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
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

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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 SO2 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 SO2 from DMS oxidation range from 27% to 54%. Even with low yields, DMS is the dominant source of SO2 in this region. Estimates of vertical entrainment velocities based on the tropospheric ozone budget suggest that vertical entrainment is a minor source of SO2. The relative rates of various loss mechanisms for SO2 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 (DMSO2) [Vin 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 (SO2) is an intermediate in the production of sulfuric acid from DMS oxidation in the marine boundary layer. It is this SO2 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 SO2 in the remote marine boundary layer. Hydrogen sulfide (H2S), another biogenic reduced sulfur gas, also oxidizes to form SO2. However, H2S is present only at very low concentrations over the remote open ocean and is not considered to be a significant source of SO2 [Saltzman and Cooper, 1988, Yvon et al., 1993].

Recently, simultaneous measurements of atmospheric DMS and SO2 have been made at the ship's stack exit [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 SO2 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 SO2 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 SO2 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
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]. SO2 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 Naflon membrane dryer. The resulting dry airstream is then drawn through a gas/liquid exchange coil. The gas phase SO2 is absorbed into an aqueous absorber solution containing 10 µM formaldehyde and 0.84 mM Na2EDTA. The resulting solution is then serially mixed with (1) ethanolamine in a pH 9 borate buffer, (2) orthophthalaldehyde (OPA), and (3) a 2.5-M sodium acetate solution buffered at pH 5.7. At pH 9, SO3 exists primarily as SO42-, 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 SO2 during the NASA/GTE/CITE 3 project indicated that the methods most commonly used for measuring the low levels SO2 found in the remote marine boundary layer are not reliable [Gregory et al., 1993]. The SO2 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 SO2 mole fraction at the site was 71 pmol mol−1 (±56 pmol mol−1, 1σ). The lack of SO2 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. SO2 appears antecorrelated with DMS during the first day at the station (JD 64); however, this trend does not continue throughout the time series. In fact, SO2 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 SO2 in this region have shown mean mole fractions of 54 pmol mol−1 using a GC/FPD technique.
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 concentration 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 [Stevering 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 [Stevering 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 x 10$^6$ cm$^{-3}$ and a 24-hour mean concentration of 7 x 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 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 x 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 x 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 dimethylsulfate or dimethylsulfoxide, 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$^{-1}$ [Rouhrer 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.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₃, nmol mol⁻¹</td>
<td>9.3</td>
<td>J. Johnson (personal. Communication, 1992)</td>
</tr>
<tr>
<td>CO₂, nmol mol⁻¹</td>
<td>60.0</td>
<td>J. Johnson (personal. Communication, 1992)</td>
</tr>
<tr>
<td>CH₄, nmol mol⁻¹</td>
<td>1.97</td>
<td>Bates et al. [1993]</td>
</tr>
<tr>
<td>H₂O₂, pmol mol⁻¹</td>
<td>580</td>
<td>Thompson et al. [1993]</td>
</tr>
<tr>
<td>NOₓ, pmol mol⁻¹</td>
<td>3</td>
<td>D. Jaffé (personal. Communication, 1992)</td>
</tr>
<tr>
<td>SO₂, pmol mol⁻¹</td>
<td>200</td>
<td>Donahue and Pinn [1993]</td>
</tr>
<tr>
<td>C₂H₆, pmol mol⁻¹</td>
<td>800</td>
<td>Donahue and Pinn [1993]</td>
</tr>
<tr>
<td>Temperature, K</td>
<td>301.5</td>
<td>J. Johnson (personal. Communication, 1992)</td>
</tr>
<tr>
<td>Total ozone column density, mmol m⁻²</td>
<td>118</td>
<td>P. Newman (personal. Communication, 1992)</td>
</tr>
<tr>
<td>Relative humidity, %</td>
<td>72</td>
<td>J. Johnson (personal. Communication, 1992)</td>
</tr>
<tr>
<td>DMS flux, μmol m⁻² s⁻¹</td>
<td>16</td>
<td>Yvon et al. [this issue]</td>
</tr>
<tr>
<td>Boundary layer height, km</td>
<td>1.30</td>
<td>Yvon et al. [this issue]</td>
</tr>
<tr>
<td>Wind speed, m s⁻¹</td>
<td>7.1</td>
<td>Yvon et al. [this issue]</td>
</tr>
<tr>
<td>Vertical entrainment velocity, cm s⁻¹</td>
<td>0.168</td>
<td>calculated</td>
</tr>
<tr>
<td>O₃ deposition velocity, cm s⁻¹</td>
<td>0.053</td>
<td>Lanceshow et al. [1982]</td>
</tr>
<tr>
<td>SO₂ deposition velocity, cm s⁻¹</td>
<td>0.87</td>
<td>calculated</td>
</tr>
<tr>
<td>In-cloud oxidation, s⁻¹</td>
<td>1.1 x 10⁻⁶</td>
<td>Hegg [1985]</td>
</tr>
<tr>
<td>SO₃ percent yield from DMS, %</td>
<td>94</td>
<td>Saltzman et al. [1986]</td>
</tr>
</tbody>
</table>

