Ammonia exists in five phases in the remote marine environment; the atmospheric gas, NH_3 (g), and aerosol particle phases, NH_4^+ (p); rainwater, NH_4^+ (r); cloudwater, NH_4^+ (c); and seawater in both unionized, NH_3 (s), and ionized NH_4^+ (s), forms (Figure 1). Ammonia moves from seawater to the atmosphere via the air/sea exchange of NH_3 (s) with NH_3 (g). Once in the atmosphere, NH_3 (g) can dissolve directly into cloud or rainwater. Alternatively, gas phase ammonia can react with submicrometer acidic sulfate aerosol particles to form NH_4^+ (p). The NH_4^+ containing particles then can act as cloud condensation nuclei (CCN) [*Pruppacher and Klett*, 1980] and become incorporated into cloud droplets. NH_4^+ in a cloud droplet can either be returned to the particulate phase as NH_4^+ (p) when the cloud evaporates or it can be removed from the atmosphere in rainwater.

Biogenic aqueous dimethylsulfide, DMS (s), is a major oceanic source of S to the atmosphere [*Andreae*, 1986; *Bates et al.*, 1987]. DMS (s) is a product of the enzymatic cleavage of dimethylsulfonium proprionate [*Cantoni and Anderson*, 1956; *Dacey and Blough*, 1987], which is produced by certain species of phytoplankton in the seawater photic zone. DMS is emitted to the atmosphere where it is oxidized to SO_2 or methanesulfonic acid (MSA). The rate of production of SO_2

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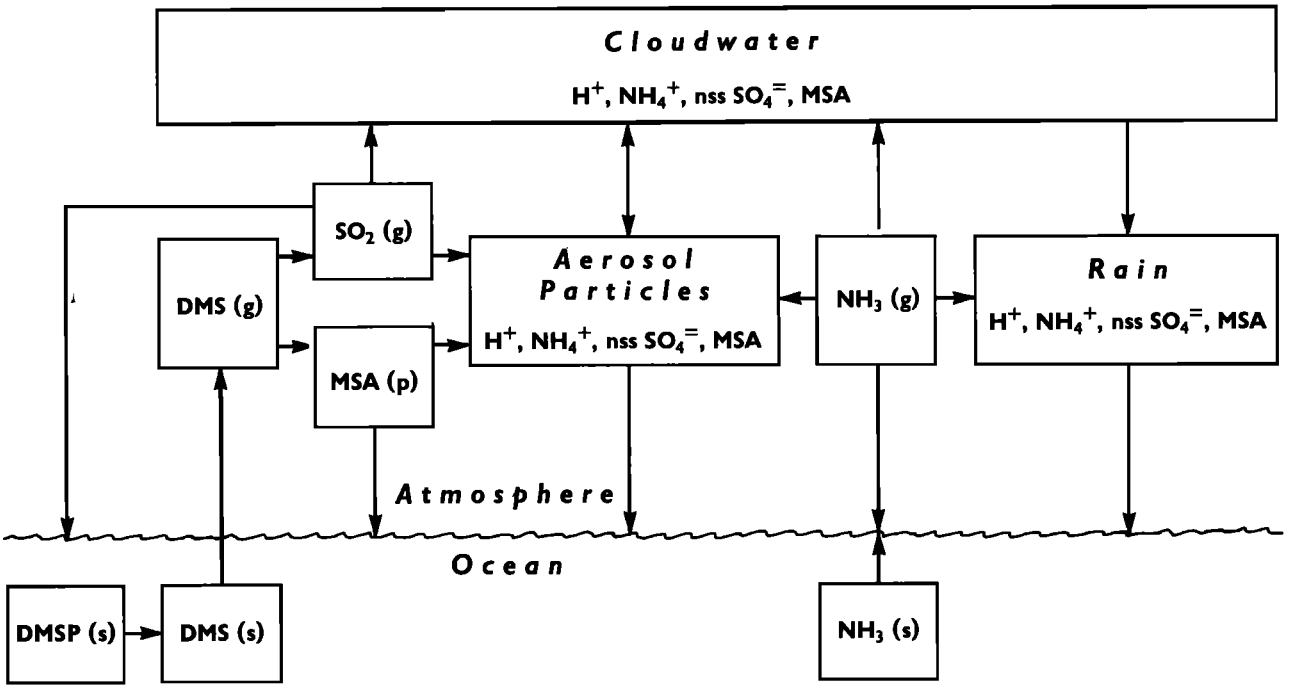

Fig. 1. Interactions of the sulfur and reduced nitrogen cycles in the remote marine troposphere.

and MSA depends at least on the relative concentration of oxidants present (OH, NO_3, or IO radicals), the rate constants of the relevant reaction mechanisms, and temperature [*Grosjean and Lewis*, 1982; *Hynes et al.*, 1986]. SO_2 undergoes gas to particle conversion to form acidic sulfate particles or is absorbed into cloudwater droplets and is oxidized to sulfate. Both MSA and nss $SO_4^=$ occur in submicrometer particles which can act as CCN and become incorporated into clouds. MSA and nss $SO_4^=$ can be removed from the atmosphere when the cloud rains or they can be returned to the particle phase upon cloud evaporation (Figure 1).

In spite of the important acid-base reaction of NH_3 (g) with H_2SO_4 aerosol particles, there are few reported simultaneous concentration measurements of NH_3 (g), NH_4^+ (p), and nss $SO_4^=$ (p). Likewise, in spite of the impact of air/sea exchange on the S and reduced N marine cycles, there are no reported simultaneous concentration measurements of NH_3 (g), NH_3 (s), DMS (g), and DMS (s). Certainly, none of these measurements has been made over a wide spatial range of the marine environment. We report here the first latitudinal distributions of simultaneous measurements of NH_3 (g), DMS (g), SO_2 (g), NH_4^+ (p), nss $SO_4^=$ (p), MSA (p), DMS (s), NH_3 (s), and total seawater ammonia, NH_3 (s,tot) = NH_3 (s) + NH_4^+ (s).

2. MEASUREMENTS

Samples were collected aboard the NOAA ship *Oceanographer* along 170°W from 53°N to 14°S (Figure 2) from April 6 to May 5, 1988. A strict sampling protocol was followed to prevent contamination of the air samples by the ship itself. Samples were taken when the total particle (CN) count was less than 1000 cm^{-3} for particles having a diameter greater than 0.01 μm, the wind direction was forward of the ship's beam, and the relative wind speed was greater than 3 m s^{-1}. In addition, after the cruise, isentropic back trajectories for 1000, 950, 850, and 700 mbar arrival heights at the ship's location were calculated enabling the course of sampled air masses to be followed 4 days back in time. All gas and particle phase concentrations are reported in nmol m^{-3} at 25°C and 1 atm. All times are reported in GMT.

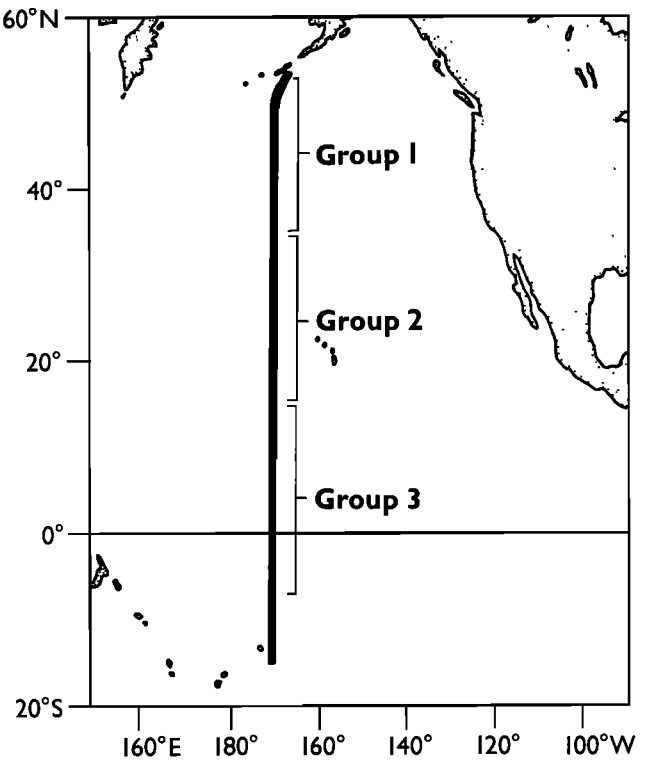

Fig. 2. Cruise track from 53°N to 11°S along 170°W. The latitude range of the three groups of atmospheric gas and particle phase samples are indicated.

