

Observations of the Atmospheric Sulfur Cycle on SAGA 3

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During the Soviet/American Gases and Aerosols (SAGA) 3 program in February and March 1991 we measured a wide variety of sulfur compounds simultaneously in the equatorial Pacific marine boundary layer. We made measurements of atmospheric dimethyl sulfide (DMS), sulfur dioxide (SO₂), and size-resolved aerosol non-sea-salt sulfate (NSS), and methane sulfonate (MSA). Some of our observed ratios contradict commonly held views of the marine sulfur cycle: the large DMS/NSS ratio implies that NSS may not be the primary product of DMS oxidation under some conditions. We also found much more DMS than SO₂, which may suggest that SO₂ is not always an intermediate in DMS oxidation. The small SO₂/NSS ratio also supports the idea that most NSS was not formed from SO₂. Although our measured ratios of MSA/NSS were similar to previous observations in this region, much of the MSA was contained on supermicron particles, in contrast to both the NSS and the earlier MSA observations at higher latitudes. This implies that MSA/NSS ratios in ice cores may not accurately reflect the MSA/NSS ratios in their source areas.

INTRODUCTION

Naturally produced sulfate aerosol may be an important factor in determining the Earth's climate. It is an important source of cloud condensation nuclei (CCN) in remote areas [Ayers *et al.*, 1991], which affect the droplet distributions and radiative properties of clouds [Twomey, 1980; Charlson *et al.*, 1987; Slingso, 1989; Albrecht, 1989]. Sulfate aerosol also has a significant direct impact on the radiative budget on Earth [Charlson *et al.*, 1991, 1992] since it scatters sunlight to space. While the role of anthropogenic sulfur has been studied extensively [Schwartz, 1988], there is still considerable uncertainty about the magnitude and impact of natural sources on the concentrations and properties of sulfate aerosols in nonpolluted areas [Andreae *et al.*, 1988; Bates *et al.*, 1987, 1989].

The flux of natural, biogenic sulfur from the oceans to the atmosphere is dominated by the gas dimethyl sulfide (DMS) [Bates and Cline, 1985; Andreae *et al.*, 1986]. In the atmosphere, DMS is oxidized on time scales of 1 to 2 days. Most authors assume that it first forms SO₂ [Toon *et al.*, 1987; Thompson *et al.*, 1990; Yin *et al.*, 1990b], which is then oxidized to sulfate aerosol, but it may also be directly oxidized to sulfate [Yin *et al.*, 1990b; Bandy *et al.*, 1992]. A fraction of the DMS (5 to 50%) becomes methane sulfonic acid [Berresheim, 1987; Berresheim *et al.*, 1990; Ayers *et al.*, 1991; Pszenny, 1992; Andreae *et al.*, 1985; Bates *et al.*, 1993]. The atmospheric oxidation of DMS is the only known source of methane sulfonate (MSA).

The third Soviet/American Gases and Aerosol's (SAGA 3) experiment was conducted in the equatorial Pacific Ocean, where the natural sulfur cycle experiences minimal influence from anthropogenic sources. Since the site of the SAGA 3 experiment is located 4000 km from major landmasses, the majority of anthropogenic SO₂ emissions will have been removed during the lengthy transit to the central Pacific. Trajectory analyses [Johnson, this issue] indicate that no sampled air mass had contacted a continent within the previous 7 days.

The R/V *Akademik Korolev* made five transects across the equator between 15°N and 10°S in the region of 145°W to 165°W during February and March 1991. The simultaneous measurement of many of the major sulfur species during this cruise makes it possible to evaluate the major terms in the natural sulfur budget.

EXPERIMENT

Atmospheric DMS was measured by an ECD-S system which was developed at PMEL [Johnson and Lovelock, 1988]. Sulfur compounds were chromatographically separated on a Caropak B/XE-60/H₃PO₄ column, fluorinated to SF₆ using F₂ in N₂ and a silver catalyst, and detected with a conventional electron capture detector. The system had a minimum detectable limit of 40 parts per thousand by volume (pptv) (2 nmol/m³), but the useful minimum detectable limit, where peaks could easily be integrated, was 200 to 300 pptv (9–13 nmol/m³). Most of the atmospheric DMS values were in this range and thus had a S/N of 5 or greater.

Air samples for DMS were collected through a 90-m continuously pumped Teflon sampling line that extended to the top of the starboard cargo mast. Standards were generated in zero air from a low-loss permeation tube. Because every other injection was a standard and the samples alternated between air and air equilibrated with seawater, each sample stream was repeated every 40 min. The atmospheric DMS system was only operational on transects 4 and 5.

The SO₂ in air was measured using the pararosaniline-formaldehyde (modified West-Gaeke) method [Rovinsky and Wiersma, 1987]. Air was pumped through a glass tube containing glass granules coated with the fine-film sorbent, disodium tetrachloromercurate, and glycerin. The air was sampled from 2.5 m above the bow. Samples were exposed for

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either 12 or 24 hours (changed at 0900 or 2100) at a flow rate of 6 to 9 L/min. The lower limit of detection for SO_2 was 0.15 nmol/m^3 , with an accuracy of $\pm 10\%$. It should be noted that this method has not been rigorously intercompared with other techniques at these low concentration levels.

Non-sea-salt (NSS) sulfate aerosol was measured in two ways, using a microorifice uniform deposit impactor (MOUDI) impactor and a thermally conditioned optical particle counter. There was no bulk measure of NSS during SAGA 3.

The size distribution of sulfate, MSA, and sodium was measured about 12 m above the water at the bow of the ship, using a MOUDI manufactured by MSP Corporation [Marple *et al.*, 1991]. The MOUDI had no inlet lines but sampled directly from unobstructed air. Aerosols in eight size ranges (cuts of 9.9, 6.2, 3.1, 1.8, 1.00, 0.56, 0.32, and 0.18 μm aerodynamic diameter) were deposited onto Teflon sheets which were extracted with dilute oxalic acid solution and analyzed by ion chromatography. Samples were exposed for between 10 and 48 hours at a flow rate of 30 L/min. Immediately after sampling, the samples were sealed into individual microclean polyethylene bags and stored at room temperature until returned to Rhode Island for analysis, as much as 2 months later. A sector controller interrupted sampling whenever the wind speed dropped below 2.5 m/s, the wind direction was more than 90° off the bow, and/or the CN count was greater than $1000/\text{cm}^3$. The detection limit of this system for the shortest sampling time was 0.2 $\text{nmol SO}_4/\text{m}^3$ and 0.005 $\text{nmol MSA}/\text{m}^3$ per stage. Since there were four logarithmically spaced stages per decade of size, each stage spanned a radius range of about a factor of 1.8. Sodium was used to correct the total sulfate on each stage for the sea-salt contribution. Although the uncertainty for MSA and NSS varied with sampling time, it was generally in the range of ± 10 to 20%.

