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DMS and SO_2 at Baring Head, New Zealand: Implications for the Yield of SO_2 from DMS

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Abstract. Atmospheric dimethyl sulfide (DMS) and sulfur dioxide (SO_2) concentrations were measured at Baring Head, New Zealand during February and March 2000. Anti-correlated DMS and SO_2 diurnal cycles, consistent with the photochemical production of SO_2 from DMS, were observed in clean southerly air off the ocean. The data is used to infer a yield of SO_2 from DMS oxidation. The estimated yields are highly dependent on assumptions about the DMS oxidation rate. Fitting the measured data in a photochemical box model using model-generated OH levels and the Hynes *et al.* (1986) DMS + OH rate constant suggests that the SO_2 yield is 50–100%, similar to current estimates for the tropical Pacific. However, the observed amplitude of the DMS diurnal cycle suggests that the oxidation rate is higher than that used by the model, and therefore, that the SO_2 yield is lower in the range of 20–40%.

Key words: dimethyl sulfide, oxidation, Southern Ocean, sulfur dioxide, sulfate aerosols.

1. Introduction

Sulfate aerosols alter the radiation balance of the earth both directly, by scattering incoming solar radiation, and indirectly by acting as cloud condensation nuclei and changing the albedo of clouds (Shaw, 1983; Charlson *et al.*, 1987; IPCC, 2000). Over the remote oceans, sea surface emissions of dimethylsulfide (DMS) are probably the primary source of aerosol sulfate. The physical and chemical processes by which dimethylsulfide is converted into sulfate aerosols are not fully understood. Oxidation by OH is believed to be the primary reaction pathway for DMS in clean marine air, although other mechanisms such as reaction with halogen atoms have been suggested (Keene *et al.*, 1996; Sander and Crutzen, 1996). Although DMS oxidation has been the focus of numerous laboratory, field, and modeling studies, the overall product distribution and its spatial/temporal variability are not well understood. The difficulty in unraveling the gas-to-particle conversion process for DMS is a result of the complexity of the gas-phase reaction mechanisms involved, and the difficulty of analyzing precursors and intermediates at ambient levels in the atmosphere. Laboratory reaction chamber studies have demonstrated that the reaction products of DMS oxidation include sulfur dioxide (SO_2), dimethysulfoxide (DMSO), dimethylsulfone ($DMSO_2$), and methanesulfonate (MSA) (Grosjean, 1984; Hatakeyama *et al.*, 1985; Barnes *et al.*, 1988). Field measurements of DMS and its reaction products have been carried out using a variety of analytical techniques; however the available data base is limited.

One of the key questions involved in the gas-to-particle conversion of DMS is the yield of SO_2. SO_2 is a direct precursor for sulfuric acid via reaction with OH, and a contributor to marine aerosol nucleation and growth. Laboratory studies indicate that the mechanism of the DMS + OH reaction is highly sensitive to temperature, as a result of the strong negative temperature dependence of OH addition and the relatively weak positive temperature dependence of OH abstraction (Hynes *et al.*, 1986). This alone does not necessarily imply temperature dependence of the SO_2 yield, as SO_2 could be produced from either reaction pathway. Attempts to estimate the yield of SO_2 from DMS oxidation using field measurements of both compounds, have produced widely divergent yields ranging from 0–100% (Bandy *et al.*, 1992; Yvon and Saltzman, 1996; Bandy *et al.*, 1996; Ayers *et al.*, 1997; de Bruyn *et al.*, 1998; Davis *et al.*, 1999; Mari *et al.*, 1999; Chen *et al.*, 2000; Shon *et al.*, 2001). Various studies have also reached quite different conclusions regarding the temperature-dependence of the SO_2 yield ranging from zero temperature dependence (Chen *et al.*, 2000) to an approximate doubling of the yield from polar regions to the tropics (de Bruyn *et al.*, 1998).

In this study we report measurements of atmospheric DMS and SO_2 concentrations at Baring Head (41°24.6′ S, 174°52.2′ E), New Zealand, in February and March of 2000. Baring Head is often exposed to clean boundary layer air originating over the Southern Ocean. Model calculations and simulations of the observed conditions are presented and used to infer SO_2 yields from the measurements. The results are compared with those of previous studies conducted at high Southern latitudes (Ayers *et al.*, 1997; de Bruyn *et al.*, 1998; Mari *et al.*, 1999; Shon *et al.*, 2001).

2. Experimental

2.1. METHODOLOGY

DMS and SO_2 were measured using an isotope dilution GC/MS instrument with cryogenic preconcentration. This approach has been developed for use in the analysis of atmospheric sulfur gases by Drs Alan Bandy and Don Thornton (Drexel University; Bandy *et al.*, 1993). This is a relatively well tested method, having been successfully deployed on both land-based and aircraft platforms (Bandy *et al.*, 1993; Thornton *et al.*, 1996; Bandy *et al.*, 1996). This method has also been validated by two formal intercomparisons: the NASA/Chemical Instrumentation Test and Evaluation program (CITE-3; Hoell *et al.*, 1993) and the NSF-sponsored Gas-Phase Sulfur Intercomparison Experiment (GASIE; Stecher *et al.*, 1996). The primary advantage of using an internal standard is that the system self-corrects for inlet losses and detector drift. For DMS analysis, the deuterated isotopomer ($^{12}C^2H_3{}^{32}S^{12}C^2H_3$) is used as the isotope spike. For SO_2, the sulfur atom is isotopically labeled ($^{34}S^{16}O_2$). The natural abundance of ^{34}S is approximately 4%, so there is a contribution to both mass 66 and 64 from the naturally occurring SO_2.

Air is drawn into the system through a single 3/8″ Teflon tube inlet at flow rates of 10–15 L/min and dried to below 10% RH using a high-capacity Nafion membrane dryer. The air is spiked as it enters the inlet with the isotopically labeled dimethylsulfide and sulfur dioxide in nitrogen, to generate a concentration of a few hundred pptv of the labeled compounds. Two separate sample streams, for DMS and SO_2, are drawn from the main manifold through 1/16″ Teflon tube traps at flow rates of 300–1000 mL/min. Both sample flows are further dried with secondary Nafion dryers prior to the traps. The downstream ends of the secondary Nafion dryers are cooled to 0 °C to further depress the dew point of the air sample (Driedger *et al.*, 1987). The DMS sample stream is scrubbed of oxidants by passing the stream through a canister of cotton (Andrea *et al.*, 1993). The SO_2 stream is passed through a final dry-ice/ethanol trap to lower the dew point to –70 °C before the sample air enters the trap. The cryotraps are cooled to liquid argon temperatures to preconcentrate the sulfur gases. After sample collection, the traps are heated and injected onto separate columns for analysis. The chromatographic separation of sulfur gases is carried out on isothermal, packed columns. SO_2 is analyzed using 12% polyphenyl ether/1% H_3PO_4 on 40/60 Chromosorb T (Supelco) and DMS is analyzed using Carbopack B/1.5% XE-60/1% H_3PO_4 (Supelco). The effluent from each column is alternately directed into a Hewlett Packard model 5973 mass selective detector (MSD). Electrically actuated multiport Valco valves are used for the injection and column switching functions. The gas chromatographic oven is a simple small heated zone holding the column and valve bodies at 50–100 °C. All gas flows are mass flow-controlled.

