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DMS and SO_2 Measurements in the Tropical Marine Boundary Layer

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Abstract. Dimethyl sulfide (DMS) and sulfur dioxide (SO_2) mixing ratios were measured in the boundary layer on Oahu, Hawaii in April and May 2000. Average DMS and SO_2 levels were 22 ± 7 ($n = 488$) pmol/mol and 23 ± 7 ($n = 471$) pmol/mol respectively. Anti-correlated DMS and SO_2 diurnal cycles, consistent with DMS + OH oxidation were observed on most days. Photochemical box model simulations suggest that the yield of SO_2 and total SO_2 sink are $\sim$85% and $\sim 2 \times 10^4$ molec cm^{-3} s^{-1} respectively. On several days the rate of decrease in DMS and increase in SO_2 levels in the early morning were larger that predicted by the model. Dynamical and chemical causes for the anomalous early morning data are explored.

Key words: dimethyl sulfide, dynamics, halogens, marine boundary layer, oxidation

1. Introduction

The atmospheric oxidation of dimethylsulfide emitted from the sea surface is an important process in the formation of sulfate aerosols in marine air. Both laboratory and field research efforts have been directed at elucidating the reaction mechanism and product distributions, but our understanding is far from complete. In marine air, DMS oxidation is initiated primarily by the OH radical. In polluted air, the nitrate radical is also believed to contribute significantly to DMS oxidation at night. Several workers have suggested that halogen radicals (Cl, ClO, Br, BrO) also contribute significantly to DMS oxidation (Keene *et al.*, 1996, 1990; Pszenny *et al.*, 1993; Chin *et al.*, 1996, 1998). The evidence for oxidation via halogen radicals is largely indirect, consisting of model calculations and estimates derived from hydrocarbon measurements (Vogt et al., 1996; Sander and Crutzen, 1996; Jobson *et al.*, 1994, Wingenter *et al.*, 1996). Direct observation of Cl_2 in coastal air has been reported, at levels which suggest that Cl radical chemistry should occur (Spicer *et al.*, 1998).

The diurnal cycle of DMS in marine air can also provide indirect insight into the oxidation process. Several previous studies have demonstrated that the diurnal cycle of DMS in clean marine air exhibits late afternoon minimum and early morning maximum expected for a well-mixed boundary layer with a sea surface DMS source and daytime oxidation by OH (Andreae *et al.*, 1995; Bandy *et al.*, 1996, Yvon *et al.*, 1996). Although previous modeling studies have shown that the amplitude of the diel cycle is larger than predicted using the currently accepted rate constant for DMS + OH (Hynes *et al.*, 1986), the phase and shape of the observed diel profiles in earlier studies is consistent with OH as the principle oxidant of DMS in clean marine air.

In this study we present measurements of DMS and SO_2 mixing ratios made in the remote marine boundary layer. Anti-correlated diel cycles, generally consistent with a DMS + OH oxidation process were observed on most days. The phase and shape of the cycles suggest a second chemical or dynamical process occurring in the early morning. The cycles are compared to the output from a photochemical box model to estimate the DMS flux, SO_2 yields, the total SO_2 sink and to explore whether the second process is chemical or dynamical.

2. Methods

2.1. FIELD SITE LOCATION AND METEOROLOGY

Measurements were carried out in the North Pacific trade winds at the University of Hawaii's atmospheric research station at Bellows Air Force Base on Oahu during the period of April 20–26, 2000. The site is located on the eastern side of the island on a sandy stretch of beach in Waimanalo Bay. The instrument was housed in a van immediately below the site-sampling tower, which was located approximately 7 m from the high tide mark. The air inlet was positioned on the tower at a height of 13 m. The site experienced clean trade winds off the ocean for the entire sampling period. Back trajectory calculations suggest that the sampled air originated over the North Pacific Ocean and did not pass over any significant land mass.

