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Authors

Yvon, S. A

Saltzman, E. S

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Atmospheric sulfur cycling in the tropical Pacific marine boundary layer (12°S, 135°W): A comparison of field data and model results 2. Sulfur dioxide

S. A. Yvon[1] and E. S. Saltzman

Rosenstiel School of Marine and Atmospheric Science, University of Miami, Miami, Florida

Abstract. The atmospheric chemistry of sulfur dioxide over the tropical South Pacific Ocean is investigated by using results from field measurements and numerical models. Simultaneous real time measurements of sulfur dioxide and its biogenic precursor dimethylsulfide were made at 12°S, 135°W for a 6-day period from March 3 through March 9, 1992. The mean SO_2 and DMS mole fractions were 71 ± 56 pmol mol^{-1} (1σ) and 453 ± 93 pmol mol^{-1} (1σ) respectively. These concentrations are compared to those predicted by a time-dependent photochemical box model of the marine boundary layer. Model estimates of the yield of SO_2 from DMS oxidation range from 27% to 54%. Even with low yields, DMS is the dominant source of SO_2 in this region. Estimates of vertical entrainment velocities based on the tropospheric ozone budget suggest that vertical entrainment is a minor source of SO_2. The relative rates of various loss mechanisms for SO_2 are dry deposition to the sea surface (58%), in-cloud oxidation (9%), OH oxidation (5%), and uptake by sea-salt aerosols (28%).

Introduction

Dimethylsulfide (DMS) is ubiquitous in the marine atmosphere. It is produced in the surface ocean by certain species of phytoplankton and is emitted to the atmosphere through air/sea exchange processes. In the marine boundary layer, DMS is oxidized by OH radicals to produce sulfuric acid, methanesulfonic acid (MSA), and possibly dimethylsulfoxide (DMSO) and dimethylsulfone ($DMSO_2$) [*Yin et al.*, 1990a, b, and references therein]. The relative yields of these products in the remote marine boundary layer is not well established owing to the difficulties in creating a laboratory environment that is suitably similar to that found over the remote oceans.

Sulfur dioxide (SO_2) is an intermediate in the production of sulfuric acid from DMS oxidation in the marine boundary layer. It is this SO_2 and its oxidation product sulfuric acid that are thought to be the major sources of non-sea-salt sulfate (nss sulfate) in aerosols in the remote marine boundary layer. Oxidation of DMS is the largest biogenic source of SO_2 in the remote marine boundary layer. Hydrogen sulfide (H_2S), another biogenic reduced sulfur gas, also oxidizes to form SO_2. However, H_2S is present only at very low concentrations over the remote open ocean and is not considered to be a significant source of SO_2 [*Saltzman and Cooper*, 1988; *Yvon et al.*, 1993].

Recently, simultaneous measurements of atmospheric DMS and SO_2 have been made in the marine boundary layer [*Berresheim* 1987; *Andreae et al.*, 1988; *Ferek et al.*, 1991; *Yvon et al.*, 1991; *Bandy et al.*, 1992; *Huebert et al.*, 1993; *Thornton et al.*, 1995]. With the exception of those of *Ferek et al.* [1991], these measurements have shown surprisingly low SO_2 mole fractions given the amounts of DMS present. The measurements reported by *Ferek et al.* [1991] were made from an aircraft in the same region and during the same time period as the shipboard measurements reported by *Yvon et al.* [1991] and *Bandy et al.* [1992] as part of the Pacific Stratus/Sulfur Investigation (PSI 3). The above mentioned studies focused on the spatial rather than temporal distributions of these species. Of the various methods employed in the studies mentioned above, only the methods used by *Yvon et al.* [1991] and *Bandy et al.* [1992] utilize sampling times that are short enough to allow the results to be examined for diel cycles and short timescale trends.

Simultaneous measurements of atmospheric DMS and SO_2 were made during a recent cruise aboard the R/V *John V. Vickers* in the equatorial Pacific Ocean. This field campaign was part of the International Global Atmospheric Chemistry/Marine Aerosols and Gases Experiment (IGAC/MAGE). A station at 12°S, 135°W was occupied for 6 days (Julian days 64.0-70.5, GMT) in March 1992 in order to study the diel cycles of these and other trace atmospheric and surface seawater species. The results of these atmospheric DMS and SO_2 measurements are investigated by using a gas phase photochemical box model [*Yvon and Saltzman*, 1993].

Experimental Methods

The sample inlets were mounted approximately 15 m above sea level on the forward facing side of a laboratory van which was bolted to the deck of the flying bridge. The van was located forward of the ship's stacks. The ship was positioned with its bow facing into the wind while we were at the station to prevent contamination of the air samples by stack gases. Samples were

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[1]Now at National Oceanic and Atmospheric Administration, Climate Monitoring and Diagnostics Laboratory, Boulder, Colorado.

taken only when the wind was coming from forward of the beam.