Air samples were taken from the ship's flying bridge on a horizontal boom extending 6 m in front of the bridge and 20 m above the sea surface. A tandem sampling system was used for the collection of gas phase NH_3 and SO_2 and particle phase species [*Quinn and Bates*, 1989]. Collection times ranged from 12 to 36 hours. The system consisted of a cyclone separator followed by a 47 mm Millipore Teflon particle filter (1.0 μm pore size) and four 47 mm Whatman 41 filters coated with either oxalic acid or potassium carbonate for the collection of NH_3 (g) and SO_2 (g), respectively. Six sets of tandem sampling systems were deployed; three were used for the collection of NH_3 (g) and three for SO_2 (g). In each set of three, two collected sample and one served as a sampling and analytical blank (average sample flow rate = 45 slpm and blank flow rate = 0 slpm). Each set of duplicate samples were individually blank corrected.

The particle filters have a greater than 99% collection efficiency for particles with diameters larger than 0.035 μm [*Liu and Lee*, 1976]. The cyclones were calibrated in an air stream containing sea-salt particles [*Quinn and Bates*, 1989] and were found to have a 50% collection efficiency at 0.9 μm for NaCl particles at 85% RH. The collection efficiencies for NH_3 (g) and SO_2 (g) were determined by comparison with gravimetrically calibrated permeation tubes. At room temperature and 75% RH, the oxalic acid coated filters had an NH_3 (g) collection efficiency of 103 ± 30% and the potassium carbonate coated filters had an SO_2 (g) collection efficiency of 100 ± 21%.

The cyclones and filter packs were soaked for 2 to 4 hours in 1.2 M HCl and rinsed with distilled deionized water prior to use. The Whatman 41 filters for NH_3 (g) collection were washed with 4 L of 1.2 M HCl followed by 4 L of distilled deionized water and for SO_2 (g) collection were washed with 8 L of distilled deionized water. They were vacuum dried and stored frozen in sealed acid-washed petri dishes. One to 36 hours before use, the filters to be used for collection of NH_3 (g) were coated in an NH_3 free glove box with 0.01 M oxalic acid in a 16/84 glycerol/methanol ("Photrex" reagent grade methanol) solution. Similarly, the filters for SO_2 (g) collection were coated in an SO_2 free glove box with 0.1 M K_2CO_3 in a 20/70/10 water/methanol/glycerol solution. NH_3 and SO_2 free glove boxes were obtained by passing lab air through citric acid and potassium carbonate scrubbers, respectively, and then into the glove boxes. After coating, the filters were left to dry in the glove box. Weighing of a representative number (based on the weighing error and a 95% confidence level) of filters before and after the coating showed that 6.5 ± 0.4 μmol of oxalic acid and 46 ± 2 μmol of K_2CO_3 were deposited onto the respective filters.

After sample collection, the cyclone was removed from the tandem sampling system and the filter pack was transferred to either an NH_3 or SO_2 free glove box depending on sample type. Once in the glove box, each oxalic acid coated filter was put into a centrifuge tube containing 10 mL of distilled deionized water. Each K_2CO_3 coated filter was placed into a centrifuge tube containing 10 mL of 0.04 M H_2O_2 to oxidize all S (IV) to $SO_4^=$. Each Teflon filter was put into a centrifuge tube, wetted first with 1 mL of methanol and then with 10 mL of distilled deionized water. The filter solutions were sonicated for 30 min and centrifuged for 10 min.

The NH_4^+ samples (filter extracts) were analyzed within 1 to 4 hours of sample collection by the phenolhypochlorite colorimetric technique [*Solarzano*, 1969] using a Technicon Autoanalyzer II (Technicon Corp., Tarrytown, New York). A calibration curve was generated for each set of samples from the absorbances of five solutions that were serially diluted from a 0.0555 M NH_4^+ (as NH_4Cl) stock standard. When necessary, the samples were diluted to between a factor of 2 to 10 to correspond to the range of the calibration curve.

The Na^+, $SO_4^=$, and MSA^- samples (filter extracts) were analyzed with a Dionex 2120i Ion Chromatograph (Dionex Corp., Sunnyvale, California). Na^+ analysis was performed with a CS-1 column, 0.5 mM HCl eluent, and 68 mM tetramethylammonium hydroxide monohydrate regenerant. $SO_4^=$ analysis was done with an AS-4 column, 0.75 mM $NaHCO_3$/2.0 mM Na_2CO_3 eluent, and 12.6 mM H_2SO_4 regenerant. MSA^- analysis was performed with an AS-4 column, 0.6 mM $NaHCO_3$ eluent, and 12.6 mM H_2SO_4 regenerant. The nss $(SO_4^=)_p$ was calculated from $(Na^+)_p$ and the mass ratio of sulfate to sodium in seawater of 0.252 [*Holland*, 1978].

The mean NH_3 (g) blank concentration was 40% of the sample concentration. NH_4^+ (p) and MSA (p) blank concentrations were below the detection limits of 0.009 and 0.01 nmol m^{-3}, respectively. The nss $SO_4^=$ (p) blank value was on the average 8% of that of the sample.

Atmospheric DMS samples were collected continuously regardless of the relative wind speed and direction. The samples were pulled through a 70 m Teflon line from the boom on the ship's flying bridge, into the lab, and through a KOH impregnated glass filter to eliminate oxidant interferences. The sample line was continuously flushed with an air flow of 6.0 L min^{-1}. Water vapor was selectively removed from the stripper gas stream in a Teflon loop held at –50°C, while the sulfur gases were trapped in a narrow bore Teflon loop held at liquid argon temperature [*Bates et al.*, 1989]. To determine the sample volume, the pressure increase of an evacuated known volume used to draw the sample was monitored. Sample size was typically 1 L. The liquid argon trap was electrically heated and the volatile compounds were transferred to a DB-1 thick film (5 μm) mega-bore fused silica column (J&W Scientific). The sulfur compounds were separated using a temperature program from 5° to 105°C and were quantified with a flame photometric detector. The flame was modified with the addition of approximately 60 ppbv SF_6 to increase sensitivity and to provide a linear detection range from 0.15 to 15 pmol of sulfur [*Goldan et al.*, 1987]. The detector was modified with a chimney over the jet to minimize flame (peak) broadening and enhance sensitivity [*Barinaga and Farwell*, 1986]. The performance of the system was tested by adding a low-loss (1.75 ng S min^{-1}) permeation tube in the upstream end of the intake air line. Based on standard addition, typical recoveries were 96 ± 4%.

Bulk seawater samples for the analysis of NH_3 (s,tot) and DMS (s) were taken from a depth of 5 m using the ship's seawater pumping system. The samples were analyzed for NH_4^+ immediately after sample collection using the colorimetric method described above [*Solarzano*, 1969]. A standard addition method was used for calculation of the sample concentration.

Aliquots of the seawater samples for DMS (s) analysis were gently filtered (<5 psi) through a 0.4 μm Nuclepore filter. Two to ten mL of the sample were valved to a Teflon gas stripper. The samples were purged with ultrapure hydrogen at 60 mL min^{-1} for 5 to 20 min. The entire purge and trap system was Teflon except for the Nitronic 60 Valco valves. DMS was analyzed on the same system used for atmospheric DMS samples. The precision of the technique, based on

periodic replicate analyses of a single water sample, was about ±10%. The performance of the system was monitored regularly by running blanks and standards through the entire system. Recovery of DMS from seawater was generally greater than 90%, while system blanks were below the detection limit. Values reported here have been corrected for recovery losses.