Sulfate was also inferred from thermally conditioned optical particle counter (OPC) measurements and a differential mobility analyzer [Clarke and Porter, this issue]. Air was drawn from an intake atop a cargo mast into a forward laboratory for analysis. The OPC used three parallel inlet systems, which were heated to 40° , 150° , and 300° . That aerosol mass (inferred from the volume) which disappeared at 150° was interpreted as sulfuric acid, while the additional loss at 300° was assumed to be ammonium bisulfate. These systems could produce average size-distributions in 15 to 20 min, a much faster time response than the other sulfate-measuring devices on board. Further details are provided by Clarke and Porter [this issue].

RESULTS

Some of the sulfur species were sampled on relatively long time scales (12 to 24 hours for the impactor and SO_2), while others were sampled much more frequently (up to several times an hour for inferred optical particle counter/differential mobility analyzer (DMA), sulfate and DMS). To meaningfully compare measurements taken on such widely different time scales, we put them all on a common 6-hour time base. The rapid measurements were averaged for 3 hours before and 3 hours after 0600, 1200, 1800, and 2400 LT, while values from the slower measurements were entered into each of the intervals during which the sample was collected. Naturally, this averaging results in the loss of some temporal information on the most frequently measured species. Additional discussions of short-term variability are included in papers on the

individual species [Clarke and Porter, this issue; Johnson *et al.*, this issue].

Averaging over a common interval does, however, allow us to compare measurements which were not started and stopped in unison, a perennial problem for interpreting multispecies experiments. This procedure also ensures that statistics for each species will fairly weight samples of different duration. Days during which maintenance may have required that a particular instrument be off-line much of the time (and therefore generate fewer analyses) are not underrepresented in averages relative to days with the highest density of measurements. All of the ratios and statistics discussed below are based on this 6-hour time base and may therefore differ slightly from average values computed using different assumptions.

Figure 1 is a compilation of all the sulfur concentrations on the five transects of SAGA 3. (The long periods of apparently constant NSS and SO_2 concentrations represent lengthy integrated samples whose values were entered for each of the latitude bands over which the sampling took place.) It is apparent that although the transects each covered roughly the same latitude range, they are in many respects very different from one another. The clear north-to-south increase in total non-sea-salt sulfate (NSST) (aerosol from the MOUDI impactor) on transects 2 and 3, for instance, is much less evident in transects 1, 4, and 5. DMS, which was only measured on the last two transects, is more concentrated than any of the other sulfur species.

In Table 1 we have tabulated statistics for each substance, by transect and by latitude band. Since standard deviations in our 6-hour time base do not realistically represent those in nature, we have included maximum and minimum values as an indication of the observed variability. Again, the difference between the transects is apparent, but when averaged over all transects, there appears to be little change with latitude in DMS, MSA, or NSST.

Although only the NSST from the MOUDI is used below for computing ratios of sulfur species, four other sulfate values are included in Table 1. These include the total MOUDI sulfate (uncorrected for sea salt), $\text{SO}_4\text{T-MDI}$; submicron NSS from the MOUDI, $\text{NSS}<1\text{-MDI}$; and sulfate inferred from the DMA and OPC, $\text{SO}_4\text{-DMA}$ and $\text{SO}_4\text{-OPC}$. The last two should compare favorably with $\text{NSS}<1\text{-MDI}$, since (1) the DMA and OPC inlets do not pass most supermicron mass and (2) these devices thermally distinguish between NSS and sea-salt sulfate. In fact, the average values of NSS from these three methods are remarkably similar. The slightly greater values from the OPC relative to the DMA may result from the fact that it measures larger particles than the DMA can. However, the thermal techniques may also count some nonsulfate volatiles (such as organics) as sulfate, resulting in slightly larger values than those from the MOUDI. $\text{SO}_4\text{T-MDI}$ is of course much larger than the others since it still includes sea-salt sulfate.

Several ratios are of interest because they reveal information about the relative rates of formation and removal processes. These include the ratios of MSA to NSS, DMS to NSS, DMS to SO_2 , and SO_2 to NSS. Table 2 shows their average values on each transect and in each latitude band. MSA was about 7% of NSS, which is typical of the equatorial Pacific [Andreae *et al.*, 1985; Pszenny, 1992; Bates *et al.*, 1993]. On those transects when atmospheric DMS was measured, it was roughly twice the concentration of NSS.