Atmospheric DMS was measured by using an automated gas chromatograph with flame photometric detection [*Cooper and Saltzman*, 1993; *Yvon et al.*, this issue]. SO_2 was measured with an automated technique involving high pressure liquid chromatography with fluorescence detection. The method and instrument are described, in detail, in *Saltzman et. al.* [1993]. A brief description of the analytical technique is given here.

A sample air stream is drawn at 1 standard liter per minute through a coarse (10 μm) Teflon particle filter and a Nafion membrane dryer. The resulting dry airstream is then drawn through a gas/liquid exchange coil. The gas phase SO_2 is absorbed into an aqueous absorber solution containing 10 μM formaldehyde and 0.84 mM Na_2EDTA. The resulting solution is then serially mixed with (1) ethanolamine in a pH 9 borate buffer, (2) orthopthalaldehyde (OPA), and (3) a 2.5-M sodium acetate solution buffered at pH 5.7. At pH 9, S_{IV} exists primarily as SO_3^-, which reacts with ethanolamine and OPA to form a fluorescent isoindole derivative. After the addition of the OPA, the reaction mixture flows through a 2-min mixing coil. The pH is then lowered through the addition of the strong sodium acetate solution. This decrease in pH slows further reaction with the OPA and reduces degradation of the column packing material. The aqueous solution containing the derivative flows continuously through a 600-μL injection loop. A sample integrated over 1.5 min is injected onto a reversed phase C-18 HPLC column once every 10 min. The chromatographically separated derivative is then detected by using a Hitachi F1000 fluorescence spectrophotometer with excitation wavelength at 330 nm and emission wavelength at 380 nm.

The instrument blank or zero point was obtained by drawing outside air through a carbonate-impregnated filter. Calibration was carried out by adding gas standards downstream of the carbonate filter. Gas phase standards were generated by passing dry nitrogen (100 standard cubic centimeters per minute) over a wafer-type permeation device held at 40°C. A variable fraction of the total gas flow over the device was pumped to waste via a mass flow controller and vacuum pump. The remainder of the gas flow was directed to the inlet of the instrument during calibration. This technique allows the delivery of low-level sulfur dioxide standards without passage of the analyte through a mass flow controller, where large losses have been found to occur. Using a 2-ng/min permeation tube, we were able to generate mole fractions as low as 10 pmol mol^{-1} in the airstream being sampled. The calibration system also provides the capability to spike ambient air samples to carry out standard addition tests. The lower limit of detection for this instrument is approximately 7 pmol mol^{-1} under normal operating conditions. Because of excessive fluorometer noise during this cruise, the detection limit during the course of this experiment was approximately 20 pmol mol^{-1}, and the accuracy was ±(10-15)%.

The results of a recent airborne intercomparison of the different techniques for measuring SO_2 during the NASA/GTE/CITE 3 project indicated that the methods most commonly used for measuring the low levels SO_2 found in the remote marine boundary layer are not reliable [*Gregory et al.*, 1993]. The SO_2 instrument used in this study was not part of this intercomparison. During CITE 3, very little agreement between the various instruments involved could be seen in their results. However, results from this instrument agreed well with results from measurements made by using an isotope dilution gas chromatography/mass spectrometry (GC/MS) technique during the PSI 3 project [*Yvon et al.*, 1991; *Bandy et al.*, 1992].

Results and Discussion

The measurements made at the MAGE station are shown as a time series in Figure 1a. The mean DMS mole fraction was 453 pmol mol^{-1} (±93 pmol mol^{-1}, 1σ) with a pronounced diel cycle of 85 pmol mol^{-1}. There is a slightly decreasing trend in the DMS mole fractions approaching Julian day 66 and an increasing trend toward the end of Julian day 67. This data and simultaneous seawater DMS measurements are discussed in detail by *Yvon et al.* [this issue].

The mean SO_2 mole fraction at the site was 71 pmol mol^{-1} (±56 pmol mol^{-1}, 1σ). The lack of SO_2 data near the beginning and end of the time series is due to instrument problems. Substantial short-term variability can be seen in the data. SO_2 appears anticorrelated with DMS during the first day at the station (JD 64); however, this trend does not continue throughout the time series. In fact, SO_2 and DMS are positively correlated on Julian day 67. In order to further examine diel variations in sulfur dioxide the measurements were sorted according to the time of day of each sample and averaged over 3-hour intervals (Figure 1b). Averaged in this way, the sulfur dioxide data do not exhibit a significant diel cycle.