2.2. ANALYSIS OF DMS AND SO_2

Atmospheric DMS and SO_2 were measured using a gas chromatograph with mass spectrometric detection (GC/MS). An isotope dilution technique was used, in which a stable isotopically labeled isotopomer of each analyte ($^{12}C_2H_3{}^{32}S^{12}C^2H_3$ and $^{34}SO_2$) is added to the air stream prior to sampling. This provides an internal standard and compensates for losses in the process of sample preconcentration and analysis. This technique has been used extensively in ground-based and aircraft studies (Bandy *et al.*, 1993; Thornton *et al.*, 1996; Bandy *et al.*, 1996, De Bruyn *et al.*, 2001), and has been evaluated in two formal instrument intercomparisons (Hoell *et al.*, 1993, Stecher *et al.*, 1996). Details of the system and its performance are given in De Bruyn *et al.* (2001). In brief, air is drawn through two traps, one for DMS and one for SO_2, held at liquid argon temperatures to pre-concentrate the samples. The air streams are spiked with the isotopically labeled standards and then dried and scrubbed of oxidants prior to reaching the traps. During this experiment two-liter samples were trapped every 8 minutes. The cryo-traps are resistance heated and injected onto the GC/MS columns for analysis. The estimated lower limit of detection is 3–5pmol/mol and the accuracy and precision of measurements is better than ±10% and ±5% respectively.

2.3. MODELING

A time-dependent photochemical box model has been used to simulate the observed DMS and SO_2 diel cycles. The model simulates the photochemistry of the boundary layer using a multi-stream radiation code, 11 photolysis reactions and 140 thermal reactions (Yvon *et al.*, 1996). Input parameters were taken from measurements made at the site (temperature, relative humidity), the literature (ozone, methane) or long-term observations made at Cape Kumukalu (CMDL) on the island of Hawaii (column ozone, carbon monoxide). In all simulations the column ozone and carbon monoxide levels were set at 280 Dobson Units and 130 ppb respectively. Boundary layer ozone levels were estimated from Logan (1996) to be 30 ppb and methane levels were estimated from Koga and Tanaka (1993) and Spivakovsky *et al.* (1990) to be 1.7 ppb. In these simulations, NOx was conserved, and held at 20 pmol/mol. The average temperature and relative humidity measured at the site were 24 °C and 70% respectively. DMS and SO_2 levels above the boundary layer were assumed to be 0 and 60 pmol/mol respectively and the boundary layer height and entrainment rate were assumed to be 1 km and 0.5 cm s^{-1} respectively. The model only considers loss of DMS via OH, NO_3 oxidation and entrainment into the layer above. SO_2 is produced in the model from NO_3 oxidation, OH oxidation of DMS, entrainment from above, and is lost via heterogeneous processes and OH oxidation. The DMS flux, yield of SO_2 from DMS oxidation and total SO_2 sink are adjustable parameters.

3. Observations and Analysis

Three days of DMS and SO_2 measurements (days 111, 112 and 115) are shown in Figure 1. DMS levels reached maxima of 30–35 pmol/mol in the early morning and minima of 10–15 pmol/mol in the late afternoon. SO_2 reached maxima of 30–35 pmol/mol in the late afternoon and minima of 10–15 pmol/mol in the early morning. The observed diel patterns and anticorrelation of the two compounds is expected if DMS is emitted from the sea surface continuously, and is oxidized photochemically during daylight hours. The diel amplitude of DMS may be damped by nighttime oxidation by NO_3 radicals (Andreae *et al.*, 1995), but in low NO_x environments like Hawaii, this is a minor effect. By contrast, SO_2 is produced via DMS oxidation during the day, and is lost principally by heterogeneous deposition (to clouds, aerosols, and the sea surface). Heterogeneous loss of SO_2 is not believed to vary on a diel basis.

