UC Irvine

UC Irvine Previously Published Works

Title

DMS and SO₂ measurements in the tropical marine boundary layer

Permalink

<https://escholarship.org/uc/item/1t03s1mc>

Journal

Journal of Atmospheric Chemistry, 53(2)

ISSN

0167-7764

Authors

De Bruyn, WJ

Dahl, E

Saltzman, ES

Publication Date

2006-02-01

DOI

10.1007/s10874-005-9000-z

Copyright Information

This work is made available under the terms of a Creative Commons Attribution License, available at <https://creativecommons.org/licenses/by/4.0/>

Peer reviewed

DMS and SO₂ Measurements in the Tropical Marine Boundary Layer

WARREN J. DE BRUYN¹, ELIZABETH DAHL² and ERIC S. SALTZMAN²

¹*Department of Physical Science, Chapman University, Orange CA 92866,
e-mail: debruynd@chapman.edu*

²*Earth System Science, University of California at Irvine, Irvine, CA 92697-3100*

(Received: 26 August 2005; accepted: 29 August 2005)

Abstract. Dimethyl sulfide (DMS) and sulfur dioxide (SO₂) mixing ratios were measured in the boundary layer on Oahu, Hawaii in April and May 2000. Average DMS and SO₂ levels were 22 ± 7 ($n = 488$) pmol/mol and 23 ± 7 ($n = 471$) pmol/mol respectively. Anti-correlated DMS and SO₂ diurnal cycles, consistent with DMS + OH oxidation were observed on most days. Photochemical box model simulations suggest that the yield of SO₂ and total SO₂ 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 SO₂ levels in the early morning were larger than 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 Cl₂ 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 SO₂ 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, SO₂ yields, the total SO₂ 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 SO₂

Atmospheric DMS and SO₂ 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 (¹²C₂H₃³²S¹²C₂H₃ and ³⁴SO₂) 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 SO₂, 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 3–5 pmol/mol and the accuracy and precision of measurements is better than $\pm 10\%$ and $\pm 5\%$ respectively.

2.3. MODELING

A time-dependent photochemical box model has been used to simulate the observed DMS and SO₂ 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, NO_x 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 SO₂ 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, NO₃ oxidation and entrainment into the layer above. SO₂ is produced in the model from NO₃ oxidation, OH oxidation of DMS, entrainment from above, and is lost via heterogeneous processes and OH oxidation. The DMS flux, yield of SO₂ from DMS oxidation and total SO₂ sink are adjustable parameters.

3. Observations and Analysis

Three days of DMS and SO₂ 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. SO₂ 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 NO₃ radicals (Andreae *et al.*, 1995), but in low NO_x environments like Hawaii, this is a minor effect. By contrast, SO₂ 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 SO₂ is not believed to vary on a diel basis.

Also shown in the figure are model-produced DMS, SO₂ 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 SO₂ levels for days 111, 112 and 115. The solid lines are simulated DMS and SO₂ profiles. The dashed lines are model produced OH levels.

the observed DMS levels, then the SO₂ production efficiency and total SO₂ sink were adjusted until the model best reproduced the observed SO₂ levels. The DMS fluxes, SO₂ sinks and SO₂ yield used to simulate the observed DMS and SO₂ 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 SO₂ levels on days 111,112 and 115

Day	DMS flux $\mu\text{mol m}^{-2} \text{ day}^{-1}$	SO ₂ sink ($\times 10^4 \text{ molec cm}^{-3} \text{ s}^{-1}$)	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 SO₂ sinks and SO₂ 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, SO₂ sink and SO₂ 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 SO₂ sink had to be decreased by 10% to balance sources and sinks. The SO₂ yield did not change. Decreasing the entrainment rate to 0.3 cm s^{-1} increased the DMS flux by 31%, decreased the SO₂ sink by 10% and also did not change the yield significantly. Decreasing the NO_x level to 10 pmol/mol decreased the flux by 11%, and decreased the SO₂ 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 SO₂ 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 SO₂ 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 SO₂ 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 SO₂ 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 SO₂. 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 $3 \mu\text{mol m}^{-2} \text{ day}^{-1}$, a total SO_2 sink of $1.9 \times 10^4 \text{ molec cm}^{-3} \text{ s}^{-1}$ 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:

$$\begin{aligned} \text{DMS}_{i+\Delta t} = & \text{DMS}_i + F_{\text{DMS}}\Delta t - \text{DMS}_i(k_{\text{OH}}\text{OH}_i \\ & + k_{\text{NO}_3}\text{NO}_{3i} + X_i + V_{\text{ex}}/\text{BLH})\Delta t \end{aligned}$$