In order to automate sample collection, the teflon cryotraps are mounted inside the neck of a 10 L pressurizable dewar. The liquid argon level is pneumatically raised and lowered to immerse and expose the traps (Andreae *et al.*, 1993). The traps are resistance heated while exposed to desorb the analyte gases. Traps are cooled to –190 °C in less than 30 seconds and reach 100 °C in under 1 minute. The 10 L dewar operates for over 24 hours running a sample every 10 minutes on a single fill. The master controller for the system is a single-board computer running Win98. The PC is programmed to carry out control functions for valve switching, cryotrap operation, and data logging of flow rates and temperatures to monitor system performance. Data acquisition and control of the mass spectrometer is accomplished by multi-tasking with the Windows-based Chemstation software designed for the HP MSD (G1701AA and HPIB interface).

Based on the mass spectrometer (HP 5973) signal to noise ratio, we estimate the detection limits ($S/N = 3$) for both SO_2 and DMS to be better than 1.5 femtomoles. This implies that, with no loss of SO_2 or DMS in the system, the instrument is capable of detecting less than 5 pptv in a 1 L sample. However, the effective detection limit depends on the loss of analyte in the system, the isotope ratios in the standards and the concentration of the standard in the manifold. During this deployment, isotope standard concentrations in the inlet manifold were typically 350 pptv SO_2 and 500 pptv DMS. 2 L samples were collected and the recovery of DMS through the system was quantitative. The recovery of SO_2 was generally better than 70%. The ^{34}S standard contained 5.3% ^{32}S and the DMS standard contained less than 1% undeuterated DMS. Chromatograms for a typical air sample at Baring Head are shown in Figure 1. The DMS is analyzed on a 3 ft Carbopack B column at a flow rate of 3 mL/min and 85 °C. The SO_2 is analyzed on a 12 ft 12% polyphenyl ether/1% H_3PO_4 on 40/60 Chromosorb T column at a flow rate of 3 mL/min at 60 °C. We estimate the lower limit of detection to be 5 pptv of DMS and SO_2 and the accuracy and precision of measurements to be better than ±10% and ±5% for both DMS and SO_2 respectively. In this configuration, both species elute in less than 7 minutes and overall sample turn-around time was approximately 10 minutes. The second peak in the m/e 66 spectrum has not been assigned yet. It does not vary significantly over the course of a day and has little impact on overall precious and accuracy.

Pure DMS and SO_2 isotopes were obtained from Aldrich and Icon Services, respectively. Gas isotope standards of 20–50 ppbv were prepared in the laboratory in pressurized, aluminum acculife-treated cylinders (Scott Gases) and calibrated against permeation devices (Vici Metronics). Permeation device loss rates were determined gravimetrically. A duplicate set of permeation devices was used to check standard tank stability in the field.

In addition to the isotope dilution GC/MS measurements, DMS was also measured during the experiment using a National Institute for Water and Atmospheric Research (NIWA) automated tenax preconcentrator coupled to a gas chromatograph with flame photometric detection (GC/FPD). The instrument has been previously used to measure DMS during a number of field experiments from both ship and land platforms (e.g., Boyd *et al.*, 2000). Details of the detection system performance are given in Walker *et al.* (2000). A comparison of results of simultaneous measurements by the two instruments shows that they are highly correlated ($r^2 = 0.91$) and the NIWA GC/FPD instrument has a response of 0.88 relative to the isotope dilution GC/MS instrument (Figure 2). Because the measurement period of the GC/FPD is 30 minutes compared to 10 minutes for the isotope dilution GC/MS, each isotope dilution GC/MS point in Figure 2 is an average of 3 points. The difference in response between the two instruments is within the estimated uncertainty of the absolute calibrations of the instruments.

The New Zealand (NIWA) air sampling site at Baring Head is located on a headland approximately 85 meters above sea level on the southeastern tip of the North Island. The isotope dilution GC/MS instrument was housed in a hut 5 meters from the cliff edge and air was sampled via a 3/8″ Teflon line attached to a flagpole. The inlet was approximately 3 meters above the hut and exposed to onshore winds.

