Evaluation of the DMS flux and its conversion to SO$_2$
over the southern ocean

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Abstract

A total of 16 boundary layer (BL) DMS flux values were derived from flights over the Southern Ocean. DMS flux values were derived from airborne observations recorded during the Aerosol Characterization Experiment (ACE 1). The latitude range covered was 55°S–40°S. The method of evaluation was based on the mass-balance photochemical-modeling (MBPCM) approach. The estimated flux for the above latitude range was 0.4–7.0 μmol m$^{-2}$ d$^{-1}$. The average value from all data analyzed was 2.6 ± 1.8 μmol m$^{-2}$ d$^{-1}$. A comparison of the MBPCM methodology with several other DMS flux methods (e.g., ship and airborne based) revealed reasonably good agreement in some cases and significant disagreement in other cases. Considering the limited number of cases compared and the fact that conditions for the comparisons were far from ideal, it is not possible to conclude that major agreement or differences have been established between these methods. A major result from this study was the finding that DMS oxidation is a major source of BL SO$_2$ over the Southern Ocean. Model simulations suggest that, on average, the conversion efficiency is 0.7 or higher, given a lifetime for SO$_2$ of ~ 1 d. A comparison of two sulfur case studies, one based on DMS–SO$_2$ data generated on the NCAR C-130 aircraft, the other based on data recorded on the NOAA ship Discoverer, revealed qualitative agreement in finding that DMS was a major source of Southern Ocean SO$_2$. On the other hand, significant disagreement was found regarding the DMS/SO$_2$ conversion efficiency (e.g., 0.3–0.5 versus 0.7–0.9). Although yet unknown factors, such as vertical mixing, may be involved in reducing the level of disagreement, it does appear at this time that some significant portion of this difference may be related to systematic differences in the two different techniques employed to measure SO$_2$. It would seem prudent, therefore, that further instrument intercomparison SO$_2$ studies be considered. It also would be desirable to stage new intercomparison activity between the MBPCM flux approach and the air-to-sea gradient as well as other flux methods, but under far more favorable conditions. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Marine; Sulfur; Chemistry; DMS; SO$_2$; ACE 1

1. Introduction

Oceanic emissions of dimethyl sulfide (DMS: CH$_3$SCH$_3$) are known to be a major primary source of natural sulfur in the remote marine atmosphere (Andreae and Raemdonck, 1983; Andreae, 1986; Bates et al., 1987). One of its oxidation products, SO$_2$, is also known to be a major source of sulfate aerosol. Hence, via its formation
of CCN, sulfate aerosol derived from the oxidation of DMS has the potential for influencing the Earth’s radiative budget (Charlson et al., 1987). This suggests that both accurate assessments of the DMS flux and its conversion efficiency to SO$_2$ and sulfate represent critical inputs to climate models.

At present, the efficiency with which DMS forms SO$_2$ is still problematic. Laboratory chamber type studies have been qualitatively informative; but as pointed out in recent reviews of marine sulfur chemistry (e.g., Berresheim et al., 1995 and references therein), because of the inability of these chambers to simulate actual marine conditions, the resulting product distributions still lack credibility.

More surprising have been the conflicting results that have emerged from marine sulfur field studies. For example, given that the typical boundary layer (BL) DMS lifetime with respect to OH is in the range of 0.5–2 d (e.g., Wine et al., 1981; Hynes et al., 1986), and that for SO$_2$ is typically less than 1 d (e.g., Berresheim et al., 1995; Bonsang et al., 1987, and references therein), it follows that one should see a strong anticorrelation between these two species. This is particularly true if the sampling times are restricted to a temporal resolution of much less than 1 d. However, in one of the earliest studies in which both species were measured (Bandy et al., 1992), no anticorrelative behavior was observed. The resulting estimated conversion efficiency was thus quite small, e.g., < 0.2. This ship study was carried out in the northeastern Pacific at 48°N latitude. By contrast, in a later ground-based study near the equator, Bandy et al. (1996) reported a strong anticorrelation between DMS and SO$_2$. In this case the conversion efficiency for DMS to SO$_2$ was estimated at 0.62 ± 0.15. At the same site (i.e., Christmas Island, 2°N, 157°W), but using DMS–SO$_2$ data collected from an airborne sampling platform, Davis et al. (1999) reported an analysis of sulfur data gathered again by Bandy and co-workers that also revealed a strong anticorrelation between DMS and SO$_2$. These investigators estimated a conversion efficiency only slightly higher than that reported by Bandy et al., e.g., 0.72 ± 0.15. Considerably at odds with the conclusions of the previous two tropical studies, Yvon and Saltzman (1996) have reported shipboard data (i.e., 12°S, 135°W) that showed only a weak anticorrelation between DMS and SO$_2$. In this case the conversion efficiency dropped to 0.27–0.54. Huebert et al. (1993) also analyzed ship data in the tropical Pacific but in their study the sampling resolution for SO$_2$ was a half day or longer. Thus, under these conditions one might expect to see a positive correlation between DMS and SO$_2$. This was a result not observed. Yet, at two other ground-based sites, one at Amsterdam Island at 38°S, 77°E (Putaud et al., 1992) and the other at Cape Grim at 41°S, 144°E (Ayers et al., 1997), “long-term” daily (Amsterdam) and weekly (Cape Grim) averaged DMS and SO$_2$ data were recorded that did result in positive correlations between DMS and SO$_2$. For the Amsterdam Island study the reported conversion efficiency was in the range of 0.64–0.69 whereas that for Cape Grim was significantly lower.