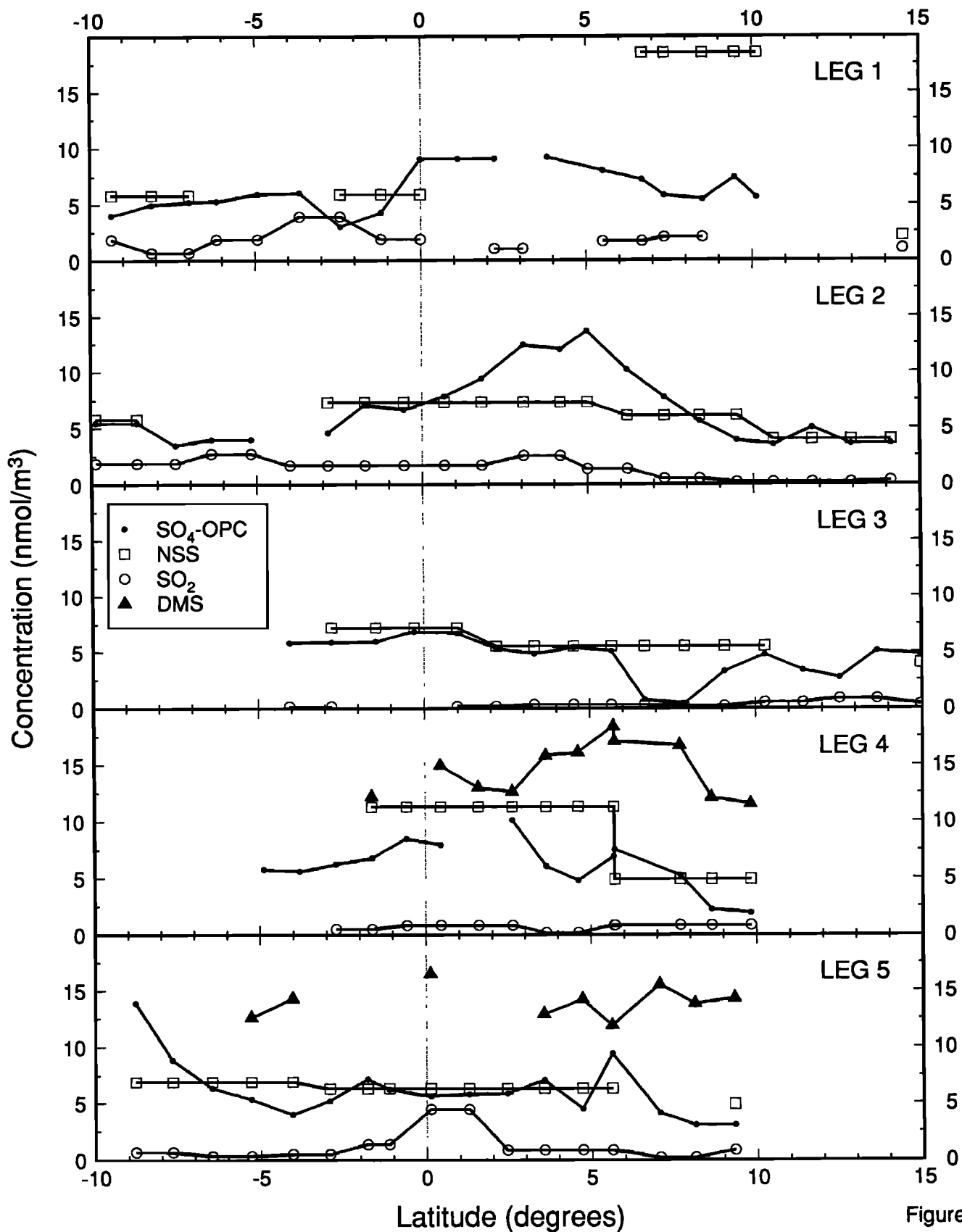


Figure 1

Fig. 1. Concentrations of DMS, SO₂, total non-sea-salt sulfate (NSS), and optical particle counter (OPC) sulfate versus latitude on the five cruise transects. The NSS and SO₂ data represent 10- to 48-hour integrated samples, so that the value from a single sample may be assigned to several latitude bands.

TABLE 1. Concentration Statistics

	DMS	SO ₂	MSA	SO ₄ T MDI	NSST MDI	NSS<1 MDI	SO ₄ DMA	SO ₄ OPC
<i>All SAG</i>								
Avg	14	1.1	0.43	17.7	7.1	5.0	5.0	6.1
Max	18	4.5	0.76	52.2	18.5	7.0	11.4	13.9
Min	11	0.2	0.13	8.5	2.2	2.0	0.6	0.4
<i>Transect 1</i>								
Avg		1.8	0.36	17.4	9.6	4.8	6.3	6.4
Max		3.9	0.46	27.4	18.5	6.6	10.4	9.2
Min		0.7	0.13	8.5	2.2	2.0	2.8	3.0
<i>Transect 2</i>								
Avg		1.5	0.56	15.4	6.2	5.4	5.7	6.6
Max		2.7	0.76	18.4	7.3	7.0	11.4	13.7
Min		0.2	0.23	12.2	4.0	3.2	2.0	3.5
<i>Transect 3</i>								
Avg		0.4	0.49	11.7	5.9	5.2	4.3	4.5
Max		0.9	0.52	12.7	7.2	6.1	7.9	6.8
Min		0.2	0.23	11.1	4.0	3.2	0.6	0.4
<i>Transect 4</i>								
Avg	15	0.7	0.48	35.8	9.2	4.9	5.4	6.1
Max	18	0.9	0.58	52.2	11.3	5.8	9.5	10.1
Min	12	0.2	0.29	27.6	4.9	3.2	2.4	1.9
<i>Transect 5</i>								
Avg	14	1.1	0.33	13.7	6.4	5.5	4.2	6.2
Max	17	4.5	0.70	52.2	6.9	5.9	6.0	13.9
Min	12	0.2	0.14	10.2	4.9	3.2	3.2	3.1
<i>10°/15°</i>								
Avg		0.5	0.28	13.5	5.8	3.7	3.7	4.2
Max		1.0	0.51	27.4	18.5	6.6	7.3	5.6
Min		0.2	0.13	8.5	2.2	2.0	2.0	2.7
<i>5°/10°</i>								
Avg	15	0.9	0.45	26.4	8.5	4.9	4.8	5.6
Max	18	2.1	0.76	52.2	18.5	7.0	11.4	13.7
Min	12	0.2	0.14	10.2	4.9	3.2	0.6	0.4
<i>0°/5°</i>								
Avg	15	1.3	0.48	17.1	7.8	5.9	6.5	7.4
Max	17	4.5	0.76	27.6	11.3	7.0	11.0	12.4
Min	13	0.2	0.14	10.2	5.5	5.0	3.6	4.5
<i>-5°/0°</i>								
Avg	13	1.5	0.49	15.2	7.3	5.7	4.9	6.0
Max	14	3.9	0.76	27.6	11.3	7.0	7.2	9.0
Min	12	0.2	0.14	10.2	5.9	4.1	2.8	3.0
<i>-10°/-5°</i>								
Avg	13	1.4	0.53	13.5	6.3	5.5	4.9	6.1
Max	13	2.7	0.70	14.6	6.9	5.9	6.0	13.9
Min	13	0.3	0.40	12.3	5.8	5.1	3.2	3.5

In nanomoles per cubic meter. DMS, dimethyl sulfide. SO₄T-MDI is the sum of sulfate on all the microorifice uniform deposit impactor (MOUDI) stages, NSST-MDI is the total of non-sea-salt sulfate (NSS) on all MOUDI stages, NSS<1-MDI is the sum of all submicron NSS from the MOUDI, SO₄-DMA is sulfate inferred from the differential mobility analyzer, and SO₄-OPC is the sulfate inferred from thermally conditioned optical particle counter measurements.

Two techniques had the capability to evaluate the size distribution of sulfate aerosols. The MOUDI impactor stages were individually analyzed for sulfate and MSA, while the thermally conditioned optical particle counter data were used to infer sulfate from the volatility of aerosols in each size range upon heating [Clarke and Porter, this issue]. The MOUDI samples were collected at ambient relative humidity, while the OPC diameters were measured at 20–30% relative humidity, which will result in slightly larger MOUDI sizes.

Figure 2a shows a typical MOUDI distribution of MSA and NSS sulfate. It is clear that most of the NSS is contained in a

submicron mode, centered at about 0.35 μm aerodynamic diameter. The MSA, by contrast, is bimodal with most of its mass in a mode whose peak is around 2 μm . The project-average MSA peak diameter is also around 1–2 μm (Figure 2b), while that of NSS is about 0.3 μm . Seventy percent of the MSA was in particles of 1 μm or greater aerodynamic diameter, as contrasted with NSS, of which only about 30% was on supermicron particles.