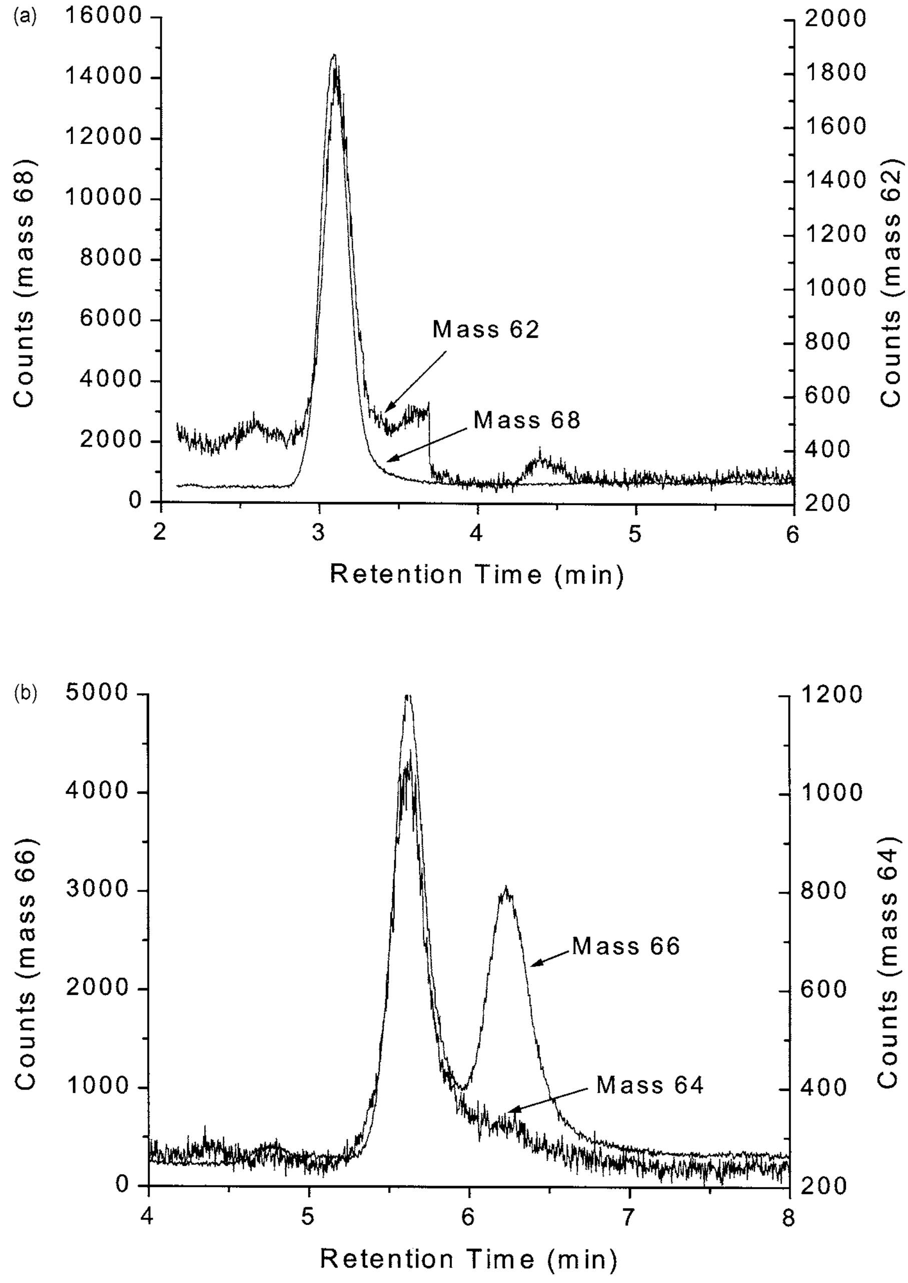

Figure 1. Analysis of DMS and SO_2 in an air sample from Baring Head, Zealand. (a) Selected ion monitoring at m/e 62 (CH_3SCH_3) and 68 (CD_3SCD_3) of 18 pptv ambient DMS. (b) Selected ion monitoring at m/e 64 ($^{32}SO_2$) and 66 ($^{34}SO_2$) of 47 pptv ambient SO_2. The peak in the m/e 66 spectrum at 6.3 min has not been assigned yet (see text).

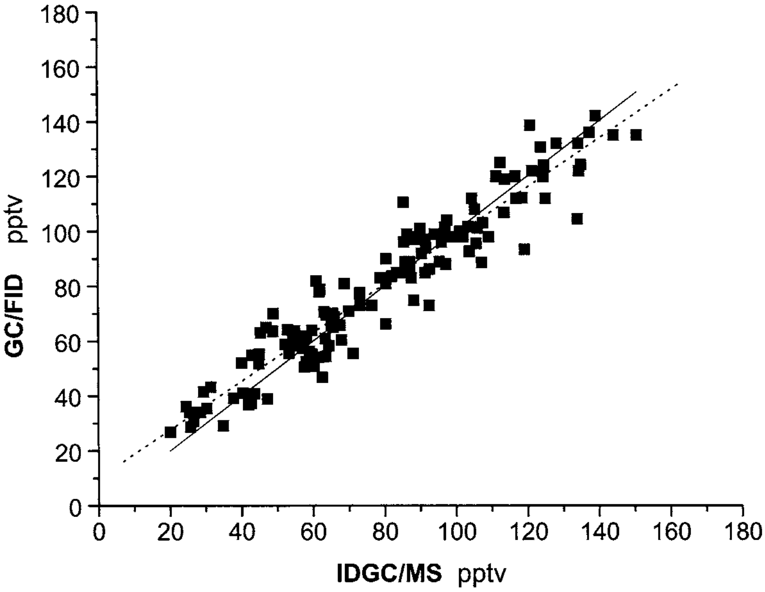

Figure 2. DMS levels measured by the NIWA GC/FPD plotted against DMS levels measured by the isotope dilution GC/MS for the whole deployment. The dashed line is a best fit to the data ($y = 0.88412x + 9.983558$; $r^2 = 0.91$). The solid line is the 1:1 line.

The NIWA GC/FPD instrument was co-located with an adjacent air inlet on the flagpole.

3. Results and Discussion

3.1. MEASUREMENTS

This study was conducted over a three week period towards the end of the austral summer (10 February–10 March 2000). Baring Head is frequently impacted by frontal passages associated with cyclonic weather systems. These events often increase in frequency and duration throughout the fall, as the frontal systems move further north. Due to the funnelling effect of the Cook Strait, winds at the site are essentially bi-directional. Southerly wind directions at the site are commonly associated with marine air trajectories originating over the Southern Ocean. Northerly winds arrive at Baring Head after passage over the North Island. These winds still have a strong marine character and are often deflected westerlies that may have tracked from the west coast which is only 30 km distant. The northerlies are associated with higher particle numbers and gaseous pollutant levels from the nearby urban centres of the Wellington region (population ~350,000). Sulfur dioxide levels in northerly winds generally exceeded 100 pptv, reaching mixing ratios as high as 1000 pptv. The distinction between these two types of air masses is easily made on the basis of condensation nuclei (CN) and wind direction. A typical transition from anthropogenically-influenced northerly winds to southerly marine air occurred on the 29th February (Figure 3). During northerly winds, CN counts were typically above 1000 cm^{-3} and SO_2 levels were elevated above 100 pptv. In southerly air, SO_2 levels dropped to below 50 pptv. DMS mixing ratios showed the opposite trend, reaching a maximum when winds were out of the south, reflecting either higher DMS emissions from the biologically productive region of the subtropical front (Chatham Rise) (Bates *et al.*, 1998) or a local source off Baring Head itself. The average DMS and SO_2 levels measured in northerly winds were 66 ± 40 pptv (1σ; $n = 354$) and 192 ± 385 pptv (1σ; $n = 354$) respectively. The average DMS and SO_2 levels measured in clean southerly air were 95 ± 35 pptv (1σ; $n = 218$) and 16 ± 12 pptv (1σ, $n = 218$) respectively. For the purposes of studying the relationship between DMS oxidation and SO_2 production, we utilized only samples collected with a wind direction between 120° and 220° and CN counts below 1000 cm^{-3}. Such conditions were typically obtained 1–3 times a week for periods of ~24 hours.

3.2. PREVIOUS MEASUREMENTS

Recent DMS and SO_2 measurements made over the Southern Ocean during summer include: (1) long term surface measurements made at Cape Grim between 1990 and 1993 (Ayers *et al.*, 1997), (2) C-130 aircraft measurements made during the ACE-1 experiment in November and December 1995 (Shon *et al.*, 2000) and (3) shipboard surface measurements aboard the R/V Discoverer during ACE-1 (de Bruyn *et al.*, 1998). Average DMS and SO_2 levels from these recent data sets are shown in Figure 4. For DMS, there is reasonable similarity between all studies. The Cape Grim data clearly shows the strong seasonal variability in atmospheric DMS levels, reflecting the annual cycle of biological activity in this region. Average levels measured on the R/V Discoverer during ACE-1 are consistent with the Cape Grim data set. However, during ACE-1, the airborne DMS levels tended to be lower than those measured at the ship. While it is impossible to discount analytical or calibration bias the differences between ACE-1 aircraft and shipboard measurements could reflect a real gradient across the boundary layer. ‘Buffer layers’ with distinctly different properties from the surface air below were observed during ACE-1 (Russell *et al.*, 1998). This incomplete mixing would result in more complete oxidation of DMS in the upper layer. Measurement differences could reflect simple sampling bias. For example, during ACE-1 the shipboard measurements were continuous and covered daylight hours and nighttime hours fairly evenly. The aircraft sampling was predominantly done during daytime, which because of the DMS diurnal cycle, could result in lower mean DMS levels. Measurement differences could also reflect spatial variability since the ACE-1 aircraft and ship were rarely co-located.