In this paper we present an analysis of airborne sulfur data recorded during the First Aerosol Characterization Experiment (ACE 1) field study. Explored here is both the issue of the confidence level one can place in current DMS flux assessments and the issue of the efficiency with which DMS is converted into SO$_2$.

2. Observational data

Data recorded during the ACE 1 field campaign are the only data used in this study. The ACE 1 campaign was carried out during the months of November and December 1995. Of the 31 marine flights flown during ACE 1, 18 of these (flights 11–28) were made over the Southern Ocean between the dates of 17 November and 12 December 1995. These flights covered the latitude range of 40°S–55°S and a longitude range of 135°E–160°E as shown in Fig. 1. The most commonly employed sampling strategy for the National Center for Atmospheric Research’s (NCAR) C-130 aircraft consisted of flying sequential circles (diameter ∼ 60 km) at 3 or 4 constant altitudes (i.e., typically 30, 150, 300, 450, 600, and/or 900 m) while moving with the wind field. Both BL and buffer layer (BuL) altitudes were flown during each field mission. (Note, the buffer layer is defined here as the transition zone between the BL and free troposphere as previously described by Russell et al., 1998.) For the

Fig. 1. Southern Ocean C-130 flight tracks during ACE 1. The number next to each track is the field program mission number.
Lagrangian missions (flights 18–20 and 23–26), a common air mass was tracked in time using “smart” balloons launched from the NOAA research vessel Discoverer (Businger et al., 1999). For further detail on all aspects of the ACE 1 sampling strategy, the reader is directed to the ACE 1 “Overview” paper by Bates et al. (1998a).

The ACE 1 airborne field program included measurements of the sulfur species, DMS, SO$_2$, and MSA as well as the aerosol species SO$_4$$. Other critical trace gas measurements included OH, O$_3$, CO, CH$_4$, NO, H$_2$O$_2$, and CH$_3$OOH. Meteorological parameters recorded included UV irradiance (e.g., Eppley radiometer), $T$, $P$ and the horizontal and vertical winds.

The C-130 DMS and SO$_2$ measurements were made using gas chromatography/mass spectrometry (GC/MS) with isotopically labeled DMS and SO$_2$ being used as internal standards. The sampling resolution ranged from 4 to 6 min and the overall system had limits-of-detection (LOD) of $\sim$ 1 part per trillion by volume (pptv) for both DMS and SO$_2$. For further details regarding this technique see Bandy et al. (1992, 1993). For details on the measurements of other trace gases and aerosol species, the reader is directed to the ACE 1 “Overview” paper by Bates et al. (1998a).

During the Southern Ocean component of the ACE 1 program, the C-130 aircraft sampled the BL 82 times. Of these, 66 sampling events were found acceptable for estimating DMS fluxes. Those runs rejected typically had poorly defined photochemical environments associated with them. From the 66 acceptable events, 16 independent flux values were estimated. The large reduction in the number of independently defined flux values reflects the fact that typically four or more BL sampling events were used in determining one independent flux value.

Median concentrations of the photochemical species, NO, CO, H$_2$O, O$_3$, H$_2$O$_2$, CH$_3$OOH, and CH$_4$ formed the basis for all input to the box model used to define both the diel profiles for OH and NO$_3$ (see Table 1). In the case of NO, most of the BL observations were at or below the 2 sigma detection limit of the chemiluminescence NO sensor (e.g., typically 5–10 pptv). Hence, the NO input to the model involved bracketing a range of values that encompassed a lower limit of 1 pptv and an upper limit defined by the 2 sigma uncertainty in the NO measurement. Using this approach, both upper and lower limiting values for OH were assigned. The best estimate of the DMS flux for these cases was that defined by the mean OH value.

### 3. Approach and model description

#### 3.1. Approach

The method used in evaluating the DMS flux ($F_{\text{DMS}}$) was based on the mass-balance photochemical-modeling (MBPCM) approach as described by Davis et al. (1999) and Chen et al. (1999). (Note, still earlier forms of this approach have been previously described by Saltzman...
and Cooper, 1989; Davison and Hewitt, 1992; Thompson et al., 1990, 1993.) As outlined by Chen et al., to achieve the most reliable results using the MPBQM approach, the region under investigation must have: (1) a reasonably high degree of surface DMS homogeneity, and (2) gas-phase levels of DMS that reflect photochemical quasi-steady-state conditions. Given that the BL is well mixed, the final form of the mass balance equation is as follows:

\[
\frac{d[DMS]}{dt} = \frac{F_{DMS}}{EMD} - (k_{OH}[OH] + k_{NO_3}[NO_3])[DMS] + \frac{1}{EMD} \int_{h_{BL}}^{h_{BL}} (\frac{\partial[DMS(z)]}{\partial z}) dz. \tag{1}
\]

Here, EMD defines the DMS equivalent mixing depth which can best be represented by

\[
EMD = \frac{[(DMS(z)]dz}{[DMS]_{BL}}. \tag{2}
\]

In this equation the quantity \([DMS]_{BL}\) represents the average DMS concentration in the marine BL. Thus, the equivalent mixing depth, EMD, is just the height of an atmospheric column that contains all DMS mass (including both BuL and BL) but at BL concentrations. Evaluation of the EMD was carried out from airborne observations of DMS recorded during descents and ascents above the BL. Although this quantity undoubtedly varies in time, as suggested by Chen et al. (1999) to a first approximation one can assume a constant value. Our making this assumption in this study reflects the fact that realistically only a very limited number of vertical DMS observations could be made during a typical flight.