Previous measurements of SO_2 in this region have shown mean mole fractions of 54 pmol mol^{-1} using a GC/FPD technique
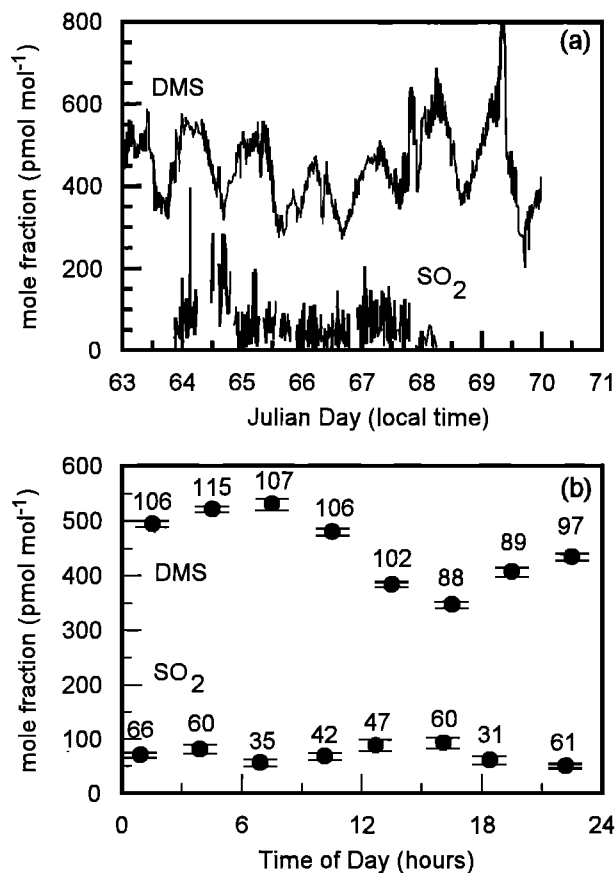

Figure 1. Results of measurements of atmospheric DMS and SO_2 mole fractions at the MAGE station (a) plotted as a time-series (LT = GMT - 9 hours) and (b) as data averaged over time of day. In Figure 1b the local time has been adjusted for the fact that solar noon occurred at 1230 hours local time, and the error bars indicate 1 standard error in the mean ($\sigma/(n^{1/2})$), where n is given above each averaged point.

[*Maroulis et al,* 1980] and approximately 50 pmol mol⁻¹ [*Yegorov,* 1990] using a modified West-Gaeke method with a detection limit of 4 pmol mol⁻¹ and an accuracy of ±10% [*Huebert et al.,* 1993]. These values are ~27% lower than the mean observed during this study.

The mole fractions of SO_2 are quite low relative to the high DMS mole fractions observed. If we assume that (1) DMS is the only source of SO_2, (2) gas phase OH chemistry controls both the production and destruction of DMS and sulfur dioxide, (3) SO_2 is the principle product of DMS oxidation, and (4) SO_2 and DMS are in steady state, then one would expect an DMS/SO_2 ratio of about 0.15, based on the ratios of their respective OH rate constants. The ratio observed in this study is approximately 6   High DMS/SO_2 ratios have been seen in results from measurements in the remote marine boundary layer before [*Berresheim* 1987; *Andreae et al.,* 1988, *Huebert et al.,* 1993] The measurements discussed by *Huebert et al.* [1993] were made in this region in 1990. The ratio of DMS/SO_2 for that cruise was 18 with mole fractions of SO_2 as discussed above. *Berresheim* [1987] measured DMS and SO_2 in the sub-Antarctic and Antarctic Oceans. His results suggest a DMS/SO_2 ratio of 9. *Andreae et al.* [1988] measured DMS and SO_2 from an aircraft over the Northeast Pacific Ocean. Their results suggest a DMS/SO_2 ratio of 6. It has been suggested that these high ratios may be due to a low yield of SO_2 from the oxidation of DMS [*Bandy et al.,* 1992]. *Chameides and Stelson* [1992] have suggested that there is a large sink in the marine boundary layer that has been overlooked.

Clearly, the assumptions cited above are not sufficient to explain the SO_2 budget in this region. The difference must lie either in assumptions about the yield of SO_2 from DMS oxidation (as suggested by *Bandy et al.* [1992]) or in the importance of heterogeneous sinks for sulfur dioxide [*Sievering et al.,* 1991, 1992; *Chameides and Stelson,* 1992]   Several workers have recently suggested that uptake of sulfur dioxide by sea-salt aerosols may provide a large sink in the marine boundary layer which has previously been overlooked [*Sievering et al.,* 1991, 1992; Chameides and Stelson, 1992]. In order to assess the relative importance of various sulfur dioxide sources and sinks we have modified a photochemical model of marine boundary layer chemistry to include the processes thought to control the atmospheric sulfur dioxide budget in this region.

Model Description

A schematic diagram of the SO_2 budget in the remote marine boundary layer is shown in Figure 2. In this budget, SO_2 is produced via the OH-initiated oxidation of DMS and from the vertical entrainment of SO_2 from the free troposphere into the boundary layer   The sinks include gas phase oxidation of SO_2 via OH, uptake and oxidation in cloud droplets and in sea-salt aerosols, and dry deposition to the sea surface. In this paper we use a photochemical box model of the marine boundary layer to simulate these processes and to assess their relative magnitudes under the conditions of the MAGE cruise. The model used is described in detail by *Yvon and Saltzman* [1993]. A description of the gas phase chemistry and the conditions used to describe the MAGE cruise were given by *Yvon et al.* [this issue] and are summarized in Table 1. A model run using test conditions gives a midday maximum OH concentration of 3.0×10^6 cm⁻³ and a 24-hour mean concentration of 7×10^5 cm⁻³.