For sulfur dioxide, the Cape Grim data do not exhibit strong seasonal variability, which is surprising given trends observed in DMS. Again, there is good agreement

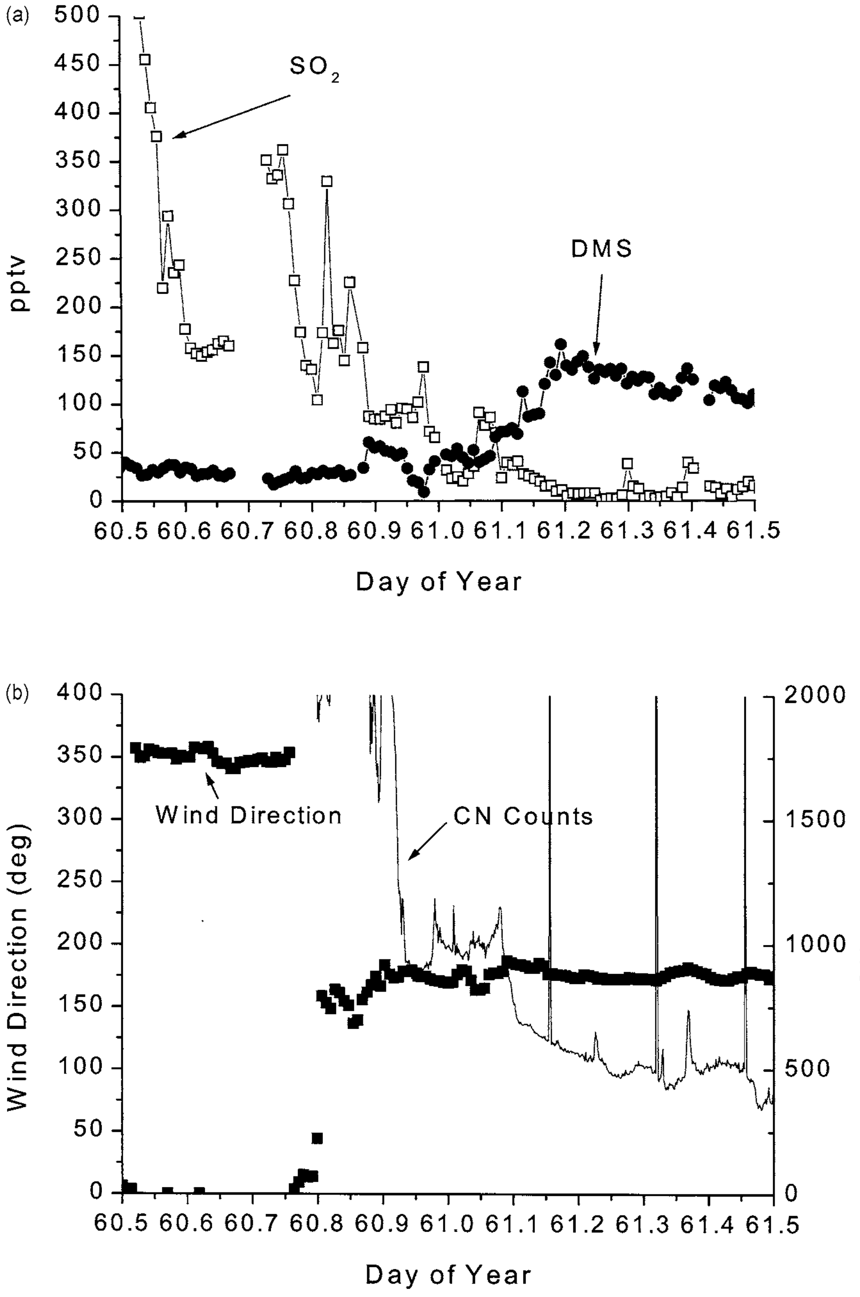

Figure 3. (a) DMS and SO_2 levels during a transition from northerly winds to southerly winds. (b) Wind direction and CN counts measured during a transition from northerly winds to southerly winds.

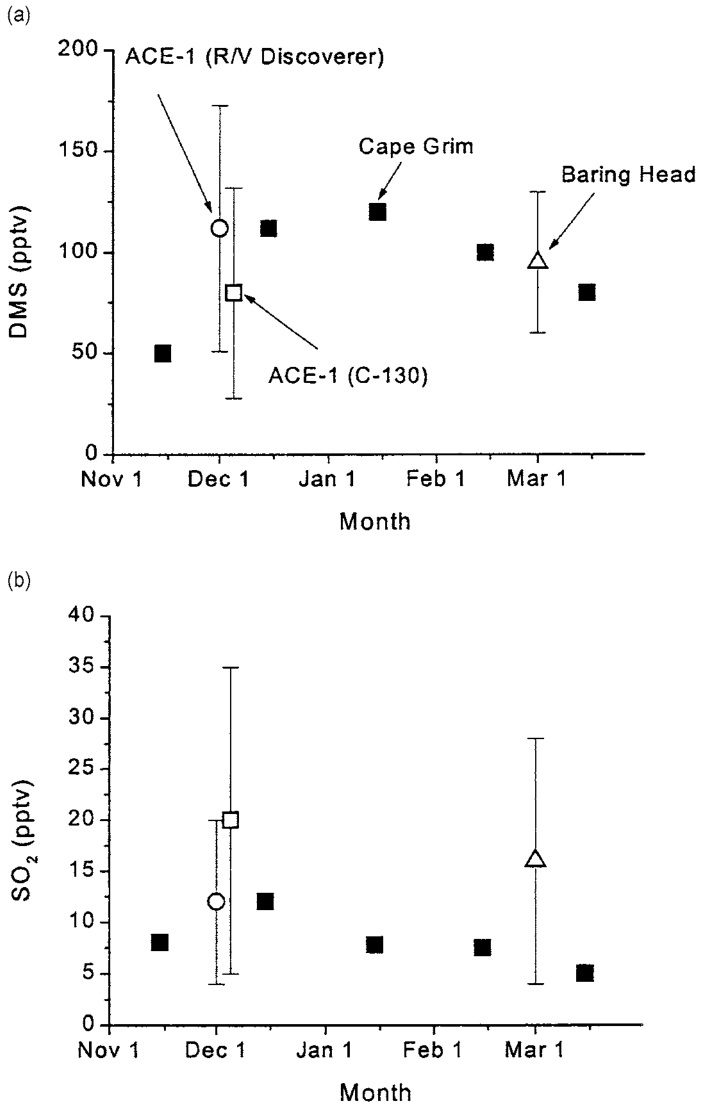

Figure 4(a, b).

between the ACE-1 shipboard SO$_2$ measurements and those at Cape Grim. However, ACE-1 aircraft measurements and the Baring Head measurements are higher than those measured at the surface during ACE-1 or at Cape Grim. Once again differences between aircraft measurements and ground or shipboard measurements are probably a result of analytical/calibration bias, spatial variability, incomplete vertical mixing or sampling bias. Incomplete mixing would not only result in more complete oxidation of DMS in the upper layer but would also result in less rapid loss of SO$_2$ to the sea surface and near-surface seasalt aerosols. Both would result

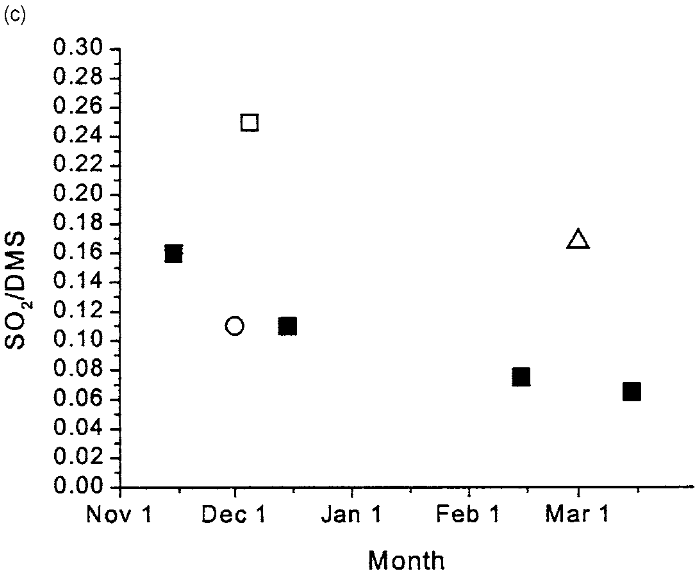

Figure 4(c).

