Dimethyl Sulfide in the Marine Atmosphere

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We have performed over 900 measurements of atmospheric dimethyl sulfide (DMS) in five different marine locations: the equatorial Pacific; Cape Grim, Tasmania; the Bahamas; the North Atlantic; and the Sargasso Sea. At all locations, DMS concentrations were usually in the range of 100–400 ng S m⁻³, with similar average concentrations of about 150 ng S m⁻³ (107 parts per thousand by volume). Highest concentrations occurred during, but were not limited to, periods of sustained high winds and overcast skies, presumably owing to faster exchange from surface seawater and less photochemical activity in the atmosphere. Lowest values occurred during airflow from continental regions, which provides higher levels of oxidants and free radicals to react with DMS. Averaged over time, the concentrations in clean marine air reached a maximum at night and a minimum in the afternoon, when concentrations were about one third lower than during the nighttime maximum. The observed concentrations of DMS in the marine atmosphere and their diurnal variability agree well with model simulations involving OH and NO₃ oxidation of DMS and are consistent with a global sea-to-air DMS flux of about 40 ± 20 Tg S yr⁻¹. DMS may represent a major sink for NO₃ in the marine troposphere.

INTRODUCTION

Dimethyl sulfide (DMS) produced by marine phytoplankton is believed to be the major source of reduced sulfur to the marine atmosphere and to be responsible for the background levels of SO₂, excess sulfate, and methanesulfonic acid observed over oceanic areas [Andreae and Raemdonck, 1983]. Numerous measurements of dissolved DMS in marine surface waters of various levels of biological productivity have led to an estimate of the overall flux from the world oceans of approximately 40 ± 20 Tg S yr⁻¹ [Andreae and Raemdonck, 1983]. Clearly, this is an important fraction of the worldwide natural sulfur flux of 60–90 Tg S yr⁻¹ required to balance the atmospheric sulfur budget [Freneny et al., 1983; Andreae, 1985a]. To investigate the behavior of DMS in the atmosphere, we have conducted field measurement programs in five marine areas: the equatorial Pacific, the northwest coast of Tasmania (Cape Grim), and three regions in the North Atlantic (see Figure 1). The equatorial Pacific cruise covered a track from Ecuador to Hawaii along the equator and represents an area with very little influence from continental air masses [Raemdonck et al., 1984]. The Baseline Air Pollution Station at Cape Grim is located in the belt of prevailing southwesterly winds from the southern ocean, which offered the opportunity to sample background marine air most of the time. The cruises in the North Atlantic offered a mixture of conditions. Marine air could be sampled when the airflow was from the south or east, but continental air masses which originated over North America would occasionally extend out over the Atlantic and perturb the chemistry of the marine atmosphere. This occurrence had a strong effect on atmospheric DMS over the oceans which was not evident in the more remote areas of the Pacific.

EXPERIMENTAL

DMS in air was determined by preconcentration on gold wool and subsequent gas chromatography with flame photometric detection. Details have been reported elsewhere [Barnard et al., 1982], and sampling and analysis in these experiments were similar with one major exception: it was found that DMS deposited on gold wool could be destroyed (possibly by ozone or other oxidants) during sampling unless a proper scrubber was used upstream of the gold tube. This negative interference was observed particularly in continental and urban air but can also occur in relatively clean maritime air. When ambient air was drawn through gold tubes on which a DMS amount typical of the size of an ambient sample (approximately 1 ng) had been deposited from a calibration gas stream, the amount of DMS found after exposure was often even smaller than the preloaded amount. On tubes which had not been preloaded with DMS and which were exposed simultaneously with the preloaded ones, a small amount of DMS was usually observed. This suggests that DMS from the air is being deposited on the gold surface and then partially destroyed while attached to the surface. During these tests it was also found that the scrubber used by Barnard et al. [1982] was ineffective in preventing loss of DMS during sampling, and thus their reported values for DMS in air over...
the Atlantic are believed to be too low by a large and unknown factor. The data presented in this paper are comparable with the results of Nguyen et al. [1984] from the remote Pacific, which were obtained using an inert-surface cryogenic trapping system (mean DMS concentration of 120 ng S (DMS) m$^{-3}$).