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 NO_{3i} are the concentrations of the different species at time i and $\text{DMS}_{i+\Delta t}$ 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 $\sim 6.5 \times 10^{-5} s^{-1}$ 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 SO₂. 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 SO₂ 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 $\text{CH}_3\text{SCH}_2+\text{HCl}$ and an addition pathway to produce the $\text{CH}_3\text{SCH}_2\text{Cl}$ 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 $X = V_{ex}[(\text{DMS}_{ft}/\text{DMS})-1]/\text{BLH}$ and DMS_{ft} is the mixing ratio of DMS above the boundary layer. Assuming that $\text{DMS}_{ft} = 0$, a minimum V_{ex} of 6.6 cm s^{-1} is required to support the observations. For $\text{DMS}_{ft} > 0$ 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 $\sim 100 \text{ m}$ 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 without 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 $\text{DMS} + \text{OH}$ 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 $\sim 2 \times 10^4 \text{ molec cm}^{-3} \text{ s}^{-1}$ respectively. On several days the rate of decrease in DMS and increase in SO_2 levels in the early morning were larger than 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.

Acknowledgements

This research was supported by NSF (ATM-0001699), NOAA (NA67RJ0149), NASA (NAG1-2002) and ONR (N0001497-1-0066). The authors would also like to thank the University of Hawaii for the use of their Bellows site and Dr. Steve Howell for logistic assistance during deployment.

References

- Andreae, M. O., Wolfgang, E., and de Mora, S., 1995: Biogenic sulfur emissions and aerosols over the tropical South Atlantic 3. Atmospheric dimethylsulfide, aerosols and cloud condensation nuclei, *J. Geophys. Res.* **100**, 11335–11356.
- Bandy, A. R., Thornton, D. C., and Driedger, A. R., 1993: III, Airborne measurements of sulfur dioxide, dimethyl sulfide, carbon disulfide, and carbonyl sulfide by isotope dilution gas chromatography/mass spectrometry, *J. Geophys. Res.* **98**, 23423–23442.
- Bandy, A. R., Thornton, D. C., Blomquist, B. W., Chen, S., Wade, T. P., Ianni, J. C., Mitchell, G. M., and Nadler, W., 1996: Chemistry of dimethyl sulfide in the equatorial Pacific atmosphere, *Geophys. Res. Lett.* **23**, 741–744.
- Bedjanian, Y. U., Poulet, G., and Le Bras, G., 1996: Kinetic study of the reaction of BrO with dimethylsulfide, *Int. J. Chem. Kinet* **28**, 383–389.
- Chin, M., Jacob, D. J., Gardner, G. M., Foreman-Fowler, M. S., and Spiro, P. A., 1996: A global three-dimensional model of tropospheric sulfate, *J. Geophys. Res.* **101**, 19667–19690.
- Chin, M., Rood, R. B., Allen, D. J., Andreae, M. O., Thompson, A. M., Lin, S. J., Atlas, R. M., and Ardizzone, J. V., 1998: Processes controlling dimethyl sulfide over the oceans: Case studies using a 3-D model driven by assimilated meteorological fields, *J. Geophys. Res.* **103**, 8341–8353.
- De Bruyn, W. J., Harvey, M., Cainey, J., and Saltzman, E. S., 2001: DMS and SO₂ measurements at Baring Head, New Zealand, *J. Atmos. Chem.* **41**, 189–209.
- Finlayson-Pitts, B. J., and Pitts, J. N., Oct 1999: Chemistry of the Upper and Lower Atmosphere: Theory, Experiments, and Applications, Elsevier Science & Technology Books.
- Hoell, J. M., Davis, D. D., Gregory, G. G., McNeal, R. J., Bendura, R. J., Joseph Drewry, W., Barrick, J. D., Kirchhoff, V. W. J. H., Motta, A. G., Navarro, R. L., Dorko, W. D., and Owen, D. W., 1993: Operational overview of the NASA GTE/CITE 3 airborne instruments for sulfur dioxide, hydrogen sulfide, carbonyl sulfide, dimethyl sulfide and carbon disulfide, *J. Geophys. Res.* **98**, 23291–23304.
- Hynes, A. J., Wine, P., and Semmes, D. H., 1986: Kinetics and mechanism of OH reactions with organic sulfides, *J. Phys. Chem.* **90**, 4148–4156.
- Jobson, B. T., Niki, H., Yokouchi, Y., Bottenheim, J., Hopper, F., and Leaitch, R., 1994: Measurements of C₂–C₆ hydrocarbons during the Polar-Sunrise 1992 Experiment: Evidence for Cl and Br atom chemistry, *J. Geophys. Res.* **99**, 25355–25368.
- Keene, W. C., Zenny, A. P. P., Jacob, D. J., Duce, R. A., Galloway, J. N., Schultz-Tokos, J. J., Sievering, H., and Boatman, J. F., 1990: The Geochemical cycling of reactive chlorine through the marine troposphere, *Global Biogeochem. Cycles* **4**, 407–430.
- Keene, W. C., Jacob, D. J., and Fan, S., 1996: Reactive Chlorine: A potential sink for dimethylsulfide and hydrocarbons in the marine boundary layer, *Atmos Environ.* **30**, i–iii.
- Koga, S. and Tanaka, H., 1993: Numerical study of the oxidation process of dimethylsulfide in the marine boundary layer, *J. Atmos. Chem.* **17**, 201–228.
- Logan, J. A., 1999: An analysis of ozonesonde data for the troposphere: Recommendations for testing 3-D models and development of a gridded climatology for tropospheric ozone, *J. Geophys. Res.* **104**, 16115–16149.
- Pszenny, A., Keene, W. Jacob, D., Fan, S., Mabel, J., Zetwo, M., Springer-Young, M., and Galloway, J., 1993: Evidence of inorganic chlorine gases other than hydrogen chloride in marine air, *Geophys. Res. Lett.* **20**, 699–702.
- Sander, R and Crutzen, P. J., 1996: Model study indicating halogen activation and ozone destruction in polluted air masses transported to the sea, *J. Geophys. Res.* **101**, 9121–9138.
- Singh, H. B., Gregory, G. L., Anderson, B., Browell, E., Sachse, G. W., Davis, D. D., Crawford, J., Bradshaw, J. D., Talbot, R., Blake, D. R., Thornton, D., Newell, R., and Merrill, J., 1996: Low