An equilibrator consisting of a closed volume of air in contact with a continual 20 L min^{-1} flow of seawater was used in conjunction with a filter pack containing 4 oxalic acid coated filters to measure the saturation concentration of NH_3 relative to the concentration in ocean surface waters, $(NH_3)_{sg}$ [*Keeling et al.*, 1965; *Quinn et al.*, 1988; *Butler et al.*, 1989]. The seawater supply to the equilibrator was the same as that for the bulk seawater samples. The lowest $(NH_3)_{sg}$ obtained from nutrient-poor waters was used as the equilibrator blank. This blank was 37% of the average sample value. In a previous experiment [*Quinn et al.*, 1988], values of $(NH_3)_{sg}$ measured directly using the equilibrator were compared with those calculated from $[NH_3]_{s,tot}$ and were found to agree within the experimental error of the two techniques. The advantage of using the equilibrator is that it does not require the use of Henry's law constant and other equilibrium constants which are not known for seawater.

Particle size distribution measurements in the range of 0.02 to 0.6 μm were made 4 times per hour [*Covert et al.*, 1988]. A condensation nucleus counter was used to detect particles in the output of a differential mobility analyzer. Mobility distributions of the aerosol were determined by measuring particle concentrations over a sequence of 17 equal, logarithmically spaced size increments. The number size distributions were calculated by a matrix inversion of the mobility distribution assuming a Boltzman-Fuchs equilibrium charge distribution of the particles.

Ancillary measurements included surface seawater *p*H [*Fuhrmann and Zirino*, 1988], NO_3^- [*Parsons et al.*, 1984], and chlorophyll *a* [*Lorenzen*, 1966]; wind speed and direction, dry and wet bulb temperature, and sea surface temperature.

3. Results and Discussion

A wide variety of oceanic conditions were encountered along the cruise track. The North Pacific Ocean has a northeastward flowing current on the west side bringing water from the coast of Asia into the Gulf of Alaska and a southward return flow on the east side. The North Pacific central gyre is a region of anticyclonic ocean surface circulation between 40°N and 15°N. It is isolated from the effects of land masses and of waters of different origins and as such is an area of relatively low nutrient concentration and productivity [*Eppley et al.*, 1973]. A series of currents around the equator propelled by the trade winds result in a region of divergence where subsurface waters are brought to the surface [*Pickard and Emery*, 1982]. This upwelling of nutrient rich waters can result in areas of high productivity ranging from tens to several hundreds of kilometers.

3.1. *Seawater Results*

From 50°N to 35°N, measured mean concentrations of chlorophyll *a*, 0.23 mg m^{-3}, and NO_3^-, 9.5 μmol L^{-1}, were seasonably high (Figure 3). The chlorophyll *a* concentration decreased to 0.19 mg m^{-3} and NO_3^- to below detection limit (0.1 μmol L^{-1}) in the North Pacific central gyre, 30°N to 10°N. In the region of equatorial upwelling, 5°N to 5°S, the concentrations of chlorophyll *a* and NO_3^- rose to 0.21 mg m^{-3} and 1.4 μmol L^{-1}, respectively. Surface seawater temperature and *p*H also changed with latitude (Figure 3). From 53°N to 14°S, the surface seawater temperature increased from 3°C to 29°C and *p*H from 7.74 to 8.45.

3.1.1. *Ammonia air/sea flux.* Bulk seawater, equilibrator, and gas phase atmospheric samples were collected simultaneously for analysis of $[NH_3]_{s,tot}$, $(NH_3)_{sg}$, and $(NH_3)_g$, respectively. The mean $[NH_3]_{s,tot}$ was 0.4 ± 0.3 μmol L^{-1} (number of samples, n = 75). The latitudinal distribution of $[NH_3]_{s,tot}$ was fairly constant with a slight decrease (0.2 μmol L^{-1}) from 30°N to 10°N, corresponding to the nutrient-poor waters of the North Pacific central gyre (Figure 4).

The air/sea flux, F, of a highly soluble gas such as NH_3 is controlled by the diffusive resistance of the gas phase side of the air/sea interface and can be modeled by

$$F = k_g[(NH_3)_{sg} - (NH_3)_g] \quad (1)$$

where k_g is the transport coefficient [*Liss and Slater*, 1974]. $(NH_3)_{sg}$ is related to $[NH_3]_s$ through Henry's law,

$$(NH_3)_{sg} = K_{hN}[NH_3]_s \quad (2)$$

where K_{hN} is the Henry's law constant. Simultaneous measurements of $(NH_3)_{sg}$ and $(NH_3)_g$ were made from 37°N to 11°S. The $(NH_3)_{sg}$ ranged from 2.8 to 21 nmol m^{-3} with a mean of 10 ± 7 (n = 9). The concurrent atmospheric $(NH_3)_g$ ranged from 0.01 to 3.4 nmol m^{-3} with a mean of 0.67 ± 0.65 (n = 9).

The flux of NH_3 was calculated using (1) and $(NH_3)_{sg}$ from the equilibrator. The transport coefficient used was that of H_2O, 3000 cm h^{-1}, as both H_2O and NH_3 are gas-phase rate controlled species and have similar molecular weights [*Liss and Slater*, 1974]. The magnitude of the flux ranged from 1.8 to 15 μmol m^{-2} d^{-1} with a mean of 7.0 ± 5.6 (n = 9). The latitudinal distribution of the NH_3 flux is shown in Figure 4. There was no correlation between the flux and the seawater concentration of total ammonia, NH_3 (s) + NH_4^+ (s). However, small-scale changes in the flux with time are obscured by the long sampling times required for the measurement of $(NH_3)_{sg}$ (10 to 30 hours). An empirically determined transfer coefficient for NH_3 would improve the accuracy of these calculations.

The flux derived from measured $(NH_3)_{sg}$ and $(NH_3)_g$ was compared to one calculated from bulk seawater measurements of $[NH_3]_{s,tot}$ using (3).

$$(NH_3)_{sg,calc} = [NH_3]_{s,tot}K_{hN}K_w(K_w + K_b[H^+])^{-1} \quad (3)$$

where K_w is the dissociation constant for water

$$K_w = [OH^-]_s[H^+]_s \quad (4)$$

and K_b is the ionization constant for dissolved ammonia

$$K_b = [NH_4^+]_s[OH^-]_s([NH_3]_s)^{-1} \quad (5)$$

All equilibrium constants were corrected for temperature and the ionic strength of seawater [*Stumm and Morgan*, 1981; *Danckwerts*, 1970].

Measured $(NH_3)_{sg}$ showed no increase as the surface seawater temperature increased. But $(NH_3)_{sg,calc}$ increased from 6.3 to 66 nmol m^{-3} as the temperature increased from 15° to 30°C. This increase is a result of the temperature dependent K_{hN}, K_w, K_b, and $[H^+]$ in (3). F_{calc} derived from (1) and $(NH_3)_{sg,calc}$ showed a corresponding increase of 4.7 to 49 μmol