The remaining terms in Eq. (1) include \(k_{OH}\) and \(k_{NO_3}\), the reaction rate coefficients for reaction with OH and NO\(_3\); \(w\), the mean vertical velocity; and \(\partial[DMS(z)]/\partial z\), the vertical gradient of DMS in the BuL. From this equation it can be seen that the first term on the right-hand side relates to the DMS sea-to-air flux, the second term defines the loss of DMS due to oxidation by OH and NO\(_3\), and the third term evaluates the effects of large-scale mean vertical motion. The 24-hr average value for \(w\) was that made available via NCEP meteorological data. The approach taken here was similar to that used for evaluating EMD; we assumed that to a first approximation the value of \(w\) was not time dependent. Note also that in Eq. (1) we have chosen not to assign any loss of DMS to chlorine oxidation or oxidation from other halogen species. Based on the recent results of Singh et al. (1996), Davis et al. (1999), and Chen et al. (2000), it would appear that for remote open ocean areas the impact from chlorine and bromine atoms is probably \(\leq 15\%\). Obviously, if halogen atoms did make a measurable contribution, the flux reported here would represent a lower limit value only.

From a practical point of view, the “best estimate” for \(F_{DMS}\) can be derived by adjusting the flux value in Eq. (1) until the difference between the model-estimated and the observed DMS profiles is minimized. The minimization routine used here was “chi-squared testing”. Given the fact that several data points at different times were available to help define the fit, as discussed by Chen et al. (1999), the resulting fit typically leads to flux errors of less than 20%. Given a reasonable estimate of the DMS flux, a diel profile for DMS was then generated from which the yield of SO\(_2\) was evaluated. The latter evaluation was carried out using Eq. (3). This expression addresses the SO\(_2\) mass balance resulting from BL-oxidized DMS and the loss of SO\(_2\) from all BL removal processes, i.e.,

\[
\frac{d[SO_2]_{BL}}{dt} = \gamma k_{OH}[DMS] - L[SO_2]_{BL, DMS}. \tag{3}
\]

Note that “\(\gamma\)” in this equation represents the overall SO\(_2\) conversion efficiency from the OH/DMS reaction. Thus, it defines contributions from both abstraction and addition channels. Similarly, the total first-order SO\(_2\) loss parameter, \(L\), includes both gas-phase chemical losses as well as the physical removal processes defined by wet/dry ocean deposition, scavenging by sea-salt aerosol and cloud droplets, as well as dilution by vertical transport. As discussed earlier in the text, given the limitations of the airborne sampling campaign, the time variability in the value of \(L\) was assumed to be negligible over a 24-hr period. Also, since the levels of NO\(_3\) were typically quite low, no effort was made here to include SO\(_2\) production from the NO\(_3\) radical which typically was \(\leq 5\%\).

As noted in the “Introduction”, results from previous field studies have led to a rather large range of DMS/SO\(_2\) conversion efficiencies. In this analysis we have chosen to use only those results from previous studies by this group, and thus, have initially limited ourselves to two initial values: 1.0 and 0.7. The first value obviously represents an upper limit for SO\(_2\) production, and defines a best-case scenario for DMS oxidation being the dominant source of BL SO\(_2\) levels. The second value of 0.7 is quite close to several values recently derived from marine-sulfur field-studies in which Bandy and co-workers have been the principal source of SO\(_2\) data. This value has thus emerged as our “best estimate” of the conversion efficiency. It was arrived at by estimating the average “\(\gamma\)” value from the field study results of Davis et al. (1998, 1999), Chen et al. (2000), and Bandy et al. (1996). A similar treatment was also adopted for the value of “\(L\)”.

In this case the range of values from field studies was that compiled by Grodzinsky et al. (2000). The recommendation for SO\(_2\) gave a lifetime range for marine conditions consisting of a low value of 0.25 d and a high of 2 d. For purposes of this work, we have taken values of “\(L\)” that correspond to SO\(_2\) lifetimes of 0.25, 1, and 2 d. Our “standard model” has been defined using an SO\(_2\) lifetime
of 1 d, coupled to our “best estimate” value for “γ” of 0.7. Hence, lower and upper limits for SO$_2$ levels are defined by the “γ” and “L” combinations: γ = 0.7, 1/L = 0.25 d and γ = 1.0, 1/L = 2 d, respectively.

3.2. Model description

The sulfur chemistry model used in this study contained 14 reactions encompassing the sources and sinks for the sulfur species: DMS, DMSO, DMSO$_2$, MSIA, MSA, and SO$_2$. Details concerning this model can be found in previous publications (e.g., Davis et al., 1998, 1999; Chen et al., 1999, 2000). The cited sulfur box model was coupled to a full HO$_x$/NO$_x$/CH$_4$/NMHC time-dependent photochemical box model as constrained by measured values of NO, CO, O$_3$, H$_2$O, H$_2$O$_2$, CH$_3$OOH, and UV irradiance. In those cases where BL OH observational data were coincident with DMS observations, these values were used to further constrain our model-generated OH profiles by adjusting critical J values. Details concerning the HO$_x$/NO$_x$/CH$_4$/NMHC time-dependent photochemical box model have been previously described by Davis et al. (1993, 1996) and Crawford et al. (1997a, b, 1999).