One method for estimating the photochemical production rate of SO_2 is to take the average observed DMS diel profile and
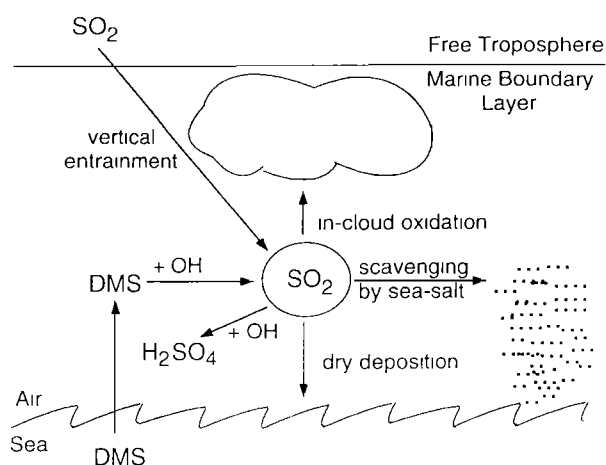

Figure 2.   Diagram of the processes controlling the concentration of SO_2 in the remote marine boundary layer.

calculate the DMS oxidation rate based on model OH concentrations and laboratory rate constants. For the data from this study this calculation gives a diurnally averaged DMS oxidation rate of 4.4×10^4 molecules cm⁻³ s⁻¹. However, *Yvon et al.* [this issue] used the model to attempt to examine the consistency between the sea-to-air flux of DMS (based on measured water column concentrations and wind fields) and the calculated OH levels. They demonstrated that by using currently accepted cross sections, quantum yields, and rate constants it is not possible to reproduce the observed mean DMS levels and the amplitude of diel variation   They concluded that the oxidation of DMS must occur at roughly twice the predicted rate, approximately 8.0×10^4 molecules cm⁻³ s⁻¹. The difference between these two estimates introduces an uncertainty of a factor of 2 into the SO_2 budget.

The SO_2 production rate is also sensitive to assumptions about the yield of SO_2 from DMS oxidation. Estimates of the yield based on laboratory studies vary widely, from <50% to more than 90%, with the more recent, low-NO_x measurements supporting the highest yields [*Thornton et al.,* 1995]. Most modeling studies have also assumed high yields of SO_2, based on the high ratios of non-sea-salt sulfate to methanesulfonate in marine aerosols [*Saltzman et al.,* 1986]. This line of reasoning assumes that other reservoirs of methylated sulfur, such as dimethylsulfoxide or dimethylsulfone, are minor. *Bandy et al.* [1992] argued that the yield of SO_2 from DMS is extremely low, based on field observations in the northeast Pacific. In this study we attempt to constrain the yield of SO_2 from our field data, based on independent estimates of DMS oxidation and SO_2 losses.

The vertical entrainment of SO_2 from the free troposphere is estimated by examining the budget of O_3. Given a free tropospheric O_3 mole fraction of 30 nmol mol⁻¹ [*Routhier et al.,* 1980] and an observed boundary layer mean mole fraction of 9.3 nmol mol⁻¹ (J. Johnson, personal communication, 1992), the vertical entrainment rate was calculated at approximately 0.168 cm s⁻¹ for a boundary layer height of 1.30 km [*Yvon et al.,* this issue]. The mole fraction of SO_2 in the free troposphere is assumed to be 90 pmol mol⁻¹ based on measurements from this region as discussed by *Maroulis et al.* [1980]. The source flux of SO_2 from the free troposphere into the marine boundary layer is calculated by using the 0.168 cm s⁻¹ entrainment rate determined from the O_3 difference.

Table 1. Input Conditions for the Photochemical Model Calculations.

Parameter	Value	Source
O_3, nmol mol^{-1}	9.3	J. Johnson (personal. Communication, 1992)
CO, nmol mol^{-1}	60.0	J. Johnson (personal. Communication, 1992)
CH_4, μmol mol^{-1}	1.97	*Bates et al.* [1993]
H_2O_2, pmol mol^{-1}	580	*Thompson et al.* [1993]
NO_x, pmol mol^{-1}	3	D. Jaffe (personal. Communication, 1992)
C_2H_4, pmol mol^{-1}	200	*Donahue and Prinn* [1993] and *Atlas et al.*[1993]
C_2H_6, pmol mol^{-1}	800	*Donahue and Prinn* [1993] and *Atlas et al.*[1993]
Temperature, K	301.5	J. Johnson (personal. Communication, 1992)
Total ozone column density, mmol m^{-2}	118	P. Newman (personal. Communication, 1992)
Relative humidity, %	72	J. Johnson (personal. Communication, 1992)
DMS flux, μmol m^{-2} d^{-1}	16	*Yvon et al.* [this issue]
Boundary layer height, km	1.30	*Yvon et al.* [this issue]
Wind speed, m s^{-1}	7.1	*Yvon et al.* [this issue]
Vertical entrainment velocity, cm s^{-1}	0.168	*Yvon et al.* [this issue]
O_3 deposition velocity, cm s^{-1}	0.053	*Lenschow et al.* [1982]
SO_2 deposition velocity, cm s^{-1}	0.87	calculated
In-cloud oxidation, s^{-1}	1.1 x 10^{-6}	*Hegg* [1985]
SO_2 percent yield from DMS, %	94	*Saltzman et al.* [1986]