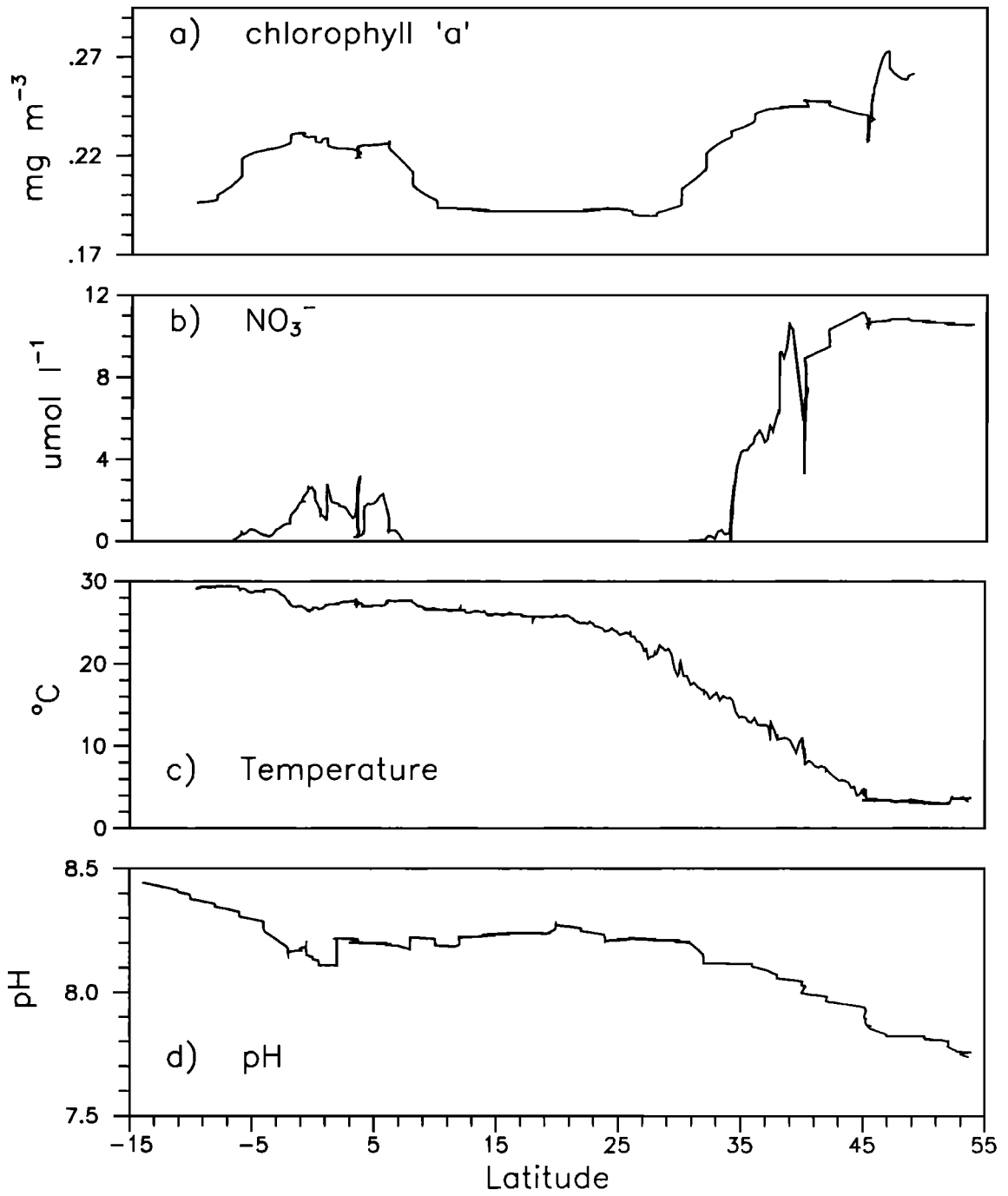

Fig. 3. Surface seawater (*a*) concentrations of chlorophyll *a* in mg m^{-3}, (*b*) concentrations of NO_3^- in μmol L^{-1}, (*c*) temperature (°C), and (*d*) *p*H during April and May of 1988 along 170°W from 50°N to 10°S.

m^{-2} d^{-1} with increasing temperature. Apparently, factors other than surface seawater temperature were significant in controlling the measured $(NH_3)_{sg}$. It is possible that temperature and biological factors such as the rate of uptake and regeneration of NH_3 interacted to maintain a nearly constant $[NH_3]_{s,tot}$ and, hence, $(NH_3)_{sg}$.

3.1.2. *Dimethylsulfide air/sea flux.* Seawater DMS concentrations ranged from 0.3 to 6.1 nmol L^{-1} (n = 70) with the highest concentrations near 52°N and 7°S and the lowest concentrations between 48°N and 40°N and in the North Pacific central gyre (Figure 4). The air/sea flux of a moderately soluble gas such as DMS is controlled by the flux resistance of the liquid side of the air/sea interface and can be modeled by

$$F = k_L[(\mathrm{DMS})_s - 1/K_{hS}(\mathrm{DMS})_g] \quad (6)$$

where k_L is the liquid phase transport coefficient derived for DMS from the method of *Liss and Merlivat* [1986] and is strongly dependent on wind speed. K_{hS} is the Henry's law constant for DMS. Since atmospheric DMS partial pressures are at least 3 orders of magnitude less than seawater DMS vapor pressures, the term $1/K_{hS}(\mathrm{DMS})_g$ is assumed to be

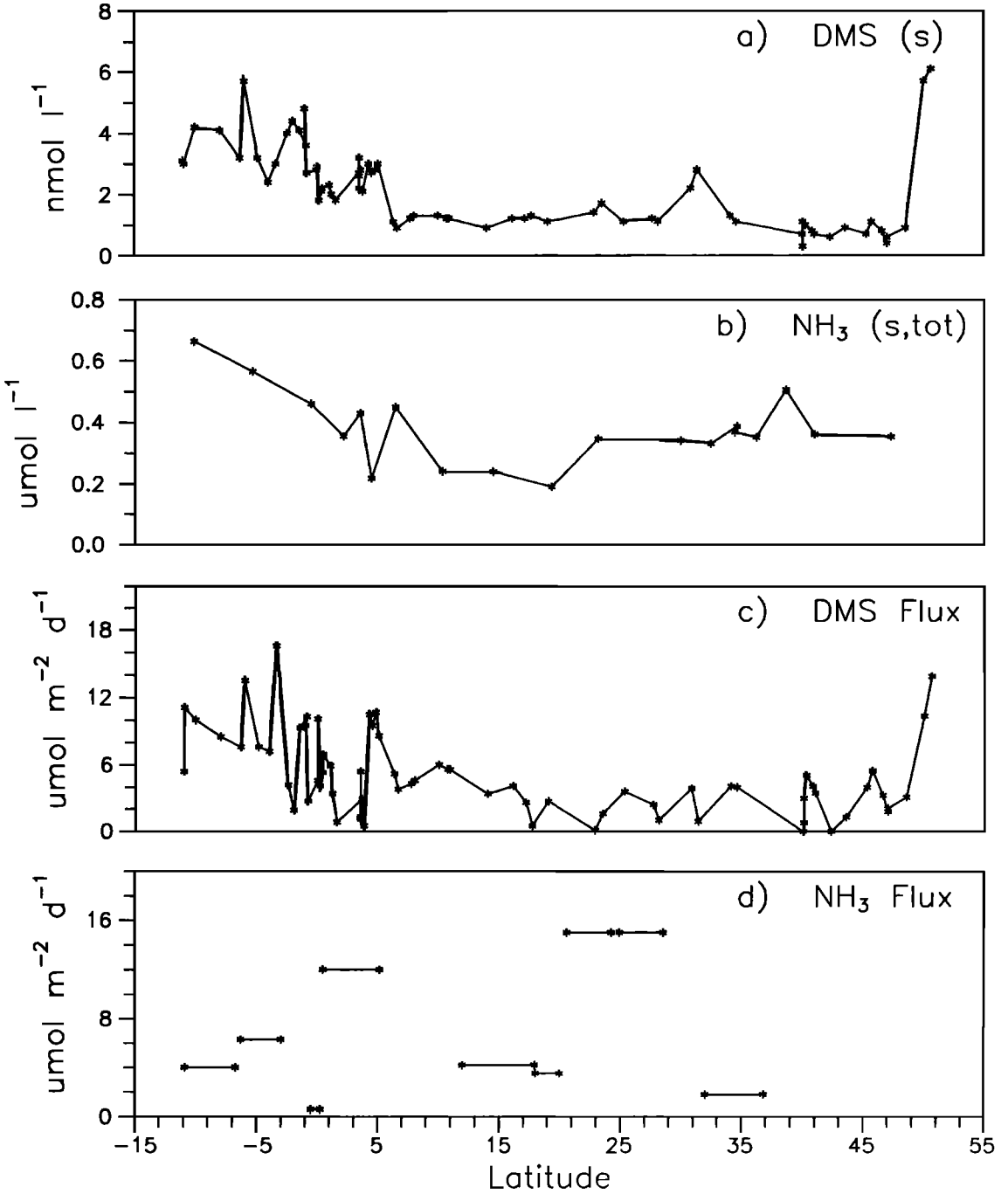

Fig. 4. (*a*) Surface seawater DMS concentrations in nmol L^{-1}, (*b*) 5° averaged surface seawater NH_3 (s,tot) concentrations in μmol L^{-1}, (*c*) DMS flux in μmol m^{-2} d^{-1} as per (6), and (*d*) NH_3 flux in μmol m^{-2} d^{-1} as per (1) during April and May of 1988 along 170°W from 50°N to 10°S.

negligible [*Cline and Bates*, 1983; *Barnard et al.*, 1982]. The DMS flux ranged from 0.1 to 17 μmol m^{-2} d^{-1} (Figure 4).