The OPC-inferred mass mode mean diameter varied between about 0.17 and 0.27 μm with typical values between about 0.2 and 0.25 μm (see Figure 2 in the work of Clarke and

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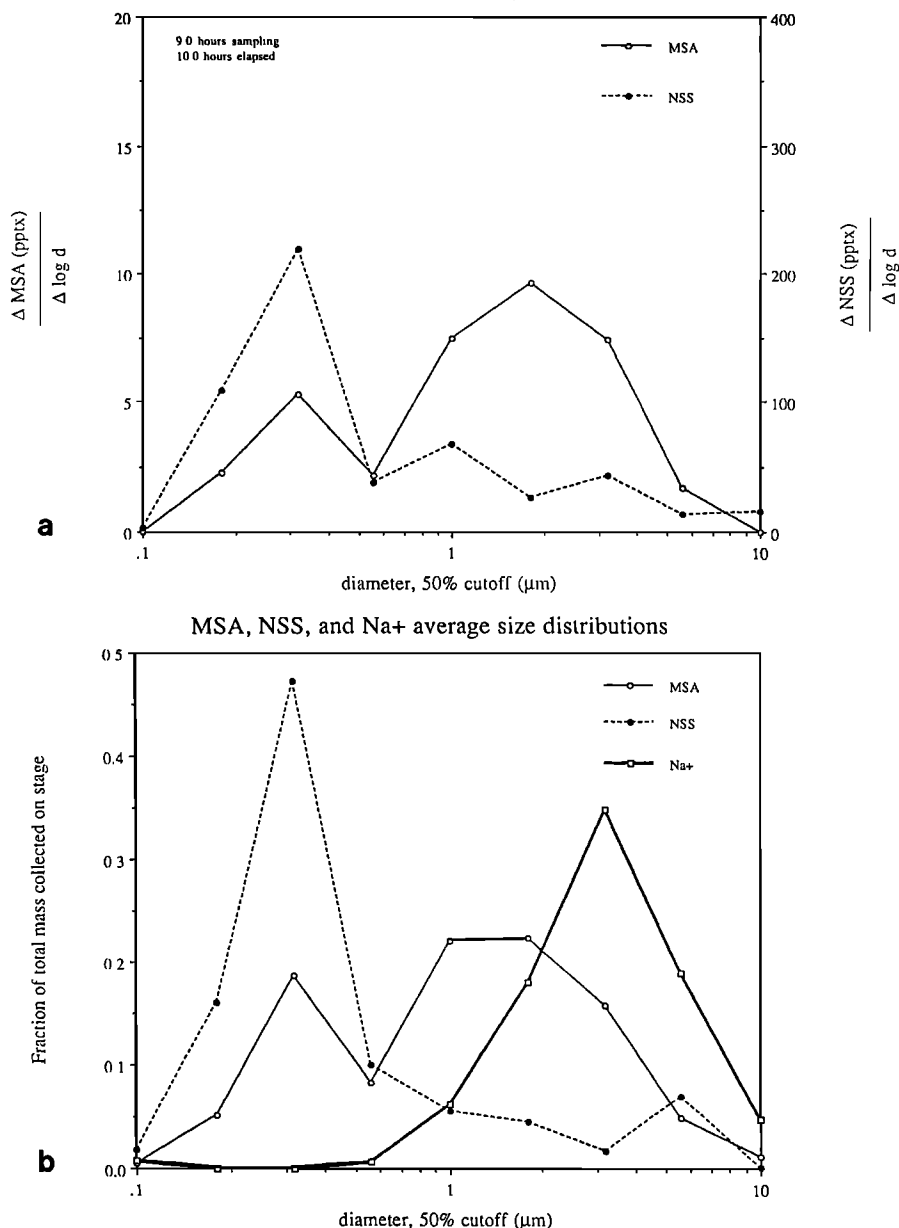


Fig. 2. MOUDI impactor size distributions: (a) concentrations of methanesulfonate (MSA) and NSS versus size on day 49 and (b) project-average fraction of MSA, NSS, and Na+ in each size range. The backup filter concentration has arbitrarily been plotted at 0.1 μm.

TABLE 2. Concentration Ratios

	DMS(Air)/ SO ₂	DMS(Air)/ NSST	SO ₂ / NSST	100xMSA/ NSST
<i>All SAGA</i>				
Avg	32	2.0	0.19	6.6
Max	94	3.5	1.19	10.4
Min	4	1.1	0.02	2.2
<i>Transect Averages</i>				
Transect 1			0.26	5.1
Transect 2			0.20	8.6
Transect 3			0.06	8.4
Transect 4	31	1.9	0.09	5.3
Transect 5	34	2.2	0.20	5.1
<i>Latitudinal Averages</i>				
10°/15°			0.15	5.8
5°/10°	36	2.6	0.13	6.5
0°/5°	30	1.7	0.18	6.3
-5°/0°	26	1.6	0.19	6.7
-10°/-5°	37	1.8	0.15	8.3

The total MOUDI NSS was used for these computations.

Porter, this issue). The DMA values showed similar variability with mass mode diameters predominantly in the 0.23- to 0.3-μm range, in excellent agreement with the average NSS MOUDI peak at 0.3 μm. This supports the use of the thermal-conditioning inferential method for estimating NSS from OPC and DMA measurements.

Examples of DMA number and mass distributions for submicrometer aerosol measured during day 48 are shown in Figure 3. The number peak is bimodal, with roughly equal concentrations in modes centered at 0.06 and 0.2 μm, while the submicrometer mass is dominated by the larger mode with its mass mean diameter at about 0.27 μm. These distributions were found to vary markedly in response to meteorological conditions and precipitation events [Clarke and Porter, this issue].

Removal and transport terms caused some of the most dramatic variations in aerosol concentrations. Around day 59 (Figure 4) the OPC sulfate climbed slowly (roughly 4 nmol/m³ d) to 6 nmol/m³, and then dropped suddenly to 0.4 nmol/m³ in

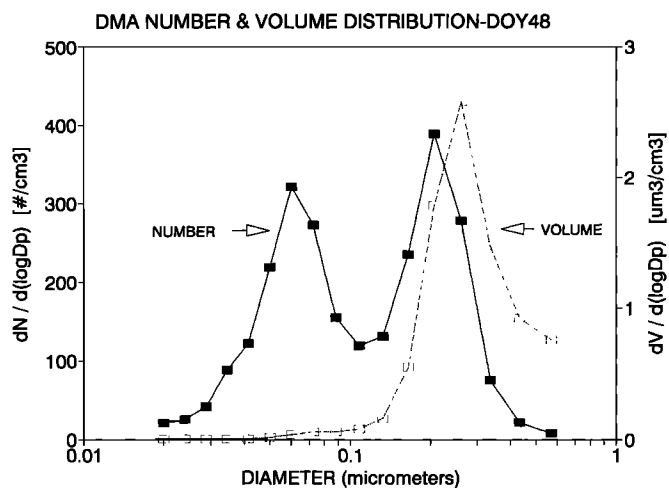


Fig. 3. Number and volume distribution of sulfate inferred from the DMA on day 48.

less than 2 hours (about 30 km), apparently due to subsidence of free tropospheric air into the marine boundary layer (MBL) [Thompson *et al.*, this issue; Clarke and Porter, this issue]. Unfortunately, none of the sampling schedules were optimized for observing the behavior of other atmospheric sulfur species during the event in Figure 4. Dramatic changes in OPC sulfate also accompanied a precipitation event on day 64.