The sinks for SO_2 include (1) homogeneous oxidation by OH radicals, (2) dry deposition, (3) in-cloud oxidation, and (4) uptake by sea-salt aerosols. Homogeneous oxidation rates are determined from the model calculated OH concentrations as discussed by *Yvon and Saltzman* [1993]. An SO_2 dry deposition velocity of 0.87 cm s^{-1} is assumed. This value was obtained using the equation for deposition velocity (v_d) as given by *Liss* [1983] ($v_d = C_{SO2}U$) where C_{SO2} is the unitless drag coefficient which has a value of 1.22 x 10^{-3}, as determined from *Hicks and Liss* [1976] and *Garratt* [1992] for a wind speed of 7 m s^{-1}, and U is the mean wind speed for MAGE station.

The rate of in-cloud oxidation of SO_2 was estimated by using the climatological approach of *Hegg* [1985]. During the MAGE cruise a camera with a wide-angle lens (180°) was used to photograph the sky during daylight hours throughout the cruise. However, the chemistry of the air mass observed at the station represents the result of conditions over several days prior to arrival. *Hegg* [1985] estimated an in-cloud oxidation rate coefficient for SO_2 of 1.275 x 10^{-6} s^{-1}, for the 0° - 15°N latitude band. He recommended an adjustment for the lower water content of the Southern Hemisphere resulting in a rate coefficient of 1.1 x 10^{-6} s^{-1}. This loss rate is considered an upper limit for the MAGE study.

The loss of SO_2 to sea-salt aerosols was parameterized in the model as a constant first-order loss. This loss rate was estimated by using an approach similar to that of *Chameides and Stelson* [1992], who used a coupled droplet/gas phase chemistry model to study the scavenging of SO_2 by sea-salt aerosols in the marine boundary layer. Their time-dependent calculations demonstrated that in a fresh sea-salt aerosol droplet, S_{IV} is rapidly oxidized by

O_3, resulting in a high initial scavenging rate. This fast rate continues until sufficient sulfuric acid is generated to lower the pH below approximately 6. This effect requires sufficient uptake to break the carbonate buffer in seawater, approximately 1/2 mole of SO_2 per equivalent of alkalinity (HCO_3^- + $2CO_3^=$). As the pH decreases, the rate of oxidation by O_3 decreases, and the oxidation of S_{IV} by free radicals (OH and HO_2) and H_2O_2 become more important. At pH 4 and below, H_2O_2 controls the rate of uptake of SO_2. *Chameides and Stelson* [1992] demonstrated that most of the uptake of SO_2 occurs by reaction with O_3 at high pH, with only about 30% occurring by other oxidants. Because the O_3 reaction is so rapid, they suggested that the uptake of SO_2 could be reasonably approximated as one half the flux of alkalinity associated with sea-salt aerosols plus 30% for the lower pH reactions.

This approach was applied to the MAGE case as follows. The production rate of sea-salt aerosols is calculated according to *Monahan et. al.* [1986] as shown here:

$$P(r) = 3.585 \times 10^5 \, W \, r(80)^{-3} \left(1 + 0.033 r(80)^{1.179}\right) \times 10^{1.19 \exp(-B^2)} \quad (1)$$

where

$$W = 3.84 \times 10^{-6} U^{3.41} \quad B = \frac{0.38 - \log(r(80))}{0.65}$$

$$r(80) = \frac{r(RH)(1 - RH/100)^{0.26}}{(1 - 0.80)^{0.26}}$$

U is the wind speed (m s^{-1}) at 10 m above the sea surface, $r(80)$ is the radius (μm) at a standard relative humidity of 80% as determined by using the equilibrium radius equation given by *Kasten* [1969], RH is the ambient relative humidity (percent), and P(r) has units of m^{-2} s^{-1} μm^{-1}. For the model calculations discussed in this paper we use the mean $U^{3.41}$ (U_x) for the MAGE station to determine the production rate of aerosols. The value of $^{3.41}\sqrt{U_x}$ is 7.3 m s^{-1} for the MAGE station. The scavenging rate of SO_2 by these aerosols is then calculated as shown below:

$$\text{scavenging rate} = \frac{1}{2}(\rho_{dry})(\text{rat}_{alk})(N_A) \sum_r \left(\frac{P(r)}{BLH}\right)(\text{Vol}_{dry})\Delta r \quad (2)$$

where ρ_{dry} is the density of the dry particle [*Hänel*, 1976], rat$_{alk}$ is the ratio (eq g^{-1}) of equivalents of alkalinity to mass of sea-salt [*Millero and Sohn*, 1992], N_A is Avogadro's number, r is the radius of the aerosols at ambient relative humidity, P(r) is the production rate of aerosols from equation (1), BLH is the boundary layer height (in meters), Vol$_{dry}$ is the volume (in cubic centimeters) of the dry particle, and Δr is the width of the radius interval, 0.05 μm.