The sinks for SO₂ 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 SO₂ dry deposition velocity of 0.87 cm s⁻¹ is assumed. This value was obtained by using the equation for deposition velocity (vₐ) as given by Liss [1983] (vₐ = C₀₂U) where C₀₂ is the unitless drag coefficient which has a value of 1.22 x 10⁻⁴ if a, as determined from Hicks and Saltzman [1983] 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 SO₂ 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 SO₂ 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 SO₂ 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 SO₂ by sea-salt aerosols in the marine boundary layer. Their time-dependent calculations demonstrated that in a fresh sea-salt aerosol droplet, Sᵥ is rapidly oxidized by O₃, 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 SO₂ per equivalent of alkalinity (HCO₃⁻ + CO₃²⁻). As the pH decreases, the rate of oxidation by O₃ decreases, and the oxidation of Sᵥ by free radicals (OH and HO₂) and H₂O₂ become more important. At pH 4 and below, H₂O₂ controls the rate of uptake of SO₂. Chameides and Stelson [1992] demonstrated that most of the uptake of SO₂ occurs by reaction with O₃ at high pH, with only about 30% occurring by other oxidants. Because the O₃ reaction is so rapid, they suggested that the uptake of SO₂ 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:

\[ P(r) = 3.585 \times 10^{-5} W \cdot r(80)^{-3} \cdot 10^{-11} \exp^{-\frac{1}{2} r(80)} \]

where

\[ W = 3.84 \times 10^{-6} U^{3.41} \]
\[ B = \frac{0.38 - \log(r(80))}{0.65} \]
\[ r(80) = r_{RH}(1 - RH/100)^{0.26} \]
\[ (1 - 0.80)^{0.26} \]

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 m² s⁻¹ μm⁻¹. For the model calculations discussed in this paper we use the mean \( t^{3.41} \) (\( U_t \)) for the MAGE station to determine the production rate of aerosols. The value of \( 3.84\times U_t \) is 7.3 m s⁻¹ for the MAGE station. The scavenging rate of SO₂ by these aerosols is then calculated as shown below:

scavenging rate = \( \frac{1}{2} \left( \rho_{dry} r_{alk} N_a \sum \frac{P(r)}{BLH} \right) \Delta r \)  

where \( \rho_{dry} \) is the density of the dry particle [Hanel, 1976], \( r_{alk} \) 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 \( \Delta r \) 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 SO₂ to break the alkalinity buffer, and extending the distribution to include larger particles does not significantly increase the calculated scavenging rate of SO₂. 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\(_2\)O\(_2\) 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 15% 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 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 case 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. 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
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 \(-25\%\) (\(\sigma\)). The rate constant for the OH + SO2 reaction has an uncertainty of \(-50\%\). A 50\% increase in the rate of oxidation would result in a predicted yield of SO2 of 28\% from the daytime oxidation of DMS, and the contribution of homogeneous oxidation to the total loss of SO2 would become 7\%. Because vertical entrainment is such a small process, changes in this parameter by even a factor of 2 would result in only a 24\% yield of SO2 from daytime DMS oxidation, (2) dry deposition equal to 52\% of the total loss of SO2, and (3) dry deposition and 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 SO2, and a substantial fraction of the DMS being oxidized does not appear to produce SO2.