Since the time scales for both DMS and SO_2 oxidation to form sulfate are generally a day or more [Toon *et al.*, 1987; Thompson *et al.*, 1990; Kreidenweis *et al.*, 1991a], it is unlikely that varying source terms could cause rapid changes in sulfate aerosol concentration. However, movement into different air masses has the potential to cause large changes in observed values. Virtually all of the rapid changes in sulfate aerosol concentration were the result of moving our experimental platform into an air mass with a different history from the one before. Localized convective events such as the one near day 59 have the potential to either scavenge the aerosols from a small area, leaving much higher concentrations in the unscavenged air around it, or entrain free tropospheric air on relatively small scales.

DISCUSSION

Comparison With Published Values

Since many of the observed values for SO_2 and DMS were

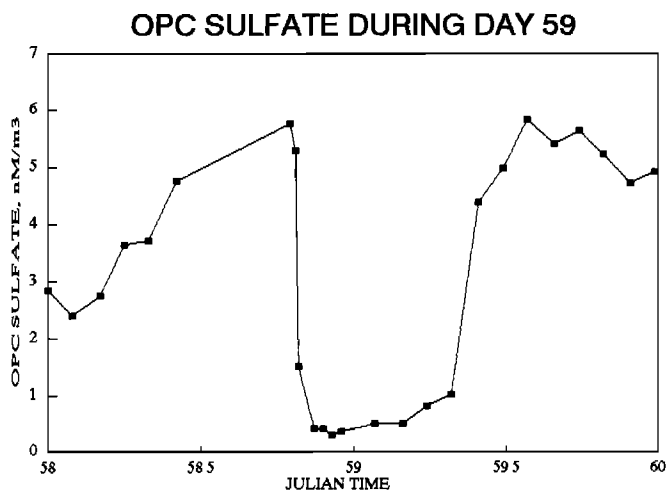


Fig. 4. OPC sulfate aerosol versus time during day 59.

only several times the detection limits for the methods used, it is particularly important that we establish how our data compares with other measurements in this and similar areas. A limited number of observations have been reported for the equatorial Pacific (Table 3). It is important to recall that during SAGA 3 all these species were measured simultaneously in the same air masses.

For DMS the 14 nmol/m^3 atmospheric DMS average here is twice that reported by Andreae *et al.* [1985] in the equatorial Pacific and about 4 times that measured by Bandy *et al.* [1992] in this region during the Equatorial Meteorological Experiment (EMEX). However, values of $8\text{--}10 \text{ nmol/m}^3$ were observed in both those programs. Perhaps the best comparisons are with Quinn *et al.* [1990] and T. Bates (unpublished Pacific Marine Aerosol and Gas Exchange (MAGE) cruise data, 1992), since both were made in virtually the same region in the late winter or early spring. Quinn *et al.* reported $11 \pm 7 \text{ nmol DMS/m}^3$, which overlaps our observed range. Bates observed DMS concentrations of $5 \text{ to } 32 \text{ nmol/m}^3$ near the equator and 140°W , which also brackets our data. Our DMS values are consistent with others reported for this area.

Our $1.1 \text{ nmol SO}_2/\text{m}^3$ average is about half the 2.4 nmol/m^3 boundary layer average reported by Maroulis *et al.* [1980], but the authors now believe that was overestimated by about 1.3 nmol/m^3 [Thornton and Bandy, 1993]. If the proposed correction to Maroulis *et al.* is valid, our data agree perfectly. Our SO_2 value is also very close to the 1.3 nmol/m^3 observed by Bonsang *et al.* [1980] and 0.7 nmol/m^3 reported by Thornton and Bandy [1993] from EMEX. It appears that our SO_2 values are quite close to others reported for this region.

Likewise, our NSS average of 7 nmol/m^3 is identical with the Fanning Island average reported by Prospero *et al.* [1985] and recent measurements by P. Quinn (unpublished data, 1992) during the Pacific MAGE cruise in this same region. It is also within the range of $5\text{--}10 \text{ nmol/m}^3$ observed from an aircraft during CPACE/PASIN (see B. J. Huebert *et al.*, unpublished data, 1990). It is several times larger than the $0.2\text{--}1.6 \text{ nmol/m}^3$ which Bates *et al.* [1989] report for this same region during SAGA 2, but a seasonal difference could be responsible. Clearly our NSS values are also in good agreement with both airborne and shipboard measurements.

Species Lifetimes

Since our discussion of the ratios in Table 2 will depend heavily on assumptions about the lifetimes of DMS, SO_2 , and NSS, we first review the existing literature on atmospheric residence times. Although numerous definitions are applied to the "lifetime" of a substance, we will try to consistently use it here as the time it takes a pseudo-first-order process to reduce the concentration of a substance to $1/e$ of its initial value. Then the lifetime, τ , is equal to the inverse of the pseudo-first-order rate constant.

For a substance whose removal can occur by more than one pathway, the mean residence time is defined by

$$\frac{1}{\tau} = \sum_i \frac{1}{\tau_i} \quad (1)$$

where τ_i refers to the characteristic removal time associated with removal path i (which may be chemical reaction, dry deposition, or wet deposition), generally assumed to be represented by a first-order loss process. In those cases where the lifetime from one process is considerably shorter than that