The results from cascade impactor samples taken at the station (1 sample spanned 24 hours) and analyzed using ion chromatography indicated that the sodium mass was found only on aerosols larger than 0.15 μm in radius (P. Quinn, personal communication, 1992). Therefore, only aerosol particles larger than 0.15 μm are used in the model calculations. Aerosols larger than 10.0 μm have a short residence time which may not be long enough to allow for the uptake of enough SO_2 to break the alkalinity buffer, and extending the distribution to include larger particles does not significantly increase the calculated scavenging rate of SO_2. Therefore we adopt the sea-salt aerosol

size range 0.15-10.0 μm in radius and obtain a scavenging rate of SO_2 of 4278 cm^{-3} s^{-1} from equation (2) for the MAGE station. Increasing this rate by 30% to account for free radical and H_2O_2 reactions yields a total rate of 5566 molecules cm^{-3} s^{-1}.

Model Results

In this section we discuss four simulations carried out with the time-dependent photochemical model. The results from all of the runs are shown in Figure 3, in which, the predicted SO_2 diel profiles are shown with their respective case numbers. There is only one DMS diel profile, and it remained the same for all runs. The measured DMS and SO_2 diel profiles are shown with their error bars for comparison to the results from the model.

Case 1. The first model simulation includes SO_2 losses by gas phase reaction, in-cloud reactions, and deposition to the sea surface. Heterogeneous losses to sea-salt aerosols are not included. The model predicts a mean SO_2 mole fraction of 307 pmol mol^{-1} (Figure 3, case 1). The results also show a diel cycle in SO_2 that is anticorrelated to that of DMS. Both the mean mole fraction and the amplitude of the diel cycle predicted by the model are considerably larger than the field results. In this case the largest source of SO_2 is from the oxidation of DMS (>99%) with entrainment of free tropospheric air providing <1% of the SO_2 in the boundary layer. Dry deposition is by far the largest sink (80%), while in-cloud oxidation and reaction with OH contribute only 13% and 7%, respectively, toward the loss of SO_2.

Case 2. Sievering et al. [1991 and 1992] and Chameides and Stelson [1992] suggested that heterogeneous loss to sea-salt aerosols is a large sink for SO_2, which may help to explain the low mole fractions of SO_2 that have been observed in the marine boundary layer. Case 2 uses the conditions given in Table 1 with a scavenging rate of 5566 molecules cm^{-3} s^{-1} for SO_2 as calculated from the alkalinity flux in the previous section The loss of SO_2 to sea-salt aerosols is a minor sink for gas phase SO_2, reducing the predicted SO_2 mole fractions by approximately 8% compared to case 1. The results of this model run show a mean SO_2 mole fraction of 283 pmol mol^{-1} with an afternoon maximum of 352 pmol mol^{-1} and a predawn minimum of 214
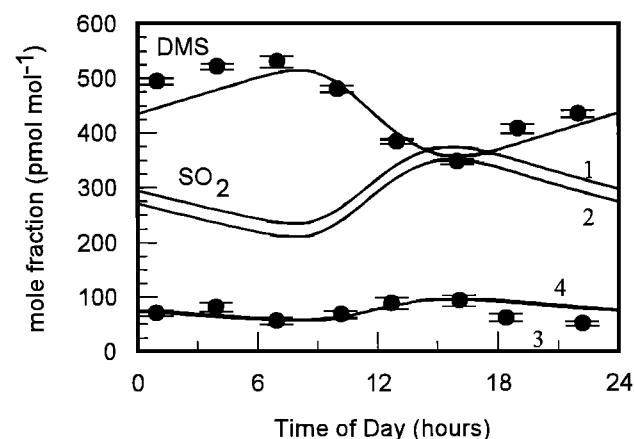

Figure 3. Results from model calculations for cases 1, 2, 3, and 4. The upper curve is the model-predicted DMS diel profile, and the bottom 4 curves are the SO_2 diel profiles for the different cases. The solid circles represent the average field data shown in Figure 1b.

pmol mol^{-1} (Figure 3, case 2). Although Chameides and Stelson [1992] concluded that the scavenging of SO_2 by sea-salt aerosols is globally important as a sink for SO_2 in the marine boundary layer, it does not appear to be fast enough at this site to account for the low mole fractions observed during this study.

Case 3. Another explanation for the presence of such low mole fractions of SO_2 in the marine boundary layer was proposed by Bandy et al. [1992]. They observed low mole fractions of SO_2 relative to the DMS mole fractions and variability in DMS which was not reflected in SO_2 off the coast of Washington. They suggest that the reaction of DMS with the OH radical does not produce SO_2 in significant quantities under low-NO_x conditions. In this scenario the SO_2 found in the marine boundary layer would originate solely from vertical mixing. For case 3, we set the yield of SO_2 from DMS equal to zero. The predicted mean SO_2 mole fraction is <1 pmol mol^{-1} (Figure 3, case 3). This is well below the observed mean of 71 pmol mol^{-1} for the MAGE station. Therefore it appears unlikely that entrainment is the only source of SO_2 to the marine boundary layer. Also, the recent results of Thornton et al. [1995] do not support the hypothesis presented by Bandy et al. [1992]. Thornton et al. [1995] observed anticorrelated SO_2 and DMS diel cycles in the remote marine boundary layer and suggests that SO_2 was produced from DMS with an efficiency of 75%.