3.2. *Atmospheric Gas and Particle Phase Data*

Calculated isentropic four-day back trajectories (Figure 5), particle size distributions (Figure 6) [*Covert et al.*, 1988], and chemical concentrations were used to classify the samples into three groups. Two groups contained samples from continentally influenced air masses, while one group appeared to be more representative of marine air. Latitudinal concentration distributions of NH_3 (g), DMS (g), SO_2 (g), nss $SO_4^=$ (p), and the NH_4^+ (p)/nss $SO_4^=$ (p) and MSA (p)/nss $SO_4^=$ (p) molar ratios are shown in Figure 7. Concentrations of atmospheric gas and particulate phase species from all three groups are given in Table 1.

3.2.1. *Group 1.* The first group contained samples collected from 50°N to 30°N from April 8 to April 18, 1988. During this time period the prevailing surface winds were westerlies. Trajectories indicate that the sampled air masses left the east coast of Asia 4 or more days prior to reaching the ship (Figure 5). Particle size distributions were representative of well-aged accumulation mode aerosol particles (0.08 to 0.6 μm diameter)

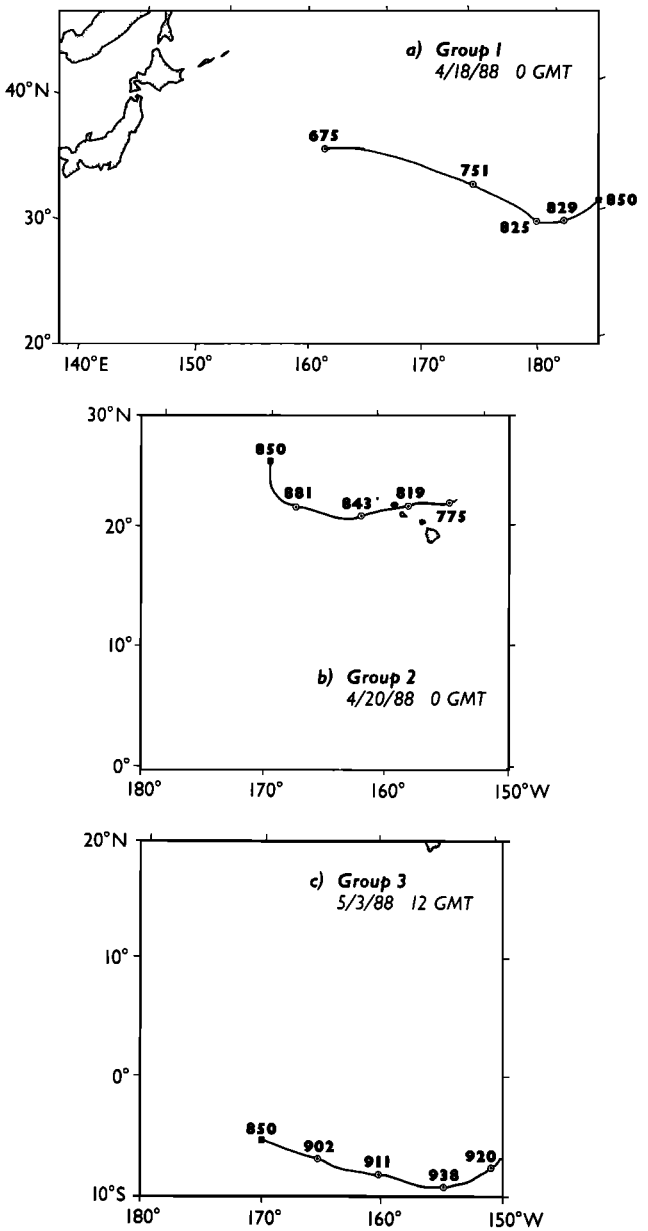

Fig. 5. Calculated isentropic 4-day trajectories at the 850 mbar arrival height from (*a*) group 1 (April 18, 1988 0000 UT), (*b*) group 2 (April 20, 1988 0000 UT), and (*c*) group 3 (May 3, 1988 1200 UT). Numbered symbols indicate the height of the calculated trajectories as atmospheric pressure in mbar at 1-day intervals.

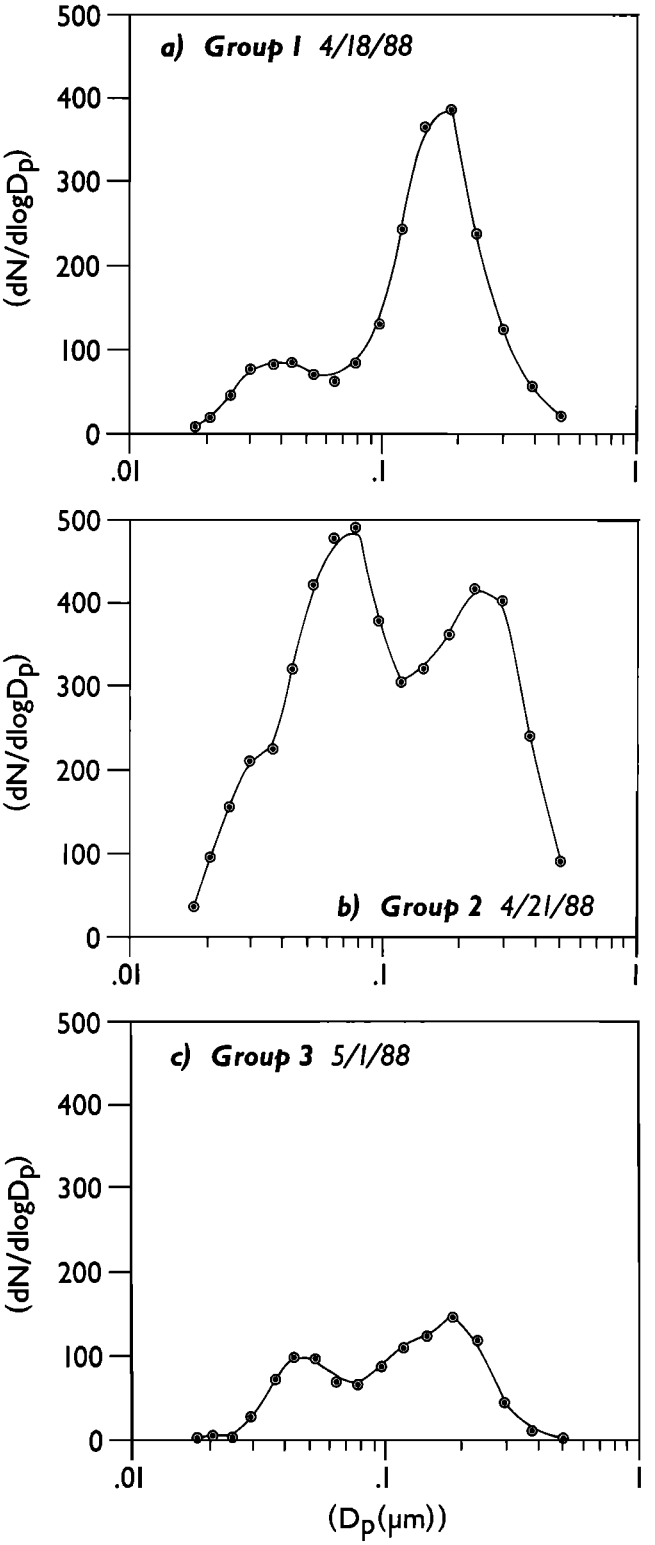

Fig. 6. Particle size distributions averaged over 24 hours from (*a*) group 1 (April 18, 1988), (*b*) group 2 (April 21, 1988), and (*c*) group 3 (May 1, 1988).

derived from continental air with relatively few particles in the nuclei mode (< 0.08 μm) (Figure 6). This concurs with the trajectory evidence indicating that the sampled air masses had passed over the western Pacific several days earlier.