Also shown in the figure are model-produced DMS, SO_2 and OH levels. The DMS flux in the model was adjusted until the simulated DMS profile best matched

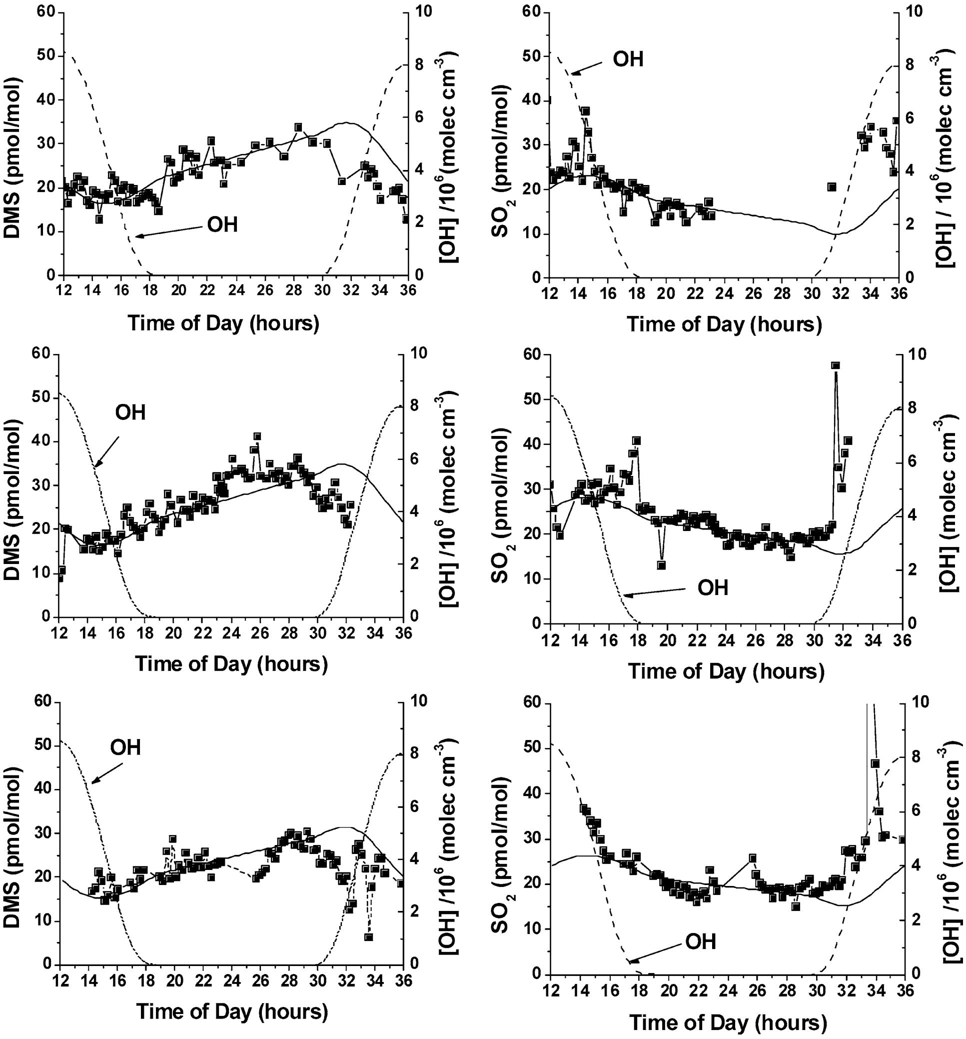

Figure 1. Observed (squares) and model produced (solid line) DMS and SO_2 levels for days 111, 112 and 115. The solid lines are simulated DMS and SO_2 profiles. The dashed lines are model produced OH levels.

the observed DMS levels, then the SO_2 production efficiency and total SO_2 sink were adjusted until the model best reproduced the observed SO_2 levels. The DMS fluxes, SO_2 sinks and SO_2 yield used to simulate the observed DMS and SO_2 levels are given in Table I. In order to reproduce the amplitude of the observed DMS diurnal cycle the oxidation rate in the model had to be increased by a factor of 1.75. Similar observations have been made in several previous attempts to reproduce dimethyl sulfide diurnal cycles with photochemical models (Suhre *et al.*, 1995; Yvon *et al.*, 1996; Chin *et al.*, 1996,1998). Explanations put forward for this inability to model