4. Results and discussion

4.1. Southern Ocean DMS flux results

Sixteen independent BL DMS flux values were derived from the ACE 1 airborne observations in the Southern Ocean. These are shown in Table 2. Individual values are seen ranging from 0.4 to 7 μmol m$^{-2}$ d$^{-1}$. The average value from this ensemble was estimated at 2.6 ± 1.8 μmol m$^{-2}$ d$^{-1}$. This value falls near the center of the most recently cited range for the global DMS flux by Chin et al. (1998), i.e., 2.0–3.2 μmol m$^{-2}$ d$^{-1}$.

Fig. 2a shows these same data plotted as a function of latitude. Also shown in Figs. 2b and c are the wind speed and sea-water DMS levels. From these collective data, one sees a weak trend of increasing DMS flux with decreasing latitude which also tracks a much stronger latitudinal trend in sea-water DMS levels (Bates et al., 1998b). Since marine DMS levels are known to be only weakly correlated with ocean biological activity (Sullivan et al., 1993; Kettle et al., 1999), the ACE 1 data were further categorized according to a different ocean surface water characteristic, namely, “water mass”. For example, during ACE 1 three different surface water masses were identified during the sampling time defined by the “intensive” campaign. These differed substantially in salinity as well as in biological activity. These have been labeled by the ACE 1 science team as: subtropical convergence zone (STCZ, < 43°S), subantarctic water zone (SAZ, 43°S–49°S), and antarctic zone (AZ, > 49°S)(Bates et al., 1998a, b). The STCZ had the highest salinity value, e.g., > 34.8 psu, while the AZ had the lowest value, i.e., < 34.2 psu.

Of the 16 DMS flux values defined by the C-130 data, five occurred in the subtropical convergence zone, seven in the subantarctic, and four in the antarctic. These data along with those for wind speed and sea-water DMS measurements are again shown in Figs. 2a–c. The average value for the flux in each zone has been estimated at 3.7 ± 2.7, 2.0 ± 0.9, and 2.0 ± 1.4 μmol m$^{-2}$ d$^{-1}$,

### Table 2

<table>
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<tr>
<th>Flight no.</th>
<th>Date (1995)</th>
<th>Latitude (negative: S)</th>
<th>Longitude (negative: W)</th>
<th>Flux (μmol m$^{-2}$ d$^{-1}$)</th>
<th>Wind speed (m s$^{-1}$)</th>
</tr>
</thead>
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<td>11</td>
<td>11/18</td>
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<td>137.9</td>
<td>1.3</td>
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<td>−40.7</td>
<td>144.2</td>
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<td>15.1</td>
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<td>150.8</td>
<td>2.6</td>
<td>5.3</td>
</tr>
<tr>
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<td>−47.4</td>
<td>145.5</td>
<td>1.2</td>
<td>6.1</td>
</tr>
<tr>
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<td>159.2</td>
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<td>6.2</td>
<td>13.2</td>
</tr>
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<td>3.2</td>
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Fig. 2. Southern Ocean ACE 1 latitudinal distributions of: (a) MBPCM DMS flux estimated from flights 11–28; (b) daily wind speed obtained from NCEP data; (c) sea-water DMS distribution measured on the NOAA ship Discoverer and (d) 1° latitude bin median values of the DMS flux based on Discoverer DMS sea-water measurements and L&M parameterization. Blue symbols in (a–d) are for Julian days 320–338, red symbols are for Julian days 338–346. The abbreviations STCZ, SAZ, and AZ signify surface water mass types for the zones: subtropical convergence, subantarctic, and antarctic polar, respectively.
respectively. For comparison purposes, the comparable DMS fluxes derived from sea-water measurements are shown in Fig. 2d. In the latter plot we have used the estimated median value for each 1° of latitude by binning all individual values appearing within each degree of latitude. (Note, the L&M parameterization was used in this assessment.) For the STCZ, although the trends in November and December were similar to those for the aircraft, the average values estimated from the ship data are seen as being nearly twice as large. This is also seen to be true for the SAZ. For the AZ, the ship data are primarily available for only the month of November and these are seen as reasonably close to those estimated from the aircraft data. Overall, the ship DMS flux values are nearly 2 times higher than those derived from the aircraft observations, or a factor of 3.6 times higher if the parameterization by Wanninkhof (1992) is used. The fact that there is a large difference in the average flux values between the two different approaches does not necessarily extrapolate to there being a systematic difference in the flux evaluation methods. For example, as stated earlier, the aircraft values were quite limited in number; and, in addition, there can be seen considerable variability in the DMS flux as well as a general lack of coordination between many of the ship and aircraft tracks. Thus, it is not totally unreasonable that the two platforms might have produced this large difference. At the same time one cannot preclude this possibility (see discussion that follows in Section 4.2).