The mean and sample standard deviation of the $(NH_3)_g$ in group 1 was 0.37 ± 0.45 nmol m^{-3} (n = 8) with an average difference between duplicate samples for all three groups of 50%. No DMS (g) concentrations were measured during this time period. The SO_2 (g) concentration ranged between 0.39 and 0.68 nmol m^{-3} (n = 2). The mean $(NH_4^+)_p$ was 16 ± 7.2 nmol m^{-3} (n = 12), with an average difference between duplicate samples for all three groups of 16%. The mean nss $(SO_4^=)_p$ was 13 ± 4.3 nmol m^{-3} (n = 12), with an average difference between duplicate samples for all three groups of 24%. The seasalt $(SO_4^=)_p$ was on the average 5% and always less than 27% of the total $(SO_4^=)_p$ for all three groups. The particulate NH_4^+/nss $SO_4^=$ molar ratio for group 1 ranged between 0.55 and 2.8 with a mean of 1.5 ± 0.88. The mean MSA (p) concentration was 0.17 ± 0.06 nmol m^{-3} (n = 12), with an average difference between duplicate samples for all three groups of 25%. The resulting MSA (p) to nss $SO_4^=$ (p)

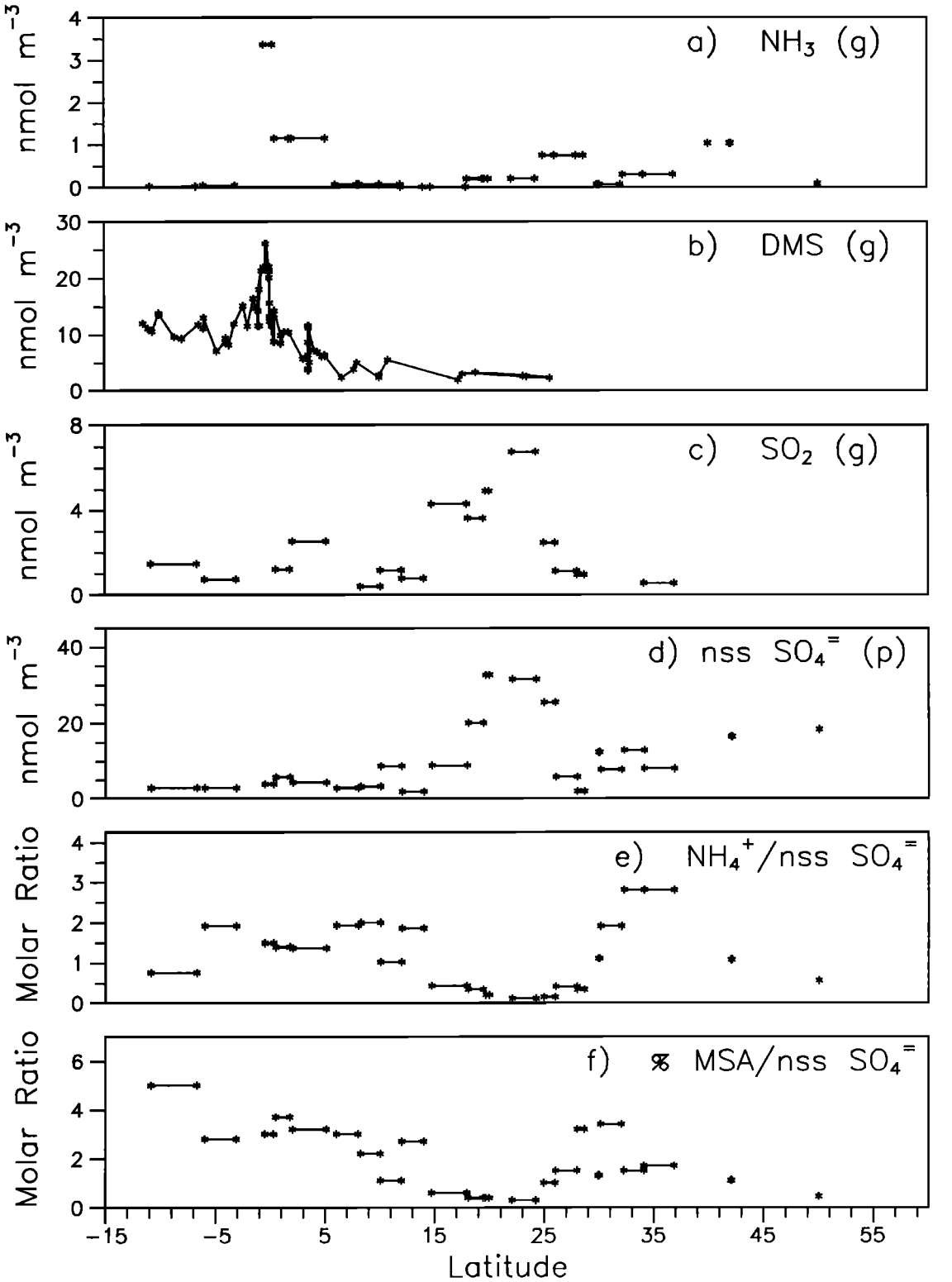

Fig. 7. Latitudinal distributions from 50°N to 11°S along 170°W during April and May of 1988 of (*a*) atmospheric NH_3 (g) concentrations in nmol m^{-3}, (*b*) atmospheric DMS (g) concentrations in nmol m^{-3}, (*c*) atmospheric SO_2 (g) concentrations in nmol m^{-3}, (*d*) nss $SO_4^=$ (p) concentrations in nmol m^{-3}, (*e*) the particulate NH_4^+ to nss $SO_4^=$ molar ratio, and (*f*) the particulate MSA to nss $SO_4^=$ percent molar ratio.

molar ratio ranged between 0.45 and 3.4% with a mean of 1.6 ± 0.99%.

The mean $(NH_4^+)_p$ for group 1 was on the high end of the range of concentrations seen by *Parungo et al.* [1986] over the Pacific Ocean. The nss $(SO_4^=)_p$ also was high compared to previously reported remote marine values, while the MSA (p) to nss $SO_4^=$ (p) molar ratio was low [*Savoie and Prospero*, 1989]. High $(NH_4^+)_p$, nss $(SO_4^=)_p$ and NH_4^+ (p)/nss $SO_4^=$ (p) molar ratios and low MSA (p)/nss $SO_4^=$ (p) molar ratios agree with the trajectories and particle size distributions in

TABLE 1. Measured Gas and Particle Phase Concentrations

Species/Phase	Number of Samples	Mean nmol m^{-3}	Range nmol m^{-3}
		Group 1 (50°N–30°N)	
NH_3 (g)	8	0.37 ± 0.45	0.07–1.0
SO_2 (g)	2	0.53 ± 0.26	0.39–0.68
NH_4^+ (p)	12	16 ± 7.2	10–29
nss $SO_4^=$ (p)	12	13 ± 4.3	7.7–18
MSA (p)	12	0.17 ± 0.06	0.08–0.25
Na^+ (p)	12	17 ± 11	2.2–30
NH_4^+ (p)/nss $SO_4^=$ (p)	10	1.5 ± 0.88	0.55–2.8
% MSA (p)/nss $SO_4^=$ (p)	12	1.6 ± 0.99	0.45–3.4
		Group 2 (29°N–15°N)	
NH_3 (g)	6	0.32 ± 0.38	0.01–0.75
DMS (g)	6	2.5 ± 0.5	1.9–3.2
SO_2 (g)	14	3.4 ± 2.1	0.94–6.7
NH_4^+ (p)	4	5.3 ± 2.2	3.8–6.8
nss $SO_4^=$ (p)	14	18 ± 12	1.9–32
MSA (p)	14	0.11 ± 0.073	0.05–0.26
Na^+ (p)	14	4.3 ± 3.3	1.6–13
NH_4^+ (p)/nss $SO_4^=$ (p)	4	0.38 ± 0.064	0.34–0.43
% MSA (p)/nss $SO_4^=$ (p)	14	1.2 ± 1.1	0.3–3.2
		Group 3 (14°N–11°S)	
NH_3 (g)	12	0.78 ± 1.3	0.01–3.4
DMS (g)	65	11.2 ± 7.12	2.3–26.1
SO_2 (g)	14	1.2 ± 0.69	0.39–2.5
NH_4^+ (p)	14	5.6 ± 1.7	2.2–8
nss $SO_4^=$ (p)	18	4.0 ± 2.1	1.8–8.6
MSA (p)	18	0.11 ± 0.05	0.05–0.21
Na^+ (p)	18	3.5 ± 3.7	1.0–16
NH_4^+ (p)/nss $SO_4^=$ (p)	14	1.5 ± 0.44	0.76–1.9
% MSA (p)/nss $SO_4^=$ (p)	18	3.0 ± 1.0	1.1–5.0

Errors are given as sample standard deviation for $n > 2$ and as sampling and analytical error for $n = 2$.

suggesting that this group of samples was influenced by continental sources.