Table I. Parameters used to simulate DMS and SO_2 levels on days 111,112 and 115

Day	DMS flux μmol m^{-2} day^{-1})	SO_2 sink ($\times 10^4$molec cm^{-3} s^{-1})	SO_2 yield (%)	SO_2 lifetime (hours)
111	3.0 ± 0.2	1.9 ± 0.15	85±10	11
112	3.0 ± 0.1	1.9 ± 0.15	85±10	11
115	2.6 ± 0.2	1.6 ± 0.10	85±10	13

DMS diurnal variability include unknown DMS oxidation processes, underestimating diurnal variability in vertical mixing and underestimating OH levels. The DMS flux values are similar to those estimated by Bates *et al.* (1987) for this region and total SO_2 sinks and SO_2 yields are consistent with those reported by Bandy *et al.* (1996) and Davis *et al.* (1999) for the tropical Pacific Ocean.

The uncertainties given in Table I reflect only the uncertainty in the fit of the model to the data. Simulations were carried out to test the sensitivity of the DMS flux, SO_2 sink and SO_2 yield to changes in the assumed parameters. With a boundary layer height of 1.5 km the DMS flux had to be increased by 38% and the SO_2 sink had to be decreased by 10% to balance sources and sinks. The SO_2 yield did not change. Decreasing the entrainment rate to 0.3 cm s^{-1} increased the DMS flux by 31%, decreased the SO_2 sink by 10% and also did not change the yield significantly. Decreasing the NO_x level to 10pmol/mol decreased the flux by 11%, and decreased the SO_2 sink by 9%. Simulations were also carried out without increasing the oxidation rate in the model. With a normal oxidation rate the model would require a 20% lower DMS flux and a 50% higher SO_2 yield in order to support the observations. However, the overall quality of the DMS fit to the data deteriorates. The uncertainty in the DMS flux is controlled by the uncertainties in entrainment rate, boundary layer height and DMS oxidation rate. Uncertainties in the SO_2 sink are relatively small and are controlled by the uncertainty in boundary layer height, entrainment rate, NO_x level and goodness of fit to the data. The overall uncertainty in the SO_2 yield is fairly large and is dominated by the uncertainty in the DMS oxidation rate.

On most days during this study, there was a significant discrepancy between measurements and model simulations at sunrise. The observed DMS mixing ratio decreases earlier in the morning than the model produced DMS levels. Conversely, the observed SO_2 mixing ratios increase earlier in the morning than predicted by the model. The assumed or adjustable parameters in the model have little impact on these differences. There are two possible types of explanations for the anomalous early morning observations, dynamical and photochemical. A dynamical explanation would require the dilution of the boundary layer with DMS-free air containing SO_2. Such air presumably exists aloft, above the boundary layer, where DMS has