### Table 2. Magnitudes of Various Sources and Sinks for SO2 for the MAGE Station and Their Percent Contributions.

<table>
<thead>
<tr>
<th>Sources</th>
<th>Production (molecules cm(^{-3}) s(^{-1}))</th>
<th>relative contribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMS oxidation (27% yield)</td>
<td>2.17 \times 10^4</td>
<td>98</td>
</tr>
<tr>
<td>Vertical entrainment</td>
<td>4.84 \times 10^6</td>
<td>2</td>
</tr>
</tbody>
</table>

Sinks

<table>
<thead>
<tr>
<th>Destruction (molecules cm(^{-3}) s(^{-1}))</th>
<th>relative contribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH oxidation</td>
<td>1.02 \times 10^4</td>
</tr>
<tr>
<td>Dry deposition</td>
<td>1.11 \times 10^4</td>
</tr>
<tr>
<td>In-cloud oxidation</td>
<td>1.99 \times 10^4</td>
</tr>
<tr>
<td>Sea-salt aerosols</td>
<td>5.57 \times 10^6</td>
</tr>
</tbody>
</table>

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:

\[
[nss\ sulfate] = \left( \frac{R_{oa}}{N_a} \right) M \left( \frac{10^6 \text{ mg}}{g} \right) \left( \frac{10^6 \text{ cm}^3}{\text{m}^3} \right)
\]

where \(R_{oa}\) is the rate (molecules cm\(^{-3}\) s\(^{-1}\)) of oxidation of SO2, \(N_a\) 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 \(\mu g\) m\(^{-3}\). The sulfuric acid produced from homogeneous and in-cloud oxidation of SO2 is likely to be incorporated into submicron aerosols which have a long lifetime. Assuming the homogeneous production rate of H2SO4 shown in Table 2 and a 5.0 to 10.0-day residence time for submicron aerosols [Warneck, 1988], approximately 0.06-0.14 \(\mu g\) m\(^{-3}\) of nss sulfate should be produced. In-cloud oxidation of SO2 should produce 0.13-0.26 \(\mu g\) 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 SO2 to these aerosols should be approximately 0.27-0.59 \(\mu g\) m\(^{-3}\). The total nss sulfate produced from these pathways is 0.46-0.99 \(\mu g\) m\(^{-3}\), approximately half the mean measured total nss sulfate concentration of 1.36 ± 0.35 \(\mu g\) 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 \(\mu g\) 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 SO2 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

<table>
<thead>
<tr>
<th>Pathway</th>
<th>nss Sulfate Produced ((\mu g) m(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Homogeneous oxidation of SO2</td>
<td>0.06-0.14</td>
</tr>
<tr>
<td>In-cloud oxidation of SO2</td>
<td>0.13-0.26</td>
</tr>
<tr>
<td>Sea-salt scavenging of SO2</td>
<td>0.27-0.59</td>
</tr>
<tr>
<td>Total</td>
<td>0.46-0.99</td>
</tr>
<tr>
<td>Measured</td>
<td>1.36 ± 0.35</td>
</tr>
</tbody>
</table>
Conclusions

The results of this study indicate that SO₂ 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 SO₂. Including heterogeneous sinks such as in-cloud oxidation, dry deposition to the sea surface, and losses to sea-salt aerosols significantly decreases the predicted SO₂ mole fractions, but these sinks are insufficient to achieve the observed levels of SO₂. These results suggest that the yield of SO₂ from DMS oxidation may be of the order of 27-54%. Under these conditions, DMS is still the dominant source of SO₂ in the marine boundary layer.

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