4.2. Comparison of MBPCM and air–sea gradient flux methods

The air–sea gradient method is currently the most extensively used method for determining the DMS sea-to-air flux. Our current global DMS flux picture is mostly based on values derived from this method. It requires both a measurement of sea-water DMS and the evaluation of the sea–air transfer efficiency factor, i.e., piston velocity. The piston velocity is believed to be a function of surface wind speed as well as sea-water temperature. Once evaluated for a specific set of meteorological conditions, more general forms of this “transfer velocity” can be developed via parameterization equations which take into account the dependency of the flux on wind speed. Currently, at least three different versions of wind speed parameterization have been employed (Smethie et al., 1985; Liss and Merlivat, 1986; Wanninkhof, 1992). In fact, the range of results from these different approaches has provided one basis for defining the uncertainty in our current estimates for the global DMS flux which is estimated to be as large as a factor of two (Andreae, 1986; Bates et al., 1987; Andreae and Crutzen, 1997). In the text that follows the sea–air DMS flux derived from the Liss and Merlivat (e.g., “Vp(L&M)”) and Wanninkhof parameterizations (e.g., “Vp(W)” are compared to those estimated in this work using the MBPCM approach.

Detailed flux comparisons from the ACE 1 observations were made possible as a result of two preplanned encounters between the NCAR C-130 and the NOAA ship Discoverer. During both encounters the respective sampling platforms were positioned at nearly the same location at the same time. The first of these cases involved data collected during flight 15, the second involved flight 22. As shown in Fig. 3a, during flight 15, BL circular patterns were flown in the very near vicinity of the Discoverer's ship track, with two of the sampling circles actually overlapping the ship track. We have set the area of comparison to be the latitude range of 46.7°S–47.9°S with corresponding longitude coordinates of 144.3°E–146.2°E. The ship and aircraft DMS fluxes measured during this encounter are those shown in Fig. 3b. From here it can be seen that the MBPCM flux is higher than the Vp(L&M) flux but at some locations overlaps the Vp(W) estimate. The average MBPCM flux is $1.2 \pm 0.5 \mu\text{mol m}^{-2} \text{d}^{-1}$, with the cited uncertainty reflecting the random error estimated from a propagation of error analysis. Values for the ship in the “encounter region” averaged 0.7 ± 0.08 μmol m$^{-2}$ d$^{-1}$ for Vp(L&M) and 1.2 ± 0.13 μmol m$^{-2}$ d$^{-1}$ for Vp(W), where the stated uncertainties for these two values represent the standard deviation of the mean (SDOM). Hence, all methods appear to be consistent within the specified uncertainties, but numerically the MBPCM method is closer to the Vp(W) flux estimate.

Any further effort at a quantitative comparison of these flux methods must reflect on the fact that the MBPCM flux method could have potentially been influenced by several systematic errors. One of these could have resulted from the presence of a large gradient in the local DMS flux field (see, for example, Mari et al., 1998). In the case of flight 15, for example, an examination of Fig. 3b suggests that the DMS flux may have been more than a factor of 2 higher when the Discoverer was at latitudes < 47°S. This flux enhancement could have resulted from a combination of elevated sea-water DMS and wind speed increases, as shown in Fig. 3c. Given the wind direction reported, it is also quite possible that the C-130 sampled an air mass that originated from the northwest (i.e., lower latitudes). Assuming this air mass had equilibrated with the high flux region and the photochemical and meteorological conditions there were similar to those observed during flight 15, model simulations suggest that the MBPCM flux estimate might have been shifted to values that were factors of 1.5–2 too high. If true, in this one case the correction would tend to shift the estimated MBPCM flux to values closer to the Vp(L&M) estimate.

The second aircraft–ship DMS flux comparison, flight 22, is shown in Fig. 3d. As before, it is quite apparent that there was considerable success in getting the C-130 BL
flight pattern to encompass a significant portion of the Discoverer’s ship track. For this comparison the MBPCM flux is seen as 0.9 ± 0.3 μmol m⁻² d⁻¹, while the average values derived from the ship data for Vp(L&M) and Vp(W) are 0.5 ± 0.2 and 1.5 ± 0.3 μmol m⁻² d⁻¹, respectively. As before, the stated uncertainty for the MBPCM method represents the propagated error while that for the ship-derived fluxes is defined by the SDOM. Although within the combined uncertainties all fluxes appear to be consistent, it is difficult to ignore the large changes that occurred in both the Vp(L&M) and Vp(W) fluxes during the encounter period. As shown in Fig. 3f, shipboard observations of sea-water DMS appear to have undergone a smaller variation during the encounter time period than did wind speed. Variations in the latter parameter most likely are the main cause of the large variation in the sea-water DMS fluxes shown in Fig. 3e. As discussed for flight 15, the presence of large gradients in the DMS flux field during flight 22 also could have produced a significant bias in the MBPCM flux estimate. The wind direction measurements suggest that the sampled air mass could have originated from the north. Unfortunately, there were no ship observations to the north, making it impossible to even estimate the sign of this potential error.

4.3. Comparison of MBPCM and TD-BU and DMS/aerosol budget flux approaches

Although it is of great interest to compare sea-water-based flux determinations with the MBPCM approach, it is of equal importance to know just how well different DMS flux methodologies agree when all are based on atmospheric observations. In the case of ACE 1, the
In particular, the MBPCM flux estimate for flight 26 most likely encompasses additional systematic error as a result of there being present during the flight multiple layers of clouds (Davis et al., 2000).