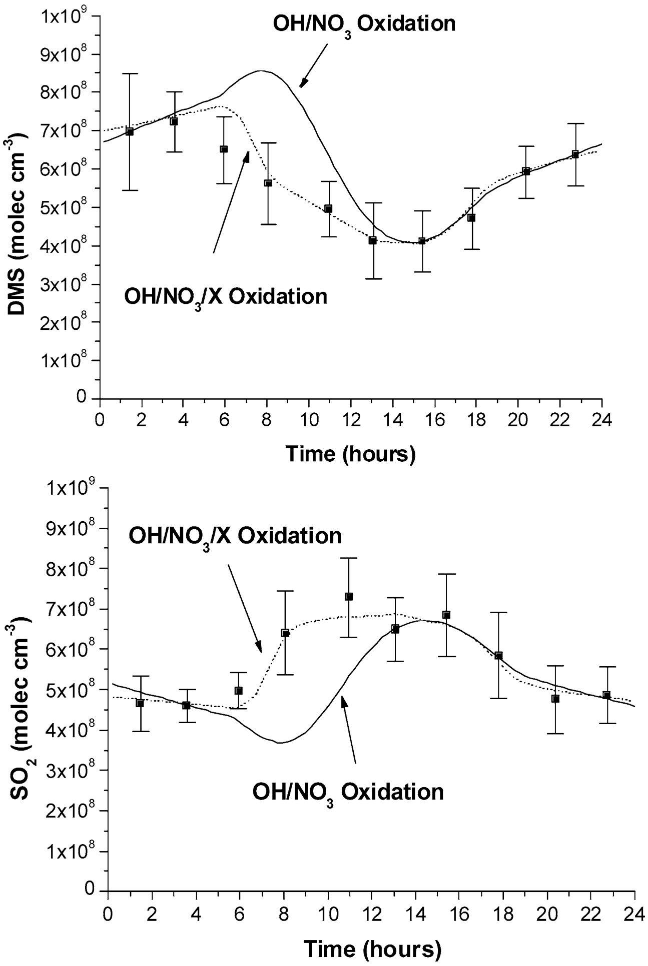

Figure 2. Composite diurnal cycles of DMS and SO_2 at Oahu, Hawaii, produced by 1-hr binning of the data in Figure 2. The error bars are one standard deviation of the mean. The solid line is a best-fit model simulation. The dashed line in (a) is a best fit to the data (see text). The dashed line in (b) is a model simulation assuming all the DMS lost via X produces SO_2 (see text).

been largely or completely oxidized to SO_2 and other products. A photochemical explanation requires the presence of an oxidant other than OH, having a different diel profile favoring morning oxidation. The most likely candidates are halogen radicals.

To determine the magnitude of the anomalous early morning DMS loss, the DMS and SO_2 measurements from 3 days (Figure 1) were averaged into hourly bins over a single 24-hour period (Figure 2). The solid lines are best-fit model simulations obtained with a DMS flux of 3 μmol m^{-2} day^{-1}, a total SO_2 sink of 1.9×10^4 molec cm^{-3} s^{-1} and an SO_2 production efficiency of 85%. The dashed

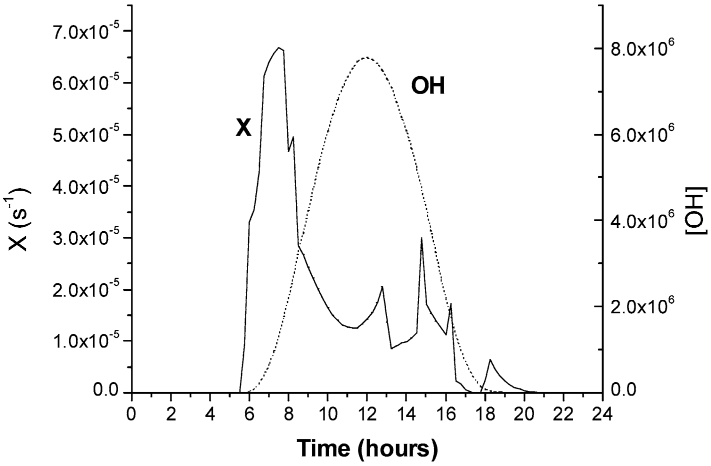

Figure 3. Diel pattern of additional process needed to simulate the DMS profile at Oahu.

line in Figure 2a is a best fit to the data. An estimate of the anomalous DMS loss rate X (s^{-1}) was obtained by evaluating the following finite difference expression for the observed DMS over the 24 hour cycle:

$$\begin{aligned}\mathrm{DMS}_{i+\Delta t} = {} & \mathrm{DMS}_i + F_{\mathrm{DMS}}\Delta t - \mathrm{DMS}_i(k_{\mathrm{OH}}\mathrm{OH}_i \\ & + k_{\mathrm{no3}}\mathrm{NO3}_i + X_i + V_{ex}/\mathrm{BLH})\Delta t\end{aligned}$$

Here, F_{DMS} is the sea-air DMS flux, V_{ex} is the entrainment rate and BLH is the boundary layer height. DMS_i, OH_i, and $\mathrm{NO3}_i$ are the concentrations of the different species at time i and $\mathrm{DMS}_{i+\Delta t}$ is the DMS concentration at time $i + \Delta t$. X is the first order rate constant for the anomalous DMS loss process. The resultant diel variation in X is shown in Figure 3. X reaches a maximum of ~6.5×10^{-5} s^{-1} in the early morning then decreases to insignificant rates at night.