Case 4. In Case 4 we adjusted the yield of SO_2 from the oxidation of DMS so that the model would produce SO_2 mole fractions with a mean similar to the observed mean mole fraction of 71 pmol mol^{-1} (Figure 3, case 4). This process requires a 27% yield of SO_2 from the total oxidation of DMS. This is substantially lower than the 75% suggested by Thornton et al. [1995]. However, the oxidation of DMS in the model described here is twice that due to oxidation by OH alone in order to model the observed DMS diel cycle [Yvon et al., this issue]. If this rate were adjusted to that produced from the oxidation of DMS by just OH while maintaining the observed DMS mole fractions, the resulting yield of SO_2 from this oxidation would have to be doubled (~54%) to maintain the observed SO_2 mole fractions. This higher SO_2 production efficiency is much closer to that suggested by Thornton et al. [1995].

Assuming a 27% yield and the DMS oxidation rate suggested by Yvon et al. [this issue], a diel cycle in SO_2 is predicted by the model which is not observed in the data with an early morning minimum of 54 pmol mol^{-1} and an afternoon maximum 94 pmol mol^{-1}. The difference between the model-predicted diel SO_2 profile and the observed SO_2 profile may be due to a diel variation in vertical entrainment that is not included in the model. Given the observed SO_2 mole fractions, this diel variation should exhibit a maximum at night and a minimum during the day. The SO_2 mole fractions measured at the station show a slight increase before dawn. The only source of SO_2 at this time of day is vertical entrainment. There is no meteorological evidence from the radiosondes taken during this cruise for a strong diel cycle in vertical entrainment [Yvon et al., this issue].

Given the conditions of case 4, the SO_2 budget would be as shown in Table 2. The OH-initiated oxidation of DMS is the largest source of SO_2 with 98% of the total production of SO_2 coming from this source even with a yield of SO_2 of just 27%. The loss of SO_2 appears to be controlled by dry deposition (58%) and scavenging by sea-salt aerosols (28%). In-cloud oxidation and homogeneous oxidation appear to be minor sinks.

The SO_2 budget shown in Table 2 is fairly insensitive to the known uncertainties involved with our model calculations. For example, the calculations of the rate of oxidation of SO_2 by OH

Table 2. Magnitudes of Various Sources and Sinks for SO_2 for the MAGE Station and Their Percent Contributions.

Sources	Production (molecules cm^{-3} s^{-1})	relative contribution (%)
DMS oxidation (27% yield)	2.17×10^4	98
Vertical entrainment	4.84×10^2	2

Sinks	Destruction (molecules cm^{-3} s^{-1})	relative contribution (%)
OH oxidation	1.02×10^3	5
Dry deposition	1.11×10^4	58
In-cloud oxidation	1.90×10^3	9
Sea-salt aerosols	5.57×10^3	28

radicals has the following sources of error (1) the calculated OH concentrations and (2) the experimental error associated with the determination of the rate constants. *Thompson and Stewart* [1991] have estimated that the error in predicting OH concentrations with a model similar to the one used here is ~25% (1σ). The rate constant for the OH + SO_2 reaction has an uncertainty of ~50%. A 50% increase in the rate of homogeneous oxidation of SO_2 would result in a predicted yield of SO_2 of 28% from the daytime oxidation of DMS, and the contribution of homogeneous oxidation to the total loss of SO_2 would become 7%. Because vertical entrainment is such a small (2%) source of SO_2, even large uncertainties in this parameter would have little or no effect on the budget.

The uncertainty in the dry deposition of SO_2 to the sea surface is a function of the uncertainty in the drag coefficient used. This drag coefficient has an error of <20% [*Garratt*, 1977; *Garratt*, 1992]. A 20% decrease in the deposition velocity would result in the following: (1) a 24% yield of SO_2 from daytime DMS oxidation, (2) dry deposition equal to 52% of the total loss of SO_2, and (3) scavenging by sea salt constituting 31% of the total loss of SO_2. The value for in-cloud oxidation is given here as an upper limit owing to the low numbers of clouds present. Changes in this parameter by even a factor of 2 would result in the following: (1) there would be a 29% yield of SO_2 from DMS oxidation, (2) in-cloud oxidation would become 17% of the total loss of SO_2, and (3) dry deposition and scavenging by sea-salt aerosols would become 53% and 25% of the total loss of SO_2. The largest source of uncertainty in the determination of the loss of SO_2 to sea-salt aerosols is the error associated with the determination of the flux of alkalinity [*Monahan*, 1986]. *Monahan* [1986] does not give any estimates of error associated with his sea-salt aerosol production model. However, he does compare globally averaged sea-salt fluxes calculated by his model with flux estimates from other sources [*Eriksson*, 1959; *Blanchard*, 1963; *Blanchard*, 1985]. If the alkalinity flux used in the model were doubled, the predicted yield of SO_2 from the oxidation of DMS would become 34%, the relative contribution of dry deposition would decrease to 45% of the total loss, and there would be a corresponding increase to 43% in the contribution of scavenging by sea-salt aerosols. If the alkalinity flux were halved, the yield of SO_2 from the oxidation of DMS would become 24%, the relative contribution of dry deposition would increase to 67% of the total loss, and there would be a decrease to 16% in the contribution of scavenging by sea-salt aerosols. The uncertainties mentioned above do not affect the