As shown in Table 2, the MBPCM flux estimates for flights 24, 25, and 26 are $2.3 \pm 0.7$, $2.2 \pm 0.5$, and $2.8 \pm 1.4 \, \text{nmol m}^{-2} \text{~d}^{-1}$, respectively. For flight 24, the average TD–BU flux is seen as a factor of 2.6 higher than MBPCM while that estimated from the AB approach is a factor of 1.9 lower. By contrast, for flight 25, the MBPCM flux is only 10% higher than the TD–BU flux, but the AB value is more than a factor of 2 lower. In the final flight, 26, both the TD–BU and AB methods are seen as factors of 2–3.5 higher. The uncertainties associated with both the TD–BU and AB approaches predominantly reflect the level of DMS inhomogeneity in the air mass sampled. Unfortunately, this was a BL property that typically was not that well defined by the limited measurements recorded during each flight. Current estimates place this as high as a factor of 2. Consideration of all three flights produced a mean value for the MBPCM approach of $2.4 \pm 0.5$ and for the TD–BU and AB methods values of $5.5 \pm 1.3$ and $3.0 \pm 1.3 \, \text{nmol m}^{-2} \text{~d}^{-1}$, respectively. The stated uncertainties reflect the calculated SDOM. If restricted to just flights 24 and 25, the three methods result in flux values of $2.2 \pm 0.4$, $4.6 \pm 1.8$, and $1.1 \pm 0.4$, respectively. Thus, in all cases the TD–BU method is higher than MBPCM by nearly a factor of two. On the hand, the AB method is somewhat higher when considering all three flights but is nearly a factor of two lower when examining only flights 24 and 25. It must be reemphasized, however, that all flux comparisons during the ACE 1 “intensive” period were limited to rather small regions, typically involving significant gradients. In particular, the TD–BU method is quite sensitive to local gradient conditions, whereas the other two methods tend to average conditions over a larger region. In summary, any conclusions drawn from the ACE 1 data should be considered as only suggestive not conclusive.

5. Contribution of DMS oxidation to BL SO$_2$

The contribution of oxidized DMS to the Southern Ocean BL SO$_2$ budget was evaluated by comparing observed SO$_2$ levels to those derived from model simulations. As discussed in Section 3.1, the calculated value for SO$_2$, [SO$_2$]$_{DMS}$, was computed from Eq. (3). Recall, this equation describes the mass balance between SO$_2$ formation from DMS oxidation and its loss via both chemical and physical processes. As per our earlier discussions, for all 16 BL sampling events in which the DMS flux was evaluated, [SO$_2$]$_{DMS}$ values were also calculated. Simulations were run for our standard case with $\gamma = 0.7$ and $1/L = 1.0 \, \text{d}$; the minimum case with $\gamma = 0.7$ and

opportunity for such a comparison arose during Lagrangian flight sequence 24, 25, and 26. For these flights the MBPCM flux was compared with two independent methods, both reported by Russell et al. (1998). These two independent methods have been labeled by their authors top-down/bottom-up (TD–BU) and DMS/aerosol budget (AB). Detailed descriptions of both approaches can be found in Russell et al. (1998) and references therein. Fig. 4a shows the flight tracks for missions 24, 25, and 26, while the corresponding flux estimates are displayed in Fig. 4b. From these plots it can be seen that with the exception of flight 26 the MBPCM fluxes generally fall between the TD–BU and DMS/AB methods. Although not shown, two independent flux determinations, based on sea-water DMS measurements (Suhre et al., 1998; Bates et al., 1998b), gave flux values that were within a factor of 1.3–2 of the MBPCM approach for flights 24 and 25. For flight 26, one method was larger by a factor of 2.5, the other by a factor greater than 5. Quite clearly, flight 26 presented problems for all methods, having a meteorological setting that was far more complex than for the other two flights (Wang et al., 1999).

![Fig. 4. Intercomparison of DMS flux methods during ACE 1 based on atmospheric measurements of DMS: (a) C-130 flight tracks during the Lagrangian flight sequence 24, 25 and 26; and (b) DMS fluxes derived from the MBPCM approach and the TD–BU and AB methods.](image-url)
The values during the ACE 1 intensive period. The symbol "c" defines the overall DMS-to-SO\(_2\) conversion efficiency and \(\tau\) is the SO\(_2\) lifetime. The top and bottom of the vertical lines within each bar define the upper and lower limit model estimates for the mixing ratio of SO\(_2\) when produced from DMS. These limits correspond to \(\gamma\) and \(\tau\) values of 1.0 and 2 d versus 0.7 and 0.25 d, respectively. The “best estimate” is defined by the top of the clear rectangular bars and corresponds to \(\gamma = 0.7\) and \(\tau = 1\) d. The top of the solid rectangular bars defines the observed mixing ratios for the SO\(_2\).