Figure 4. (a) All recent DMS measurements made over the Southern Ocean during Summer. The error bars are one standard deviation of the mean. (b) All recent SO_2 measurements made over the Southern Ocean during summer. The error bars are one standard deviation of the mean. (c) Average SO_2/DMS ratios. In all figures: closed squares = Cape Grim, Ayers *et al.* (1997); open squares = ACE-1 C-130, Shon *et al.* (2001); open circle = ACE-1 R/V Discoverer, de Bruyn *et al.* (1998); open triangle = Baring Head, this work.

in higher SO_2 levels in the upper layer. Given that SO_2 has a maximum during the day, preferential daytime sampling would also tend to result in a higher average SO_2 level. Differences between ground based observations are probably a result of instrumental bias or spatial variability.

The quoted measurement uncertainties of the various instruments used in these studies is in the range of 10–20%. For the most part these uncertainties have been confirmed by formal instrument intercomparisons of sulfur gas measurement techniques (Hoell *et al.*, 1993; Stecher *et al.*, 1996). However, these intercomparisons were generally carried out with the instruments operating well above their detection limits. This is particularly true for SO_2. The uncertainties for SO_2 could be larger at the very low levels (<10 ppt) encountered in these studies. Whether these differences in measured levels are real or a result of analytical bias, they often result in significant differences in average SO_2/DMS levels between different studies (Figure 4(c)) which in turn often results in significant differences in estimated SO_2 yields, particularly when the estimate is based on average values.

3.3. DIURNAL VARIABILITY

DMS and SO_2 levels should exhibit a consistent anti-correlated diurnal variation in a clean, marine boundary layer. If DMS is oxidized predominantly by OH radicals, then DMS levels should decrease during the day as OH levels increase, reaching a minimum in the late afternoon. When OH levels drop during the night DMS levels should increase reaching a maximum in the early hours of the morning. Conversely, SO_2 levels should increase during the day as OH levels increase and should decrease at night when OH levels decrease. The overall levels and rate of change of DMS and SO_2 levels reflect the magnitude of all the DMS and SO_2 production and destruction processes and therefore contain useful information about these processes. For example, the rate of increase in DMS levels during the night is simply the sea-air DMS flux/boundary layer depth minus the loss of DMS via the vertical exchange of air between the boundary layer and overlying air.

Because of the frequent occurrence of frontal passages, and associated wind shifts, the Southern Ocean is not an ideal location for diurnal studies. However, during this deployment anti-correlated diurnal variability was often observed in clean Southern Ocean air. Figure 5 shows anti-correlated DMS and SO_2 levels for periods of 10–18 hours on days 50, 53 and 61. Instabilities associated with wind transitions prevented the observation of diurnal cycles for longer periods of time. However, a complete 24 hour diurnal cycle is clearly observable if all the clean air is averaged into a single day (Figure 6). The averaged DMS_{max}/DMS_{min} is 1.9 and the averaged SO_{2max}/SO_{2min} is 4. This compares reasonably well with previous observations in the region. Ayers *et al.* (1995) reported an averaged DMS diurnal cycle for December 1993 at Cape Grim with a DMS_{max}/DMS_{min} ratio of 1.7. Wylie and De Mora (1996) observed DMS diurnal cycles at Leigh, New Zealand with DMS_{max}/DMS_{min} ratios of 1.2, 1.5 and 1.7 for the months of March, September and November, respectively. During ACE-1, a DMS_{max}/DMS_{min} ratio of 2 was observed in boundary layer measurements made on a single day by the C-130 aircraft (Mari *et al.*, 1999). There are fewer reports of measured SO_2 diurnal cycles over the Southern Ocean. The ACE-1 aircraft study found a SO_{2max}/SO_{2min} of 3.5 (Mari *et al.*, 1999). The ACE-1 shipboard study reported ratios of 2 on day 338 and 4 on days 339 and 340 (de Bruyn *et al.*, 1998).

3.4. MODEL SIMULATIONS AND SULFUR DIOXIDE YIELDS

Sulfur dioxide yields and total sinks have been estimated from the data in Figure 5 using a non-photochemical Lagrangian mass balance approach, described in detail by Bandy *et al.* (1996), and using a photochemical box model. In the non-photochemical approach SO_2 yields and sinks are determined directly from the observed DMS and SO_2 rates of change. Resultant SO_2 sinks, corresponding lifetimes and yields are given in Table I. The sinks and lifetimes assume that the concentration of SO_2 above the boundary layer is 30 ppt, the vertical exchange rate is 0.5 cm s^{-1} and the boundary layer height is 1 km. These lifetimes, ranging