- Ozone in the marine boundary layer of the Tropical Pacific Ocean: Photochemical loss, chlorine atoms, and entrainment, *J. Geophys. Res.* **101**, 1907–1917.
- Spicer, C. W., Chapman, E. G., Finlayson-Pitts, B. J., Plastring, R. A., Hubbe, J. M., Fast, J. D., and Berkowitz, C. M., 1998: Unexpectedly high concentrations of chlorine in coastal air, *Nature* **394**, 353–356.
- Spivakovsky, C. M., Yevich, R., Logan, J. A., Wofsy, S. C., McElroy, M. B., and Prather, M. J., 1990: Tropospheric OH in a three-dimensional chemical tracer model: An assessment based on observations of CH_3CCl_3 , *J. Geophys. Res.* **95**, 18441–18471.
- Stecher III, H. A., Luther III, G. W., MacTaggart, D., Farwell, S., Crosley, D., Dorko, W., Goldan, P., Beltz, N., Krischke, U., Luke, W., Thornton, D., Talbot, R., Scheuer, E., Lefer, R., Benner, Wu, J., Saltzman, E. S., Gallagher, M., and Ferek, R., 1996: Results of the Gas-phase Sulfur intercomparison Experiment (GASIE). Overview of experimental set-up, results and general conclusions, submitted to *J. Geophys. Res.*
- Suhre, K. and Rosset, R., 1994: DMS Oxidation and turbulent transport in the marine boundary layer: A numerical study, *J. Atmos. Chem.* **18**, 379–395.
- Suhre, K., Andreae, M. O., and Rosset, R., 1995: Biogenic sulfur emissions and aerosols over the tropical South Atlantic, 2, One-dimensional simulation of sulfur chemistry in the marine boundary layer, *J. Geophys. Res.* **100**, 11323–11334.
- Thornton, D. C., Bandy, A. R., Blomquist, B. W., Davis D. D., and Talbot, R. W., 1996: Sulfur dioxide as a source of condensation nuclei in the upper troposphere of the Pacific Ocean, *J. Geophys. Res.* **101**, 1883–1890.
- Vogt, R., Crutzen, P., and Sander, R., 1996: A mechanism for halogen release in the remote marine boundary layer, *Nature* **383**, 327–330.
- Wingenter, O., Kubo, M., Blake, N., Smith, T., Blake, D., and Sherwood Rowland, F., 1996: Hydrocarbon and halocarbon measurements as photochemical and dynamical indicators of atmospheric hydroxyl, atomic chlorine, and vertical mixing obtained during Lagrangian flights, *J. Geophys. Res.* **101**, 4331–4340.
- Yin, F., Grosjean, D., and Seinfeld, J. H., 1990: Photo-oxidation of dimethyl sulfide and dimethyl disulfide, I, Mechanism development, *J. Atmos. Chem.* **11**, 309–364.
- Yvon, S. A., Saltzman, E. S., Cooper, D. J., Bates, T. S., and Thompson, A. M., 1996: Atmospheric dimethylsulfide cycling at a tropical South Pacific station (12°S, 135°W): A comparison of field data and model results, *J. Geophys. Res.* **101**, 6899–6909.