TABLE 3. Atmospheric DMS, SO₂, and NSS Values

nmol/m ³	Reference	Location and Comment
<i>Dimethyl Sulfide</i>		
7.1 ± 3	<i>Andreae et al.</i> [1985]	equatorial Pacific
11 ± 7	<i>Quinn et al.</i> [1990]	equatorial Pacific, spring
3.2 ± 1.6	<i>Bates et al.</i> [1990]	Northeast Pacific, spring
3.5	<i>Thornton and Bandy</i> [1993]	equatorial Pacific, EMEX
2-8	<i>Bandy et al.</i> [1992]	Northeast Pacific, PSI 3
5-32	T. S. Bates, unpublished, data, 1992	equatorial Pacific, winter
14 ± 2	this work	equatorial Pacific, winter
<i>Sulfur Dioxide</i>		
2.4 ± 0.8	<i>Maroulis et al.</i> [1980]	Pacific MBL (overestimate)
1.3	<i>Bonsang et al.</i> [1980]	Pacific
1.2 ± 0.7	<i>Quinn et al.</i> [1990]	equatorial Pacific, spring
0.7	<i>Thornton and Bandy</i> [1993]	equatorial Pacific, EMEX
1.0 ± 0.5	<i>Bandy et al.</i> [1992]	Northeast Pacific, PSI 3
1.1 ± 0.9	this work	equatorial Pacific, winter
<i>Non-Sea-Salt Sulfate</i>		
7	<i>Prospero et al.</i> [1985]	Fanning Island annual average
10	<i>Clarke et al.</i> [1987]	equatorial Pacific, spring
0.2-1.6	<i>Bates et al.</i> [1989]	equatorial Pacific, summer
4 ± 2	<i>Quinn et al.</i> [1990]	equatorial Pacific
5-10	B. J. Huebert, unpublished data, 1990	equatorial Pacific, summer
7	P. K. Quinn, unpublished data, 1992	equatorial Pacific, winter
7	this work	equatorial Pacific, winter

EMEX, Equatorial Meteorological Experiment; PSI 3, Third Pacific Sulfur Stratus Investigation.

from other processes, the faster process will dominate the mean residence time. Although observations of lifetimes frequently have been presented without an explicit statement of the responsible processes, we will identify chemical lifetimes and depositional lifetimes where possible in our discussion.

There is no consensus on the lifetime of DMS in the MBL. Since it is insoluble and is emitted from the surface, its lifetime relative to deposition will be very long. If we use a rate constant for OH attack on DMS of $6.1 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ [*Yin et al.*, 1990a] and an OH concentration for this cruise of $1.2 \times 10^6/\text{cm}^3$ [*Thompson et al.*, this issue], we compute a chemical τ_{DMS} of about 2 days. In contrast, *Bates et al.* [1990] used an estimate of the DMS emission flux and its column burden to compute a residence time of just 13 hours over the Northeast Pacific. *Cooper and Saltzman* [1991] noted an apparent DMS lifetime of less than a day just off the east coast of North America but attributed it to a sea breeze circulation bringing different air masses during the daytime and nighttime. Although we do not have adequate time-resolved atmospheric DMS data from SAGA 3 to demonstrate its diurnal variation with the data reported here, several other investigators have noted a large diurnal cycle. *Bandy et al.* [1992] observed a diurnal variation in DMS during Chemical Intercomparison Test and Evaluation (CITE) 3 in the Atlantic and again during Third Pacific Sulfur Stratus Investigation (PSI-3) in the Pacific, in which a late morning peak was followed by a 40 to 50% afternoon decline and a postsunset slow climb back to the next morning's peak. *Andreae et al.* (1985) shows three days of this diurnal variation from CITE 3. The same cycling has been observed in the equatorial Pacific region by Bates and coworkers (personal communication, 1992) during the spring 1992 JGFS/MAGE cruise. This rapid afternoon loss suggests that τ_{DMS} can be of the order of half a day in clean marine air. These subday DMS residence times imply that OH may not be the only oxidant of DMS, even when one considers that OH will peak around solar noon.

During the SAGA 3 program, however [*Bates et al.*, this issue] an estimate of the DMS flux ($6.4 \mu\text{mol}/\text{m}^2/\text{d}$) and the DMS column burden ($15 \text{ nmol}/\text{m}^3 \times 1.5 \text{ km}$) yielded a DMS lifetime of 1.5 to 3 days. When the flux estimate/column burden approach was applied to the *Bates* (personal communication, 1992) MAGE data referred to above, it yielded a lifetime of the order of 2 days. There remains a substantial discrepancy between lifetime computations based on flux estimates and those from the evaluation of diurnal DMS variations. In view of this discrepancy we will consider both 0.5- and 3-day values for τ_{DMS} in our discussions below.

The mean residence time of SO₂ in the MBL (15 ± 3 hours) has been calculated and summarized by *Bonsang et al.* [1987] from the average of many observations. Most of these were based on the disappearance of SO₂ from continental plumes as they were advected through the marine boundary layer. This 15-hour value for τ_{SO_2} is much smaller than the six days that oxidation by OH would predict for a homogeneous chemical reaction time [*Kreidenweis and Seinfeld*, 1988] and must therefore represent the combined effects of wet and dry deposition and heterogeneous oxidation. Dry deposition alone would generate a 1-day lifetime if an SO₂ deposition velocity of 1 cm/s were assumed in a 1.5-km-deep boundary layer.

The lifetime of NSS is probably about a day. *Bates et al.* [1990] used a budget approach to derive a 31-hour lifetime for the northeastern Pacific in May 1987. *Vong et al.* [1988] used a statistical approach to derive a 48-hour lifetime for these submicron aerosols in the same region in 1984. Since dry deposition of NSS with a 0.1 cm/s deposition velocity would produce a lifetime of weeks and since no chemical loss mechanism has been described, it follows that wet deposition must be responsible for these shorter lifetimes.

The rainfall frequency during SAGA 3 might therefore be a reasonable way to estimate the minimum possible NSS lifetime. B. Heikes (personal communication, 1991) evaluated reports in the *Akademik Korolev's* log of precipitation at and

near the ship. His analysis shows that the interval between precipitation events at the ship was between 12 and 36 hours 50% of the time but that the time between events which were observable from the ship was shorter: it was between 4 and 26 hours 50% of the time. Since air from nonprecipitating regions might be drawn into the updrafts accompanying "observable" precipitation, the time between observable events may represent the minimum time between scavenging events for the air at the ship. This implies that τ_{NSS} with respect to precipitation removal (assuming that the scavenging of these submicron aerosols is not 100% efficient) was probably about a day.

The Use of Lifetimes to Infer Concentration Ratios

If substances *A* and *B* are related by the following sequence of first-order (or pseudo-first order) reactions or deposition processes



their concentration ratio can be predicted from their lifetimes. If we assume that *B* is in steady state between formation and loss, then

$$\frac{d[B]}{dt} = k_A[A] - k_B[B] = 0 \quad (3)$$

$$\frac{[A]}{[B]} = \frac{k_B}{k_A} = \frac{\tau_A}{\tau_B} \quad (4)$$

where τ_A and τ_B represent the lifetimes of *A* and *B*, respectively. If the observed concentration ratio disagrees with the lifetime ratio, then either (1) *B* is not in steady state, (2) the lifetimes or concentrations are incorrect, or (3) the chemistry is not properly described by equation (2). We will apply this test to some of the concentration ratios listed in Table 2. Since they are averages over several weeks, we will assume that this averaging makes the steady state assumption valid for each substance.