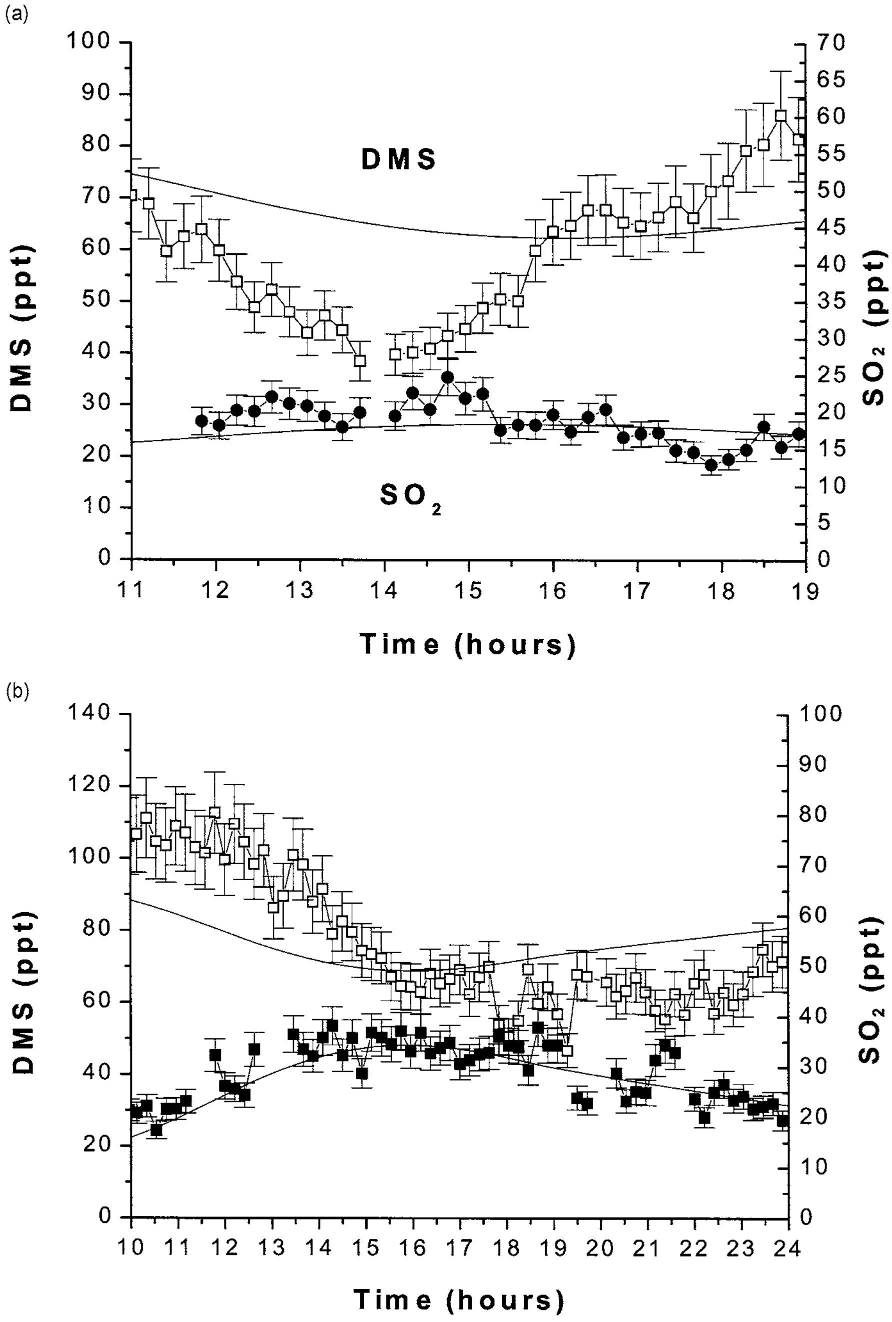
(a)
DMS
SO2
DMS (ppt)
SO₂ (ppt)
Time (hours)
0
10
20
30
40
50
60
70
80
90
100
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
11
12
13
14
15
16
17
18
19
(b)
DMS (ppt)
SO₂ (ppt)
Time (hours)
0
20
40
60
80
100
120
140
0
10
20
30
40
50
60
70
80
90
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Figure 5(a, b).

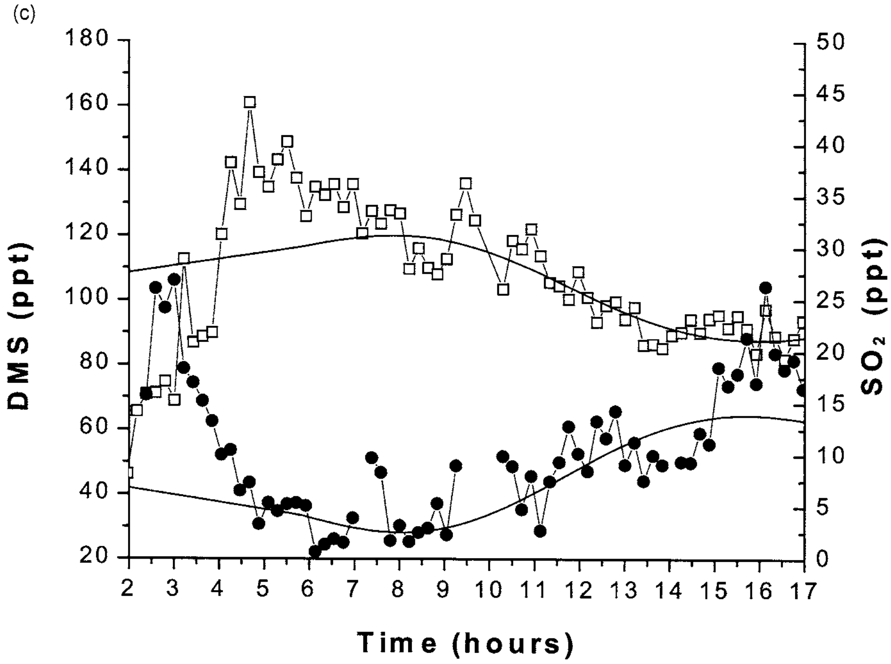

Figure 5(c).

Figure 5. Measured DMS and SO_2 level on days (a) 50, (b) 53, and (c) 61. DMS = open squares; SO_2 = filled circles.

from 5 to 18 hours, are relatively consistent with previous estimates in this region. Mari *et al.* (1999) estimated the SO_2 lifetime to be 11 hours and de Bruyn *et al.* (1988) estimated the lifetime to be 8–10 hours and 12–16 hours for two different days in 1995. Estimated SO_2 yields are 29 ± 6%, 43 ± 11% and 20 ± 10% for days 50, 53 and 61, respectively. If the vertical exchange rate was zero the SO_2 sinks would decrease by approximately 13%, 1% and 8% for days 50, 53 and 61, respectively. Conversely the lifetimes would increase by the same amount. The quoted uncertainties are based on the uncertainty of fits to the observed rates of change.

The photochemical box model simulates the photochemistry of the boundary layer using a multi-stream radiation code, 11 photolysis reactions and 140 thermal reactions (Yvon and Saltzman, 1993; Yvon *et al.*, 1996). Input parameters used to simulate the three days shown in Figure 5 are given in Table II. The boundary layer height and vertical exchange rate were initially assumed to be 1 km and 0.5 cm s^{-1}, respectively, and concentrations of DMS and SO_2 were assumed to be 0 and 30 ppt, respectively, in the free troposphere (FT) or buffer layer (BuL). Model generated OH levels reach a maximum of 2–4 × 10^6 molec cm^{-3} at noon. While there is no

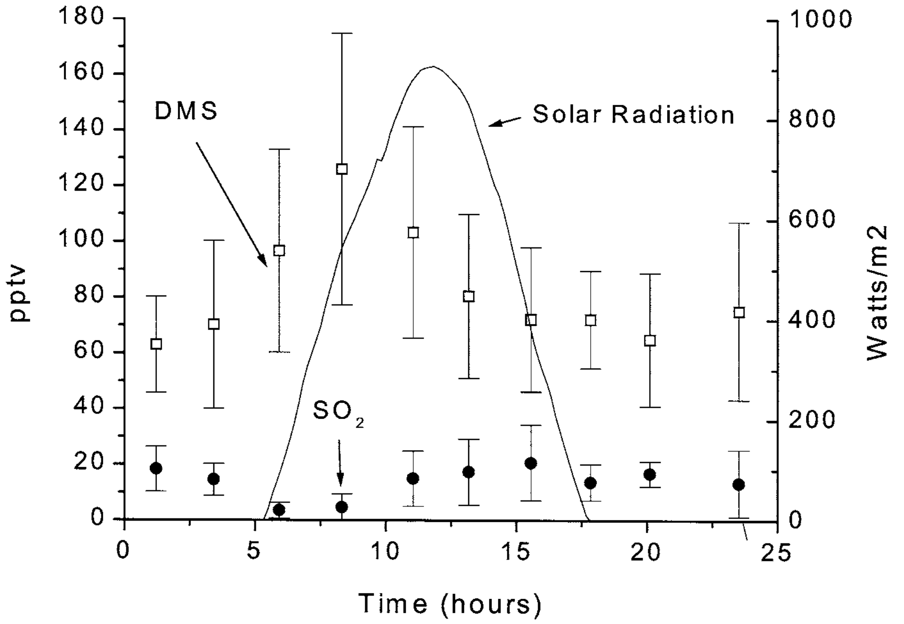

Figure 6. All southerly DMS and SO_2 measurements averaged into hourly bins over a single day. The error bars represent one standard deviation of the mean. The solid line is a plot of solar radiation for Julian Day 52.