major conclusions of this modeling study. Dry deposition and sea-salt scavenging remain the dominant sinks for SO_2, and a substantial fraction of the DMS being oxidized does not appear to produce SO_2.

Non-sea-salt sulfate concentrations. If we accept the budget shown in Table 2, we can calculate the expected steady state aerosol nss sulfate concentrations (Table 3). The nss sulfate concentration is determined by using the following equation:

$$[\text{nss sulfate}] = (R_{ox})(\tau_{aero}) \left(\frac{1}{N_A} \right) (M) \left(10^6 \frac{mg}{g} \right) \left(10^6 \frac{cm^3}{m^3} \right) \quad (3)$$

where R_{ox} is the rate (molecules cm^{-3} s^{-1}) of oxidation of SO_2, τ_{aero} is the residence time (seconds) of the aerosol, N_A is Avogadro's number, M is the molecular weight (96 g mol^{-1}) of sulfate, and the last two numbers are for converting the units to μg m^{-3}. The sulfuric acid produced from homogeneous and in-cloud oxidation of SO_2 is likely to be incorporated into submicron aerosols which have a long lifetime. Assuming the homogeneous production rate of H_2SO_4 shown in Table 2 and a 5.0 to 10.0-day residence time for submicron aerosols [*Warneck*, 1988], approximately 0.06-0.14 μg m^{-3} of nss sulfate should be produced. In-cloud oxidation of SO_2 should produce 0.13-0.26 μg m^{-3} of nss sulfate. The supermicron sea-salt aerosol particles are assumed to have a shorter residence time (~2.5-5.0 days) [*Warneck*, 1988]. The amount of nss sulfate associated with the loss of SO_2 to these aerosols should be approximately 0.27-0.59 μg m^{-3}. The total nss sulfate produced from these pathways is 0.46-0.99 μg m^{-3}, approximately half the mean measured total nss sulfate concentration of 1.36 ± 0.35 μg m^{-3} (P. Quinn, personal communication, 1992) from the station. However, the measured nss sulfate from the station is approximately twice the mean nss sulfate concentration measured in this region by *Huebert et al.*, [1993] and at Fanning Island by *Prospero et al.* [1985].

If we assume that the products from the remaining 73% of the DMS oxidized eventually produce nss sulfate and use the 5.0 to 10.0-day residence time assigned to the submicron particles, the nss sulfate from this source should equal 4.04-11.07 μg m^{-3}. Given the measured nss sulfate concentration from the station, it would appear that 7-16% of the DMS oxidized produces nss sulfate without SO_2 acting as an intermediate. This suggests that most of the remaining 47-57% of DMS oxidized does not produce nss sulfate. One of the oxidation products is MSA, but this is a minor product in tropical air masses [*Saltzman et al.*, 1986]. The other products formed are not known, but it has been suggested that the OH-initiated oxidation of DMS may produce DMSO and $DMSO_2$ with significant yields [*Yin et al.*, 1990a and 1990b].

Table 3. Production of Aerosol Non-Sea-Salt Sulfate

Pathway	nss Sulfate Produced (μg m^{-3})
Homogeneous oxidation of SO_2	0.06-0.14
In-cloud oxidation of SO_2	0.13-0.26
Sea-salt scavenging of SO_2	0.27-0.59
Total	0.46-0.99
Measured	1.36 ± 0.35

Conclusions

The results of this study indicate that SO_2 levels at the field site (12°S, 135°W) in March 1992 were lower than those predicted on the basis of gas phase chemistry alone, if it is assumed that DMS oxidation yields primarily SO_2. Including heterogeneous sinks such as in-cloud oxidation, dry deposition to the sea surface, and losses to sea-salt aerosols significantly decreases the predicted SO_2 mole fractions, but these sinks are insufficient to achieve the observed levels of SO_2. These results suggest that the yield of SO_2 from DMS oxidation may be of the order of 27-54%. Under these conditions, DMS is still the dominant source of SO_2 in the marine boundary layer.

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E. S. Saltzman, Rosenstiel School of Marine and Atmospheric Sciences, University of Miami, 4600 Rickenbacker Causeway, Miami, FL 33149. (email: saltzman@rsmas.miami.edu)

S. A. Yvon, National Oceanic and Atmospheric Administration, Climate Monitoring and Diagnostics Laboratory, R/E/CG1, 325 Broadway, Boulder, CO 80303. (email: syvon@cmdl.noaa.gov)