DMS/NSS Ratio

The first question is whether DMS is the source of most of the NSS in the MBL. Although this process is not a single pseudo-first-order reaction, we can still test the hypothesis that virtually all DMS forms NSS and virtually all NSS originates from DMS. As Table 2 demonstrates, we observed twice as much atmospheric DMS as NSS. Applying lifetime arguments to this ratio would suggest that the lifetime of NSS must be only half that of DMS. If the DMS lifetime is 3 days, this implies a 1.5-day NSS lifetime, which is consistent with the observed precipitation frequency. This agreement would be very convincing if it were not for our inability to explain the diurnal variation of DMS using this long lifetime.

If the 0.5-day DMS lifetime is correct, τ_{NSS} would have to be just a few hours, which is physically unreasonable for a submicron aerosol. Thus $\tau_{\text{DMS}} = 0.5$ days would be consistent with the observed ratios only if the majority of DMS is not oxidized to sulfate. This possibility could obtain if the OH addition pathway [Yin *et al.*, 1990a] predominates over hydrogen abstraction, thus forming DMSO and DMSO₂. These

soluble compounds should dry deposit rapidly to the ocean's surface without producing sulfate aerosol. Some NSS could still be formed from DMS (depending on the branching after the initial oxidant attack), but the predominance of the DMSO channel would allow us to explain why the DMS/NSS ratio exceeds unity. Since we have no alternate explanation for the observed diurnal cycle of DMS, this "DMSO rather than NSS" explanation merits serious consideration.

This hypothesized branching toward DMSO could also explain the high DMS/SO₂ ratio discussed below, since SO₂ would only be a product of the hydrogen abstraction branch of the reaction. This argument suffers from the fact that OH attack alone cannot explain the rapid daytime loss of DMS, which is well established in this area. It may be that another oxidant, such as Cl atoms, should be given further consideration as the cause of this diurnal variation in DMS.

DMS/SO₂ Ratio

The ratio of atmospheric DMS to SO₂ contains information about the link between these two sulfur gases. For the last two transects of SAGA 3 this ratio averaged 32; there was much more DMS than SO₂. Eliminating the two lowest SO₂ values (which may have been the result of recent precipitation scavenging) results in a project average ratio of 18 ± 7. Computing the ratio using transect-average concentrations (thereby eliminating the effect of simultaneously high DMS and low SO₂) yields 21 for transect 4 and 13 for transect 5.

These results present a quandary: if all but a few percent of the DMS were to form SO₂, which is then oxidized to sulfate [Bates *et al.*, 1990; Yin *et al.*, 1990b; Thompson *et al.*, 1990; Kreidenweis *et al.*, 1991b], our 0.5- and 3-day DMS lifetimes would predict DMS/SO₂ ratios of 1 and 6. (Any additional sources of SO₂, such as volcanoes or free tropospheric transport of continental SO₂ followed by entrainment into the MBL, would only make the DMS/SO₂ ratio even smaller and thus harder to reconcile with the observations.)

Clearly, the DMS/SO₂ ratio observed on SAGA 3 is several times larger than that predicted by this lifetime argument, even when the longer DMS lifetime is used. There are several possible explanations: (1) our measurements of the ratio are in error by a large factor, (2) the actual lifetime of SO₂ in the MBL is a small fraction of the DMS lifetime (of the order of an hour or so), or (3) SO₂ is not the principal product of DMS oxidation.

Option 1 seems unlikely. Although directly measuring DMS without preconcentration made values below about 5 nmol/m³ unmeasurable, the S/N for the measured values was good. Likewise, while the West-Gaeke method for SO₂ has not been rigorously intercompared in remote marine environments with other SO₂ methods, the values we found are very similar to those measured by other methods. Furthermore, other measurements in this region also point to a DMS/SO₂ ratio much larger than 1. Even when we acknowledge the uncertainty of the West-Gaeke SO₂ method at these low levels, the evidence still points to a large DMS/SO₂ ratio.

Option 2 is no more plausible: If we accept the 3-day value for τ_{DMS} , the lifetime of SO₂ would have to be 0.2 to 0.1 days. This is clearly much smaller than either observed or predicted values for τ_{SO_2} . The 0.5-day DMS lifetime produces an even more unrealistic requirement that τ_{SO_2} be only 20 to 60 min. But neither dry deposition nor any known oxidation reaction can operate that rapidly [Bonsang *et al.*, 1987]. SO₂ lifetimes of

half a day or more result from these calculations. In addition, a short SO_2 lifetime would result in much more SO_2 variability than has been observed. There seems to be little evidence of a diurnal cycle in any of the reported SO_2 measurements, which argues against a τ_{SO_2} of a few hours or less. Indeed, the constancy of SO_2 in the midst of widely varying DMS concentrations has been noted [Thornton and Bandy, 1993; Bandy et al., 1992].

Option 3 deserves serious consideration. Although most models to date have assumed that DMS oxidation proceeds via SO_2 , two other possibilities deserve consideration: one is the hypothesis advanced above, that the majority of DMS is converted to DMSO and DMSO_2 . This would imply that very little SO_2 or NSS would be formed, relative to the concentration of DMS. The second plausible alternative is a pathway proposed by Bandy et al. [1992]: DMS oxidation may form sulfate directly, without SO_2 serving as an intermediate.

Yin et al. [1990b] consider the possibility that CH_3SO_3 can undergo unimolecular decomposition to directly form SO_3 and sulfate. The limitation they see to this pathway is the lack of a reductant capable of extracting an oxygen from $\text{CH}_3\text{S}(\text{O})_2\text{OO}$. They considered only CH_3S , NO , and NO_2 for this role. But as Bandy et al. [1992] point out, HO_2 may be present at levels of 100 pptv or more in the low- NO_x environment of the central Pacific. By contrast, the model of Thompson et al. [this issue] suggests that HO_2 should not exceed 20-30 pptv under SAGA 3 conditions. Reaction with HO_2 could add a hydrogen atom to $\text{CH}_3\text{S}(\text{O})_2\text{OO}$, forming peroxy methane sulfonic acid. Photolytic cleavage of the peroxy bond then leaves CH_3SO_3 , which can either decompose to form SO_3 or react with HO_2 to form MSA. Rapid hydration of SO_3 then generates sulfate without an SO_2 intermediate. For this pathway the relative amounts of MSA and NSS formed would be controlled by the branching in the reaction of CH_3SO_3 [Bandy et al., 1992].