1/L = 0.25 d; and the maximum case with \(\gamma = 1.0\) and 1/L = 2.0 d. The results are those shown in Fig. 5. From here it can be seen that for 14 out of 16 runs, the standard case values of [SO\(_2\)]\(_{DMS}\) are equal to or somewhat larger than those observed. We interpret these results as strongly suggestive that DMS oxidation is the dominant source of SO\(_2\) in the remote Southern Ocean. This conclusion was also supported by the observation that the BL versus BuL gradient in SO\(_2\) was primarily negative or neutral when data were available for evaluation. It was also further corroborated in a more detailed sulfur budget analysis reported by Davis et al. (2000). In the latter study, the authors carried out an analysis of the Lagrangian flight sequence 23, 24, and 25. In this case a strong anticorrelation was found between DMS and SO\(_2\) in which systematic decreases in DMS were seen following sunrise and concomitant increases were observed in SO\(_2\). In a totally independent ship-based study during ACE 1 reported by De Bruyn et al. (1998), a similar conclusion was reached. Finally, Mari et al. (1999), using sea-water-derived DMS flux values and aircraft SO\(_2\) observations, also arrived at the same conclusion.

Quite interestingly, although the results reported by De Bruyn et al. (1998) qualitatively are in good agreement with those reported in this work, their "best estimate" for the value of \(\gamma\) was substantially lower, ranging from 0.3 to 0.5. Considering the similarities in the temperature field for both studies as well as in the levels of critical species like NO\(_x\), it seems unlikely that the cause of this shift in \(\gamma\) would be due to a major shift in the DMS oxidation mechanism for the two sampling platforms. Other possibilities would include: (a) systematic errors in either the measurement of DMS or SO\(_2\), (b) incorrect estimates of the OH level, or (c) lack of appropriate corrections for the effects of vertical mixing.

In the study by De Bruyn et al. (1998) the DMS-to-SO\(_2\) ratio was the principal basis upon which the value of \(\gamma\) was derived. The median value in their study for this ratio was \(\sim 8\). Corresponding median values for DMS and SO\(_2\) were 106 and 13 pptv, respectively. By contrast, the median DMS:SO\(_2\) ratio estimated from the C-130 data was \(\sim 3\). This ratio was based on median values for DMS and SO\(_2\) of 92 and 35 pptv, respectively.

The ship results of De Bruyn et al. can also be compared to the independent detailed sulfur budget study of Davis et al. (2000), again using C-130 data. The De Bruyn et al. study was performed on Julian days 338–340 whereas that by Davis et al. was based on results from the Lagrangian B flight sequence (flight 24, 25, and 26) covering Julian days 341–343. One of the interesting aspects of these two studies is the fact that although each occurred on slightly different days and at a somewhat different geographical sites in the Southern Ocean, both arrived at a similar average value for the estimated lifetime for SO\(_2\), i.e., 12–14 h (Davis et al., 2000), and 8–16 h (De Bruyn et al., 1998). However, in contrast to the SO\(_2\) lifetime findings, these two studies derived quite different values for \(\gamma\). Davis et al. evaluated \(\gamma\) at 0.7–0.9 as compared with the previously cited results of De Bruyn et al. of 0.3–0.5. Recall, the latter \(\gamma\) value range is also similar to that discussed earlier in the text involving the tropical DMS–SO\(_2\) data reported by Yvon and Saltzman (1996). Yvon and Saltzman’s \(\gamma\) values were also noted to be significantly lower than those derived by Davis et al. (1999) and Chen et al. (2000) (e.g., 0.27–0.54 versus 0.65 \(\pm\) 0.15) which also involved a tropical environment.

Of interest in each of the above studies is the question whether significant differences existed in the respective chemical and physical environments and what possible differences existed in the types of instrumentation used to make the sulfur observations. Possible differences in the vertical mixing properties of each BL environment are clearly one of the most difficult issues to evaluate. For example, only in the case of the two airborne studies reported by Davis et al. were vertical observations of chemical and meteorological parameters sufficiently complete to evaluate the role of vertical mixing. Thus, one clearly cannot rule out the possibility that this was a contributing factor in defining some of the differences reported in \(\gamma\). Possible differences in the respective chemical environments can be more easily assessed. In the case
of NO levels, for example, observations recorded in the respective tropical and Southern Ocean environments suggest that in all cases the differences were quite small. (Note, significant differences in the level of NO can be a basis for arguing that the DMS oxidation mechanism might have been different for the two studies even though they took place in the same geographical region.) As related to differences in the diurnal averaged OH level for each study, an assessment of this critical quantity using a common photochemical model, based on actual photochemical observational data recorded at each site or platform, has revealed that for the tropical studies the Yvon and Saltzman study produced the lowest value by \( \sim 20\% \) whereas for the Southern Ocean studies De Bruyn et al.'s study was \( \sim 21\% \) higher than that estimated at the site analyzed by Davis. Thus, these results do not seem to provide a simple answer to the difference in the previously cited \( \gamma \) values.

The third and final possibility listed above, namely, differences in the sulfur measuring instrumentation is addressed in the text that follows. In this context it is worth noting that in the two case studies in the Southern Ocean (e.g., De Bruyn et al.'s results and those reported by Davis et al. (2000)), the ratio of the median values of measured DMS from the two studies was 1.05; however, that for \( \text{SO}_2 \) was 2.2. As noted earlier, the difference in the average level of OH for the two studies reduces the above discrepancy slightly, but clearly is not the whole answer. Regarding the instrumentation employed, that for measuring DMS had much commonality in that both were GC based. Furthermore, both have previously been involved in a common DMS field intercomparison study, the NASA CITE-3 program. This program compared six different DMS techniques. Drexel fielded an isotopic-dilution gas-chromatography mass-spectrometric (ID-GC/MS) technique and U. Miami employed a gas chromatography-flame photometric detection system. (Note, these same systems have been used in all studies under discussion.) The intercomparison was carried out off the northeast coast of the USA and off the eastern coast of Brazil (Gregory et al., 1993). The conclusion from this double-blind airborne intercomparison was that “all” methods were without any major systematic errors and that even at DMS levels < 50 pptv this species could be measured to within a few pptv.