If the early morning DMS loss is caused by an unknown radical oxidant, then X can be expressed as a second order rate coefficient and a radical concentration (k (radical)). Of the halogen radicals Cl, ClO, Br, BrO, only Cl and BrO seem likely to have an impact on the lifetime of DMS in the boundary layer. Br reacts with DMS to form a DMS-Br adduct which decomposes thermally too rapidly for this pathway to be important in the boundary layer (Nakano *et al.*, 2001). Similarly the DMS + ClO reaction rate is believed to be too slow for ClO to be important unless ClO levels are very high (Finlayson-Pitts and Pitts, 1999).

The dashed line in Figure 2b is obtained assuming that all the DMS lost via the oxidation process X produces SO_2. Overall the agreement with observations is reasonably good suggesting that if the differences between model and observation are a result of reaction with an unknown oxidant then the reaction produces SO_2 with near unit efficiency. Neither BrO nor Cl is expected to do this (Pitts and Pitts, 2000 and references therein). BrO+DMS produces DMSO + Br with a yield of almost 1 (Bedjanian *et al.*, 1996). The Cl+DMS reaction is expected to proceed via both an abstraction pathway to produce CH_3SCH_2+HCl and an addition pathway to produce the CH_3SCH_3Cl adduct with equivalent yields (Stickel *et al.*, 1992) and the CH_3SCH_2 pathway is not expected to produce SO_2 with unit efficiency (Yin *et al.*, 1990). While there are numerous assumptions and adjustable parameters in these calculations it is difficult to produce a yield significantly lower than 100%.

If the early morning decrease in DMS is caused by air being mixed down into the boundary layer at sunrise then the loss rate constant X can be expressed as an entrainment velocity, where $X = V_{ex}[(DMS_{ft}/DMS)-1]/BLH$ and DMS_{ft} is the mixing ratio of DMS above the boundary layer. Assuming that $DMS_{ft} = 0$, a minimum V_{ex} of 6.6 cm s^{-1} is required to support the observations. For $DMS_{ft} > 0$ a larger entrainment velocity would be required to explain the observations. The required entrainment velocity is inversely proportional to the assumed boundary layer height. A boundary layer of ~100 m would be required to obtain exchange rates typically associated with the trade wind regime. It is difficult to determine conclusively whether an early morning mixing event is responsible for the observed changes in dimethyl sulfide and sulfur dioxide mixing ratios with out an independent chemical tracer of atmospheric dynamics. However, the above calculations suggest that it is the most likely explanation. It is also possible that some combination of the above two processes is responsible but an assessment of the likelihood is beyond the scope of this paper.

4. Summary

DMS and SO_2 mixing ratios were measured in the tropical boundary layer by isotope dilution GC/MS. Average DMS and SO_2 levels were 22 ± 7 ($n = 488$) pmol/mol and 23 ± 7 ($n = 471$) pmol/mol respectively. Anti-correlated DMS and SO_2 diurnal cycles, consistent with DMS + OH oxidation were observed on most days. Photochemical box model simulations suggest that the yield of SO_2 and total SO_2 sink are ~85% and $\sim 2 \times 10^4$ molec cm^{-3} s^{-1} respectively. On several days the rate of decrease in DMS and increase in SO_2 levels in the early morning were larger that predicted by the model. The rate and timing of the early morning loss are consistent with chemical oxidation of DMS by halogen radicals, but the quantitative yield of SO_2 is not, suggesting a dynamical explanation.

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