If this reaction pathway were responsible for a significant fraction of the DMS oxidation, it would explain why high levels of SO_2 are not generally observed along with high DMS levels. Yet as long as some fraction of the DMS formed SO_2 , it would not eliminate the possibility of a seasonal coherence between DMS and SO_2 at long-term monitoring sites where entrainment of SO_2 from the free troposphere is insignificant.

SO₂/NSS Ratio

The SO_2/NSS ratio averaged 0.2, yet varied from 0.26 on transect 1 to 0.06 on transect 3. If we accept the 15-hour SO_2 lifetime, this implies that τ_{NSS} should be around 3 days, with a transect 1 minimum of 2.4 and a transect 3 maximum of 10 days. These NSS lifetimes are somewhat longer than the literature values discussed above. Another way to look at this ratio is to assume that the lifetimes above are correct at roughly 0.5 days for SO_2 and 1 day for NSS. This suggests that the ratio SO_2/NSS should be about 0.5, whereas we observed 0.2 or less. In other words, we observed too little SO_2 for the observed NSS, by a factor of 2 to 10. This supports the idea that some NSS is formed by a mechanism that does not involve SO_2 . These data argue that between 10 and 50% of the NSS is derived from SO_2 oxidation, while the remainder is formed from something like the SO_2 -free DMS oxidation pathway.

MSA/NSS Ratio

Our observation that MSA is about 7% of the NSS concentration agrees with Savoie and Prospero [1989] (6.5%)

and Andreae et al. [1985] (7%). Kreidenweis et al. [1991] used an empirical method to estimate the change in this ratio with latitude and predicted that it should be about 20% larger at 5°N than at 5°S. This slight change in the mass ratio is ascribed to the effect of temperature differences on the vapor pressures of the acid gases. As Table 2 shows, we found very little variation in this ratio in the latitude zones nearest to the equator. The trend at the extreme latitudes is for slightly higher values to the south, in contrast to the predictions of Kreidenweis et al. [1991a,b]. Our observed MSA/NSS ratios vary in the same manner as the seawater DMS concentrations do, maximizing between 5°S and 10°S.

Implications of the Size Distribution of MSA

It is clear from Figure 2a that during SAGA 3, MSA was being deposited on larger particles than the NSS was, in contrast to observations by Andreae et al. [1985] near North America and Pszenny et al. [1989] in the Antarctic. However, Pszenny [1992] noted the same size distribution that we did while making measurements in the equatorial Pacific only a few weeks before SAGA 3 arrived in the area. Since his similar observations were made using a different type of impactor (a Sierra), it leaves little doubt that our observations are valid for that place and time.

Figure 2b demonstrates that the project-average mass peak for MSA occurs at about 1-2 μm aerodynamic diameter, which is between the 0.3- μm NSS peak and the 3+ μm sodium peak. This may indicate that the MSA was depositing on sea-salt aerosol, according to its surface area. This hypothesis is supported by the inferred SAGA 3 sea-salt area distribution measured by Clarke and Porter [this issue], which peaked at 1.0 to 1.5 μm .

As a further test of this hypothesis, we examined the mass and area peaks of a lognormally distributed sea-salt aerosol having the characteristics described by Ahr et al. [1989]. For this aerosol the mass peak occurred at 7.0 μm and the area peak at 3.0 μm . While the precise diameter of the mass peak will be a function of local factors such as wind speed, the ratio of the two should translate fairly well to our conditions. Since our sodium mass peak was at 3 μm , the sodium area peak should be around 1.3 μm , which is just what we observed for MSA and Clarke and Porter [this issue] inferred for sodium. It appears then that MSA is condensing onto sea-salt aerosol in proportion to its available surface area.

As Clegg and Brimblecombe [1985] have shown, MSA has a very high vapor pressure. Pure MSA has a vapor pressure of 10^{-6} atmospheres, or 1 ppm by volume. Its vapor pressure drops dramatically as the amount of liquid water increases, however, indicating a high solubility in dilute solutions. Thus the lower vapor pressure over dilute solutions will cause the bulk of it to distill out of aerosols with very little water mass and dissolve instead in those with more available liquid water, which here appears to be the sea-salt aerosol. The greater volume of water on sea-salt aerosols makes them the favored solvent for MSA here. This water mass argument, however, would tend to make the MSA distribution resemble that of sodium mass. The fact that it peaks near the sodium area peak argues that MSA may be in a disequilibrium controlled by surface area, rather than an equilibrium controlled by water mass.

It is not clear why this same argument would not cause the MSA in all regions to deposit on supermicron aerosols, since they should in most cases compete favorably for water with the

smaller particles. It may be that near continents the aerosol liquid water budget and surface area is shifted toward smaller particles by the greater number of small particles in continental regions. It may also be that larger aerosols near continents are made more acidic, thus increasing the MSA vapor pressure somewhat relative to that over the large aerosols in more remote regions.

Because of its high vapor pressure, MSA may not be capable of nucleating new particles under these conditions. Thus it would only have a secondary effect on climate, causing the growth of existing particles and improving their ability to serve as CCN, rather than changing the climate-critical number of particles in the marine atmosphere.

It is also important to recognize the significance of the different sizes of MSA and NSS aerosols on the use of MSA for estimating the biogenic contribution to NSS found in ice cores [Legrand et al., 1991]. Because of its larger size in the tropical marine atmosphere, MSA will have a considerably shorter lifetime than NSS aerosols, causing the MSA/NSS ratio to change as they are being transported from their source region to the site where the ice is deposited. Until we understand why NSS and MSA size distributions are different in some regions and similar in others, extreme caution must be used when interpreting their record in ice.

CONCLUSIONS

We observed gradients of sulfate aerosol with latitude on transects 2 and 3, but they were much less apparent on the other three transects. Significant differences between the transects emphasized the lack of longitudinal and temporal homogeneity in the equatorial Pacific in February and March. DMS was by far the most concentrated sulfur species.

The DMS/NSS ratio, which averaged about 2, suggests that most DMS is not oxidized to NSS. The ratio DMS/SO₂ was considerably greater than 1. This result, in combination with similar results from other measurement programs, suggests that SO₂ may not always be a major intermediate in the formation of NSS from DMS. The small SO₂/NSS ratio also supports the idea that much of the NSS is formed by a pathway that does not include SO₂.

The size distributions of MSA and NSS aerosol imply that MSA does not play a significant role in nucleating new particles but rather dissolves in the liquid water on sea-salt aerosols. The MSA mass distribution corresponds roughly to the distribution of sea-salt aerosol surface area. One result of the difference in NSS and MSA sizes is that the lifetimes of these two aerosol species will differ, causing their ratio to change with transport time. Extreme care is therefore required when trying to interpret ice core MSA/NSS ratios.

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