Concerning the \( \text{SO}_2 \) measurements, in the De Bruyn et al. and Yvon and Saltzman’s studies the HPLC/Fluorescence method was employed. In all analysis reported by Davis et al. and Chen et al., the \( \text{SO}_2 \) data were those recorded by Bandy and co-workers using the ID-GC/MS method. The only \( \text{SO}_2 \) intercomparison involving both Drexel’s ID-GC/MS and the U. Miami’s Fluorescence–HPLC instrument was that carried out at Lewes, Delaware (Stecher et al., 1997). Among the findings that can be extracted from this ground-based study (i.e., GASIE – Gas Phase Sulfur Intercomparison Experiment) are the following: (1) the ID-GC/MS and HPLC/Fluorescence instruments differed by \( \sim 27\% \) in their measurement of a standard \( \text{SO}_2 \) calibration source, the ID-GC/MS system giving the higher reading; and (2) even with normalization of all data to account for this calibration difference, the ID-GC/MS system typically was found to measure \( 15–20\% \) higher than the HPLC/Fluorescence instrument when measuring diluted ambient air samples. The resulting collective error showed up during many of the individual sampling periods involving diluted ambient air samples with mixing ratios of less than 200 pptv. This difference was frequently as high as factors of 1.4–1.5.

Given the limited information available, we can draw no final conclusions concerning the accuracy of each of these measurement systems. However, the intercomparison results would seem to suggest that there might be a significant systematic difference between measurements recorded on these two different systems when in the field.

### 6. Summary and conclusion

The MBPCM approach was used here to evaluate sea-to-air DMS fluxes for the Southern Ocean. These evaluations were based on 18 airborne flights (i.e., flights 11–28) flown during the ACE 1 field study in November and December 1995. From these 18 flights, 16 independent BL DMS flux values were defined. The latitude range covered by these was 55°S–40°S and encompassed the flux range of 0.4–7.0 \( \mu \text{mol m}^{-2} \text{d}^{-1} \). The average value was 2.6 ± 1.8 \( \mu \text{mol m}^{-2} \text{d}^{-1} \). For the same time period, the average value derived from all sea-water measurements was approximately a factor of 2 larger, based on the L&M parameterization, or a factor of 3 when using W's parameterization. That they could differ by this amount is not totally unreasonable considering the fact that a wide range of DMS fluxes presented themselves during the Southern Ocean study and that the Discoverer's sampling track was frequently nonaligned with that of the C-130’s. Obviously, one can also not rule out the possibility that there could have been a fundamental difference in the techniques employed for estimating the fluxes.

Efforts to compare the MBPCM flux method with other airborne-based approaches resulted in our finding some cases which showed reasonably good agreement and other cases that were in significant disagreement. Thus, we believe it would be premature at this time to draw any final conclusions from this intercomparison. To a very large degree, these results reflect the fact that the number of detailed comparisons was small, and that the conditions under which the comparisons were made were far from ideal.

A major result from this study was the conclusion that DMS oxidation is a major source of BL \( \text{SO}_2 \) in the
Southern Ocean, assuming in agreement with other ACE 1 investigators. Assuming that the sole source of reduced sulfur is DMS, our simulations suggest that, on average, the conversion of DMS to SO$_2$ occurs with an efficiency of $\sim 0.7$, given an assumed lifetime for SO$_2$ of $\sim 1$ d. On at least one occasion, during the second ACE 1 Lagrangian, observations were recorded under nighttime conditions which led to a direct determination of the SO$_2$ lifetime of 12–14 h. Although meteorological and chemical conditions during Lagrangian B were not typical of the ACE 1 field program overall, they still provided a basis for comparison with an independent study on the ship Discoverer. This comparison revealed that although both studies point toward DMS as a major source of SO$_2$, each arrived at a quite different estimate for the DMS-to-SO$_2$ conversion efficiency (e.g., 0.3–0.5 versus 0.7–0.9).

It was further noted that a similar difference in $\gamma$ (SO$_2$) resulted when independent tropical studies (involving two different SO$_2$ instruments) were compared. Although yet unknown factors may still be involved which are responsible for the differences noted in the conversion efficiency, the evidence now available suggests that this difference may be at least partially tied to systematic differences in the SO$_2$ calibrations and measurements. At this time there is no basis for selecting one measurement over the other. It would seem prudent, however, to recommend that a further effort be made to examine this issue in that the results could have a major impact on our interpretation of the DMS oxidation mechanism. It is also recommended that a further effort be made at intercomparing the MBPCM flux approach with the air-to-sea gradient as well as other flux methods under more favorable conditions. The location for the latter study should be one where the meteorology is relatively stable, DMS lifetimes are short, and the DMS flux field is reasonably uniform. One such possibility would be the trade wind regime in the central tropical Pacific.

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