Table I. Model output

Day	SO_2 sink (mol cm^{-3} s^{-1})	SO_2 lifetime (hours)	SO_2 yield (%)	Analysis
50	10837 ± 1604	15 ± 2.2	29 ± 6	Derivative
53	12092 ± 967	18 ± 1.4	43 ± 14	Derivative
61	25099 ± 3249	4.5 ± 0.6	20 ± 10	Derivative
50	9000 ± 3000	14 ± 4.6	60 ± 30	Photochemical model
53	19500 ± 4000	11 ± 2.3	100 ± 20	Photochemical model
61	13000 ± 3000	10 ± 2.4	40 ± 10	Photochemical model

direct observational data to compare this with the model does reproduce OH levels measured in this region during ACE-1 reasonably well (Mauldin *et al.*, 1998).

For all three days two sets of simulations were run. First the DMS sources and sinks were adjusted until the model reproduced the average observed DMS levels. Then SO_2 sources and sinks were adjusted until the model reproduced the observed SO_2 levels. With negligible DMS in the FT/BuL, the sea-air DMS

Table II. Input parameters for photochemical model calculations

Parameter				Source
Day	50	53	61	
Latitude	40° S	40° S	40° S	
Temperature (C)	14.6	14.4	16.4	NIWA
Pressure (mbars)	1014	1019	1017	NIWA
Relative humidity (%)	76	72	87	NIWA
O_3 (ppb)	11.2	15	13.7	NIWA
CO (ppb)	60	60	60	Koga and Tanaka (1993)
CH_4 (ppm)	1.63	1.63	1.63	Koga and Tanaka (1993)
Total O_3 (mmol m^{-2})	320	320	320	Spivakowsky *et al.* (1990)
Free trop SO_2 (pptv)	30	30	30	Mari *et al.* (1999)
Free trop DMS (pptv)	0	0	0	Mari *et al.* (1999); Blake *et al.* (1999)
Entrainment (cm s^{-1})	0.5	0.5	0.5	Estimated
NO_x (pptv)	20	20	20	R/V Discoverer ACE-1
Boundary height (km)	1	1	1	Estimated

flux is the only source of DMS. DMS is oxidized by OH radicals and is lost to the FT/BuL. Assuming an entrainment rate of 0.5 cm s^{-1} and a boundary layer height of 1 km, approximately 1/3 of the DMS entering the boundary layer is lost to the FT/BuL. SO_2 is produced from DMS oxidation and can be entrained into the boundary layer from above if the levels of SO_2 in the FT/BuL are relatively high. Assuming a concentration of 30 ppt above the boundary layer, a relatively small amount of SO_2 is transported downwards into the boundary layer. SO_2 losses include sea-salt scavenging, in-cloud oxidation, dry deposition to the ocean surface and gas-phase oxidation by OH. In this modeling exercise, the primary objective was to determine SO_2 yields from DMS oxidation. Therefore, the total SO_2 loss rate has been adjusted rather than individual SO_2 sinks. The solid lines in Figure 5 are model produced DMS and SO_2 levels. SO_2 yields and sinks required to produce these levels are given in Table I.

Sea-air DMS fluxes of 3.5, 5.5 and 4.3 μmol m^{-2} d^{-1} were required to support the average DMS levels observed on days 50, 53, and 61, respectively. This is consistent with current flux estimates for this region. Seawater DMS measurements suggest that the sea-air DMS flux at 40° S is about 5 μmol m^{-2} d^{-1} in summer with an uncertainty of a factor of 2 (Erickson, 1990; Bates *et al.*, 1992). Ayers *et al.* (1995) estimate that the DMS flux required to support the observed levels of atmospheric DMS at Cape Grim in February and March is 3.8 and 2.2 μmol m^{-2} d^{-1} respectively with an uncertainty of a factor of 1.5. While the model reproduces the average DMS levels reasonably well, it does not reproduce the amplitude of the observed DMS diurnal cycle. In general, the amplitude of the observed DMS cycle is larger than the amplitude of the model generated cycle, particularly on days 50 and 61. The amplitude of the model produced diurnal cycle can be increased by increasing the DMS oxidation rate. Similar observations have been made in several previous attempts to reproduce observed DMS diurnal cycles with this and other photochemical models (Suhre *et al.*, 1995; Yvon *et al.*, 1996; Chin *et al.*, 1996, 1998). Chin *et al.* (1996, 1998) had to increase the DMS oxidation rate by a factor of two in a global model to simulate DMS profiles measured at a number of different sites around the world. Increasing the oxidation rate by a factor of two would require a 50–60% larger DMS sea-air flux to support the observed levels.

The model simulates the average SO_2 levels reasonably well with total SO_2 sinks of $0.9 \pm 0.3 \times 10^4$, $1.9 \pm 0.4 \times 10^4$ and $1.3 \pm 0.3 \times 10^4$ molec cm^{-3} s^{-1} and SO_2 yields of $50 \pm 30\%$, $100 \pm 20\%$ and $40 \pm 10\%$ for days 50, 53 and 61, respectively. These sinks correspond to lifetimes of 14 ± 5, 11 ± 2 and 10 ± 2 hours, respectively. Overall the model also reproduces the observed diurnal variability reasonably well. The only exception is on day 61 where the nighttime loss of SO_2 is clearly larger than that produced by the model. Increasing the SO_2 sink would require increasing the SO_2 yield to maintain the overall average SO_2 level.

SO_2 sinks and lifetimes determined from the photochemical model are reasonably consistent with earlier estimates and the non-photochemical analysis above. However, SO_2 yields are clearly higher than those determined directly from the rates of change of the observed DMS and SO_2. This is primarily due to the photochemical model underestimating the amplitude of the DMS diurnal cycle. In the non-photochemical approach, the DMS oxidation rate is defined by the observed DMS cycle. Increasing the oxidation rate in the photochemical model by a factor of two would improve the agreement between model and observations and would decrease the SO_2 yield by a factor of two, a result which is more consistent with the mass balance analysis.