3.2.2. *Group 2.* The second group of samples consisted of those collected from 29°N to 15°N from April 18 to 23, 1988. The prevailing surface winds were southeasterlies from 29°N to 23°N shifting to northeasterlies from 23°N to 15°N. Trajectories indicate that the sampled air masses had passed over Hawaii no more than 4 days before reaching the ship (Figure 5). The size distributions were indicative of both fresh nuclei and more aged accumulation modes and relatively high particle concentrations as would be expected in an air mass influenced by a large gaseous particle precursor source (Figure 6). A volcanic eruption which occurred during the time period that the sampled air masses passed over Hawaii could have been the source of these particles.

The mean $(NH_3)_g$ was 0.32 ± 0.38 nmol m^{-3} (n = 6). Between April 20 and 23, the mean DMS (g) concentration was 2.5 ± 0.5 nmol m^{-3} (n = 6). The mean $(SO_2)_g$ was 3.4 ± 2.1 nmol m^{-3} (n = 14). The mean $(NH_4^+)_p$ was 5.3 ± 2.2 nmol m^{-3} (n = 4). The mean nss $(SO_4^=)_p$ was 18 ± 12 nmol m^{-3} (n = 14). The resulting NH_4^+ (p)/nss $SO_4^=$ (p) molar ratio ranged between 0.34 and 0.43 with a mean of 0.38 ± 0.064 (n = 4). The mean $(MSA)_p$ was 0.11 ± 0.07 nmol m^{-3} (n = 14) and the resulting MSA (p) to nss $SO_4^=$ (p) molar ratio ranged between 0.3 and 3.2% with a mean of 1.2 ± 1.1%.

The NH_4^+ (p) and NH_3 (g) concentrations in this group are typical of remote marine air [*Parungo et al.*, 1986; *Quinn et al.*, 1988]. Yet the nss $SO_4^=$ (p) concentrations are higher than those usually found in remote marine air without correspondingly high values of DMS (g) and MSA (p) indicating a strong nonmarine source of nss $SO_4^=$ (p). The relatively high $(SO_2)_g$ and low NH_4^+ (p)/nss $SO_4^=$ (p) molar ratios suggest a volcanic source of nss $SO_4^=$ (p).

3.2.3. *Group 3.* The third group was made up of samples collected from 14°N to 11°S from April 24 through May 5, 1988. NE trade winds prevailed from 22°N to 4°N and SE trade winds from 4°N to 11°S. The Intertropical Convergence Zone (ITCZ) was between 3° and 4°N as shown by sharp gradients in atmospheric CO and CH_4 concentrations [*Kelly and Gammon*, 1988]. The trajectories show an easterly flow at the 850 mbar arrival height and that the sampled air masses had not passed over land for at least 4 days prior to reaching the ship (Figure 5). Particle size distributions revealed nearly equal nuclei and accumulation mode populations (Figure 6).

The mean $(NH_3)_g$ was 0.78 ± 1.3 nmol m^{-3} (n = 12), ranging from 0.01 to 3.4 nmol m^{-3} with concentrations peaking at the

equator. The DMS (g) concentrations ranged from 2.3 to 26.1 nmol m^{-3} also with the highest concentrations at the equator. The equatorial values were higher than the range of 2.1 to 13 nmol m^{-3} measured along the equator from Ecuador to Hawaii by *Andreae et al.* [1985]. The mean $(SO_2)_g$ was 1.2 ± 0.69 nmol m^{-3} (n = 14).

The mean $(NH_4^+)_p$ was 5.6 ± 1.7 nmol m^{-3} (n = 14). This range compares well with the mean $(NH_4^+)_p$ of about 4.6 nmol m^{-3} measured by *Parungo et al.* [1986] over the same region of the Pacific. Based on 5-day trajectory analysis, they claim that these samples were not influenced by long-range transport of anthropogenic pollution. The mean nss $(SO_4^=)_p$ was 4.0 ± 2.1 nmol m^{-3} (n = 18). *Parungo et al.* [1986] measured nss $(SO_4^=)_p$ in this region of approximately 2.0 nmol m^{-3}. *Savoie and Prospero* [1989] found an annual mean nss $(SO_4^=)_p$ of 3.6 nmol m^{-3} at American Samoa (15°S, 170°W). They suggest that almost all of the nss $SO_4^=$ (p) at American Samoa originates from the oxidation of DMS. The range of NH_4^+ (p)/nss $SO_4^=$ (p) molar ratios was between 0.76 and 1.9 with a mean of 1.5 ± 0.44.

The mean $(MSA)_p$ was 0.11 ± 0.05 nmol m^{-3} (n = 18), yielding a range of MSA (p) to nss $SO_4^=$ (p) molar ratios between 1.1 and 5.0% with a mean of 3.0 ± 1.0%. *Savoie and Prospero* [1989] measured an annual mean $(MSA)_p$ of 0.26 nmol m^{-3} at American Samoa and a mean MSA (p)/nss $SO_4^=$ (p) ratio of 6.5%. If all of the nss $SO_4^=$ (p) at American Samoa is derived from the oxidation of DMS and this partitioning ratio is conservative, then this ratio may be used to estimate the marine biogenic input of nss $SO_4^=$ (p) measured in the group 3 samples. The MSA (p)/nss $SO_4^=$ (p) ratio of 6.5% and the measured $(MSA)_p$ of 0.11 nmol m^{-3} yields a calculated nss $SO_4^=$ (p) concentration of 1.7 nmol m^{-3}. As the measured nss $(SO_4^=)_p$ was 4.0 nmol m^{-3}, this suggests that 42% of the nss $SO_4^=$ (p) was of marine biogenic origin. If only the samples taken nearest to American Samoa (0° to 11°S) are considered, 53% of the nss $SO_4^=$ (p) appears to be of marine biogenic origin.

The low concentrations of NH_4^+ (p), SO_2 (g), and nss $SO_4^=$ (p) and relatively high MSA (p) to nss $SO_4^=$ (p) molar ratio indicate that the samples from group 3 were the most representative of marine air found along the cruise track. The trajectories and particle size distributions support this conclusion. Comparison of these data to those of *Savoie and Prospero* [1989] from American Samoa, however, suggests that the sampled air masses may have been influenced by continental sources. This comparison is based on the assumption that the production rate of MSA (p) and nss $SO_4^=$ (p) from DMS were comparable in the two data sets. If MSA (p) production was less favored and nss $SO_4^=$ (p) production was more favored in the time period and region of this study, then this comparison would not be valid. Previous studies have shown that the MSA (p) to nss $SO_4^=$ (p) molar ratio varies greatly [*Berresheim*, 1987; *Calhoun and Bates*, 1989] and therefore may be a poor tracer for marine air.

3.3. *Interaction of the Sulfur and Reduced Nitrogen Cycles in the Marine Environment*

From 50°N to 11°S along 170°W, the latitudinal distributions of DMS (s) and NH_3 (s,tot) were similar with concentrations higher in the northern latitudes, decreasing through the North Pacific central gyre, and increasing once again near and south of the equator. However, the change in DMS (s) concentration with latitude was more dramatic than that of NH_3 (s,tot). In nutrient-limited waters, regeneration of nitrogenous material in the form of NH_4^+ (s) becomes important in phytoplankton productivity [*Eppley et al.*, 1973]. NH_4^+ (s) is taken up by phytoplankton. Zooplankton then feed on the phytoplankton and excrete NH_4^+. The cycle is closed by phytoplankton utilizing the excreted NH_4^+. Since NH_4^+ is being produced as it is being removed, the $[NH_3]_{s,tot}$ remains relatively constant and does not decrease as markedly as does $[NO_3^-]_s$ in the central gyre.

Both DMSP, the precursor of DMS, and NH_4^+ are released from decaying phytoplankton cells and grazing zooplankton [*Nguyen et al.*, 1988; *Dacey and Wakeham*, 1986; *Eppley et al.*, 1973]. DMSP subsequently is cleaved enzymatically to form DMS and acrylic acid [*Cantoni and Anderson*, 1956; *Dacey and Blough*, 1987]. If the rate of enzymatic cleavage is constant, the biogenic production of DMS and NH_4^+ may be controlled by the same factors. As a result there might be a correlation between DMS (s) and NH_3 (s) concentrations and the air/sea fluxes of DMS and NH_3. No such correlation was found in this data set suggesting that the biological production of DMS (s) was independent of that of NH_3 (s,tot).

The utilization of NH_4^+ (s) in primary production by phytoplankton and, hence, the concentration of NH_3 (s,tot) is a complex function of the relative abundance of NH_4^+ (s) and NO_3^- (s) and the amount of available light [*Thompson et al.*, 1989]. The NH_3 (s,tot) concentration also is related to the diel periodicity in NH_4^+ (s) uptake and regeneration [*Wheeler et al.*, 1989]. Alternatively, the concentration of DMS (s) depends on phytoplankton speciation [*Andreae et al.*, 1983], the rate of enzymatic cleavage of DMSP, and the rate of microbial breakdown of DMS (s) [*Brimblecombe and Shooter*, 1986]. Only if all of these factors were constant and the release of DMS (s) and NH_4^+ (s) from phytoplankton and zooplankton were related would one expect to see a strong relationship between DMS (s) and NH_3 (s,tot) concentration.

In addition, physical parameters such as degree of mixing of the ocean surface layer and wind speed may affect the DMS (s) and NH_3 (s) fluxes differently as they are liquid and gas phase rate controlled species, respectively [*Liss and Slater*, 1974]. In this data set, it also may be that any correlation was obscured by the long sampling time required for analysis of $(NH_3)_{sg}$.

The NH_4^+ (p) to nss $SO_4^=$ (p) molar ratios for all three groups are shown in Figure 8. Group 1 had an NH_4^+ (p) to nss $SO_4^=$ (p) molar ratio of 1.5 ± 0.88, while groups 2 and 3 had molar ratios of 0.38 ± 0.064 and 1.5 ± 0.44, respectively. The mean molar ratio for all groups was 1.3 ± 0.71. Group 1 contained the highest molar ratio of 2.8. This outlier is most likely due to well-aged aerosol from Asia or Alaska or to contamination during sampling and/or analysis. If the outlier is removed from the data set, the mean molar ratio becomes 1.2 ± 0.59, with values ranging from 0.34 to 1.9. Except for the outlying sample, it appears that low NH_3 (g) concentrations resulted in only partly neutralized H_2SO_4 aerosol particles all along the cruise track. Even in regions of continental influence having relatively high NH_4^+ (p) concentrations, the NH_3 (g) concentration was low, reflecting its short lifetime in the marine boundary layer. Based on the group 3 average $(NH_3)_g$ (0.8 nmol m^{-3}), air/sea NH_3 flux (5 μmol m^{-2} d^{-1}), and boundary layer height (1750 m), the estimated lifetime of NH_3 (g) is 6 hours.

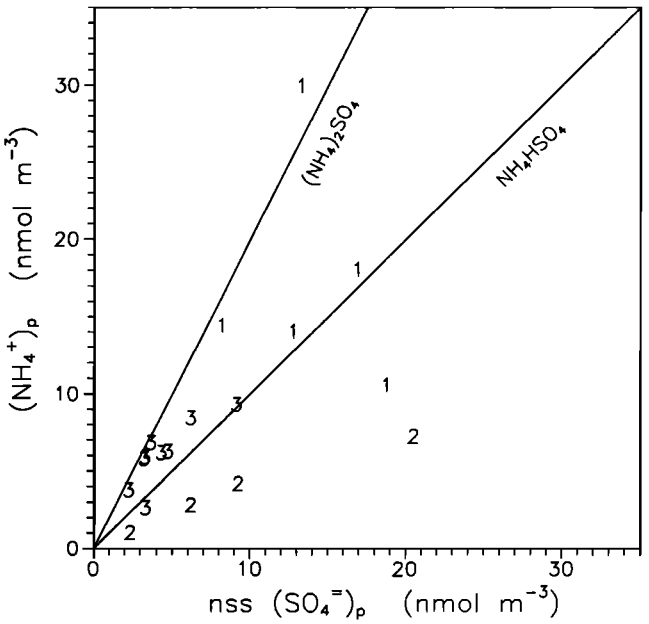

Fig. 8. Particulate nss $(SO_4^=)_p$ versus $(NH_4^+)_p$ for air masses over the Pacific Ocean during April and May of 1988 along 170°W from 50°N to 11°S. Data points are labeled 1, 2, and 3 corresponding to sample groups 1, 2, and 3, respectively. The line representing a two to one molar ratio of NH_4^+ (p) to nss $SO_4^=$ (p) is indicative of an $(NH_4)_2SO_4$ particle composition and that representing the one to one molar ratio is indicative of an NH_4HSO_4 particle composition.

4. CONCLUSIONS

Changes in the relative concentrations of the S and N species in the marine atmosphere reflect the origin of the air masses sampled. Air masses sampled between 50°N and 30°N were influenced by the Asian continent. NH_4^+ (p) and nss $SO_4^=$ (p) concentrations were high, while MSA (p) concentrations were low. Between 29°N and 16°N, the air masses sampled appeared to have passed over Hawaii during the period of a volcanic eruption. The SO_2 (g) and nss $SO_4^=$ (p) concentrations were high but the NH_4^+ (p), DMS (g), and MSA (p) concentrations were low. Trajectories and particle size distributions suggest that air masses sampled between 15°N and 10°S were more representative of marine air than those encountered further north. During this period, DMS (g) and MSA (p) concentrations were relatively high as was the MSA (p) to nss $SO_4^=$ molar ratio while the NH_4^+ (p) concentrations were low. The many potential sources of NH_4^+ (p), SO_2 (g), and nss $SO_4^=$ (p) to the central Pacific marine atmosphere contribute to the difficulty of studying the acid-base chemistry of the remote marine troposphere. Only between 15°N and 10°S were air masses encountered which were minimally influenced by continental sources.

Throughout the cruise track, the ocean acted as a local source of NH_3 to the atmosphere even in regions of low nutrient concentrations. Despite this flux, all measured atmospheric concentrations of NH_3 (g) were low, indicating that the lifetime of NH_3 (g) in the marine atmosphere is short. As a result, while the ocean may serve as a local and significant source of atmospheric NH_3, it probably has a negligible impact on continental regions. The low gas phase ammonia concentrations resulted in only partly neutralized H_2SO_4 aerosol particles. Two regimes resulted in the highest NH_4^+ (p) to nss $SO_4^=$ (p) molar ratios: a region of well-aged aerosol such that much of the NH_4^+ (p) was most likely of continental origin and a region of remote marine air with an absence of continentally derived nss $SO_4^=$ (p).

These data as well as data from the NE Pacific Ocean [*Covert*, 1988; *Quinn et al.*, 1988] indicate that the particulate NH_4^+ to nss $SO_4^=$ molar ratio is often near one in remote marine atmospheres. The consistency of this ratio given the potential range over which it might vary suggests that there may be a relationship between the factors controlling the production of biogenically produced NH_3 and nss $SO_4^=$. Even though correlations between seawater DMS and NH_3 concentrations and fluxes were lacking in this data set, the consistency of the ratio is intriguing and suggests future work. Integration of data from other portions of the interacting S and reduced N cycles, e.g., aerosol particle and rainwater data, may prove fruitful.

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