A number of simulations were carried out to test the sensitivity of the air-sea flux, SO_2 sink and SO_2 yield to changes in the estimated parameters. Increasing the boundary layer height from 1 km to 1.5 km increased the air-sea flux by 33% and did not change the yield or SO_2 loss rate significantly. Decreasing the boundary layer height to 0.5 km decreased the DMS flux by 32% and had no impact on the SO_2 sink or SO_2 yield. Decreasing the NO_X levels from 20 to 10 ppt decreased the DMS flux by 9%, decreased the total SO_2 loss rate by 14% and did not change the yield significantly. Increasing the entrainment rate from 0.5–0.8 cm s^{-1} increased the air-sea flux by 20%, increased the SO_2 yield by 6% and had little impact on the SO_2 sink. Decreasing the entrainment rate to 0.2 cm s^{-1} decreased the DMS flux by 19%, decreased the SO_2 yield by 2% and had no impact on the SO_2 sink.

The SO_2 yield and SO_2 sink uncertainties quoted above are based on the uncertainty of the fit of the model to the data. These uncertainties clearly dominate any contribution from the estimated boundary layer height and entrainment rate. The largest source of uncertainty to the yield is clearly the fit to the DMS profile. If the amplitude of the DMS diurnal cycle is allowed to define the DMS oxidation rate, then yields are at least a factor of two lower than yields estimated with photochemical model produced OH levels and the Hynes *et al.* (1986) rate constant. The entrainment rate estimate, boundary layer height estimate and the DMS profile fit all have a significant impact on the DMS flux used, resulting in an overall uncertainty on the DMS flux of approximately a factor of two. However, given the equally large uncertainties associated with current flux estimates, the fluxes used are reasonable.

3.5. PREVIOUS YIELD ESTIMATES

Each of the data sets shown in Figure 4 have been used at least once in studies attempting to model DMS oxidation chemistry. Ayers *et al.* (1997) used a yield of 15% to simulate the monthly averaged DMS and SO_2 levels observed at Cape Grim. De Bruyn *et al.* (1998) estimated the yield to be 30–50% for measurements made on the R/V Discoverer during ACE-1. Mari *et al.* (1999) estimated the SO_2 yield to be 60, 71 and 74% for the three C-130 flights (24, 25 and 26) of Lagrangian B during ACE-1. Shon *et al.* (2001) determined the yield to be 70% based on 16 ACE-1 C-130 boundary layer flights. Using a global model, Chin *et al.* (2000) required a yield of 90% to simulate both ACE-1 data sets.

Figure 4(c) is a plot of average SO_2/DMS ratios from all recent studies. The higher yields determined by Mari *et al.* (1999), Shon *et al.* (2001) and Chin *et al.* (2000) are all associated with the high SO_2/DMS ratios observed by the C-130 aircraft during ACE-1. This suggests that differences in measured levels are at least partly responsible for differences in estimated yields. However, some of the differences in SO_2 yields are directly traceable to specific differences in modeling assumptions or approach. For example, there is very little difference between the average Cape Grim levels and the measurements made on the R/V Discoverer during ACE-1, yet the yield estimated by de Bruyn *et al.* (1998) is significantly higher than that used by Ayers *et al.* (1997) to model the Cape Grim data set. Ayers *et al.* (1997) fixed the yield at 15% and treated the entrainment of SO_2 from the free troposphere as an adjustable parameter. De Bruyn *et al.* (1998) assumed the entrainment of SO_2 was negligible and treated the yield as an adjustable parameter. Had Ayers *et al.* (1997) also assumed that there was no SO_2 entering the boundary layer from above they would have required a yield of $\sim$30% to support the observed SO_2 mixing ratios. This result would be relatively consistent with the yield estimated by de Bruyn *et al.* (1998). Similarly, since the Chin *et al.* (2000) yield estimate is based on the same data as the estimates made by de Bruyn *et al.* (1998), Mari *et al.* (1999) and Shon *et al.* (2000), differences in resultant yields are probably related to differences in modeling approach or assumptions. It is not clear at this point what those differences are. Chin *et al.* (2000) suggest that their higher yields were probably a result of using higher entrainment rates. With negligible SO_2 in the free troposphere, higher entrainment rates result in larger SO_2 loss rates requiring larger yields to support observations. In the de Bruyn *et al.* (1998) and

Mari *et al.*, (1999) studies, the total SO_2 loss rate was constrained by the amplitude of the observed SO_2 diurnal cycle.

Perhaps most importantly yield estimates are a function of the choice of DMS oxidation rate. Yields derived here are consistent with the work of Ayers *et al.* (1997) and de Bruyn *et al.* (1998) assuming a DMS oxidation rate suggested by the DMS diurnal profile. However, yields derived here would be more consistent with the higher yields determined by Mari *et al.* (1999) and Shon *et al.* (2000) if an oxidation rate based on model-derived OH levels and DMS + OH kinetics is used. Given the numerous times that observed DMS diurnal cycles have suggested that the DMS oxidation rate may be higher than defined by model-calculated OH and DMS+OH kinetics (Hynes *et al.*, 1986), there is clearly uncertainty associated with the DMS oxidation rate. This uncertainty should be included in the yield estimate. Yield estimates that are based on average data where oxidation rates are not constrained by DMS diurnal profiles have no way of assessing the uncertainty in the oxidation rate and should probably be treated with caution. The DMS oxidation rate was constrained by a DMS diurnal cycle in only two of the previous studies; Mari *et al.* (1999) and Ayers *et al.* (1997). Mari et. al. (1999) found the same level of agreement between observed DMS levels and model output with and without an enhanced oxidation rate. Their yield estimate is based on the ‘normal’ lower oxidation rate. Ayers *et al.* (1997) did not require an enhanced oxidation rate to model the DMS diurnal cycle observed at Cape Grim. However, the OH levels produced by the model in the Ayers *et al.* (1997) study are considerably higher than produced by our photochemical model.

4. Conclusions

The results of this study at Baring Head, New Zealand, and examination of previous measurements and modeling efforts to determine the yield of SO_2 from DMS oxidation, suggest the following:

1. There are significant differences in observed SO_2/DMS ratios between recent Southern Ocean data sets. These differences are at least partly responsible for differences in estimated SO_2 yields. Existing instrument intercomparisons are not adequate to determine whether these differences are due to instrumental bias.
2. There are also differences in yields among various studies resulting from different model assumptions. The DMS oxidation rate appears to be most critical. In this and several previous field studies, utilizing observed diel variations to obtain oxidation rates results in a higher oxidation rate than using a rate calculation based on photochemical model-generated OH and the currently accepted rate constant (Hynes *et al.*, 1986). This difference is larger than predicted based on the estimated uncertainties of the OH calculations and probably reflects either an underestimation of the rate constant or the presence of other atmospheric oxidants. In either case, the uncertainty in determining the DMS

oxidation rate should be included when estimating the yield of SO_2. Studies which utilize only mean DMS and SO_2 concentrations have no independent basis for evaluating this uncertainty.

3. At Baring Head, New Zealand, anti-correlated DMS and SO_2 diurnal cycles were observed in the clean air data which are consistent with the production of SO_2 from DMS + OH oxidation. Assuming a DMS oxidation rate implied from the observed diurnal amplitude, simulations suggest that the yield of SO_2 is significant, ranging from 20–40%. This yield is smaller than recent tropical estimates and therefore implies that the yield of SO_2 decreases with latitude. If the DMS oxidation rate is obtained from photochemical model-derived OH and the Hynes *et al.* (1986) rate constant is assumed, then the SO_2 yield would be in the range of 50–100%, similar to tropical estimates and suggesting very little variation in yield with latitude.

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