A successful scrubber was made using a tube filled with 5% Na$_2$CO$_3$ on Anakrom C22 (40/50 mesh). When this scrubber was used upstream of the gold tubes, the amounts found on preloaded gold tubes always increased by the same amount as was found on simultaneously run unpreloaded tubes. This experiment shows that the negative interference by destruction of DMS adsorbed to the gold surface had been eliminated. The absence of negative interferences was further confirmed by inserting a DMS permeation device in the airstream upstream of the scrubber. Comparison of the results with and without the permeation device showed that the signal increased by the amount expected from the known permeation rate of the device. This experiment also shows that no loss of DMS occurs in the scrubber. No blanks are detectable when gold tubes are exposed to zero air either with or without the scrubbers. No blanks were observed in gold tubes which were installed into the sampling line but through which air was not drawn. To verify the selectivity of the procedure, gold tubes were exposed to large amounts (100–1000 ng) of H$_2$S, COS, CS$_2$, and methyl mercaptan from calibration gas streams, and then exposed as normal samples. No interference was detectable. We conclude that the combination of a highly selective preconcentration technique (chemisorption to the gold surface), gas chromatographic separation, and the use of a sulfur-specific detector effectively eliminates any positive interferences.

The gold tubes are 100% effective in removing DMS from the sample stream. This is shown by operating tubes in sequence: no DMS is found on the second tube as long as flow rates do not exceed 5 L min$^{-1}$. The absorbed DMS is recovered with an efficiency of better than 90% from new gold tubes during the analytical procedure, as is shown by comparison between the results obtained by injecting DMS directly into the system and those observed using adsorption on the gold surface. After several hundred uses, the efficiency of the tubes declines. The efficiency of each tube is monitored periodically, and deteriorating tubes are eliminated.

The system is calibrated by adding DMS either to compressed zero air or to purified (by charcoal trap and particle filter) ambient air in a dynamic dilution system (Metronics Dynacalibrator, model 340) using a gravimetrically calibrated permeation device. This device has been validated by comparison with independent, gravimetrically prepared standards [Andreae and Barnard, 1983]. A range of DMS concentrations in air is prepared this way, and the calibration stream is sampled using the scrubber and gold tubes in the same way as for ambient samples. Precision and accuracy of the measurements are somewhat variable between the different field experiments; they are typically near ±10 and 20%, respectively.

RESULTS

Figure 2 shows the results of the DMS measurements during the five field experiments. The upper two plots for the equatorial Pacific and Cape Grim represent remote marine locations, while the three lower plots from the Atlantic cruises also reflect the influence of continental air masses on DMS over the ocean. To the right of each data plot are the average concentrations plotted versus time of day for the first four data sets. The "error bars" in the diurnal plots (one standard error of the mean) do not reflect analytical uncertainty (precision is about ±10%) but rather the substantial day-to-day variability imposed by meteorological and oceanographic factors.

Remote Marine Areas

The main feature of the remote marine measurements from the equatorial Pacific cruise and Cape Grim is that the DMS concentrations are not highly variable and remain high except for the periods on January 12, 16, and 23, when continental air from Australia reached Cape Grim. The highest concentrations occur on cloudy days with periods of sustained
high wind speeds, during which more rapid exchange of volatile species from surface seawater is expected. The plots of hourly averages for both remote data sets show similar diurnal behavior, with maximum concentrations at night and minimum during late afternoon, due mainly to the oxidation of DMS by OH radical which is generated photochemically. The amplitude of the diurnal cycle is slightly greater for the equatorial Pacific averages, which may be due to greater sunlight intensity than at Cape Grim, which is at a higher latitude and has a higher frequency of cloudy days.

Fig. 2. Concentrations and diurnal variations of DMS in air for all five field experiments. Concentration plots are of individual samples. Diurnal variation plots represent means and standard errors of samples grouped into 2- or 4-hour time segments. Arrows on concentration plots indicate the onset of airflow of recent continental origin. Weather symbols above the time series plots indicate noon wind direction and strength (long barbs denote 10 knots; short barbs denote 5 knots) and cloud cover.
The DMS results from the three Atlantic cruises show much wider variability than those from the remote oceanic sites, with the lowest values occurring when air trajectories were from the North American continent. The plot of diurnal averages for the Bahamas cruise (excluding air masses of recent continental origin) shows the same features as the equatorial Pacific and Cape Grim plots (i.e., highest at night, minimum in the afternoon), but the diurnal trend is somewhat less clear, presumably owing to the interactions of continental and marine air masses and a smaller number of data points. For the North Atlantic cruise the diurnal averages were subdivided into “marine” and “continental” cases on the basis of air mass origin; both curves are plotted for these data. The DMS concentrations during “marine” conditions are approximately 3 times greater than for “continental” conditions and show a diurnal cycle similar to that of the remote marine locations. The “continental” cases, besides being lower in concentration, show little diurnal variability, suggesting that oxidation by OH is not the dominant reaction path for DMS when polluted continental air is present.

A detailed example of the effect of mixing continental and marine air is illustrated in Figure 3 for 2 days during the Bahamas cruise. Figure 4 shows the weather map (valid for November 17, 1983, 0000 UT, or November 16, 1983, 1900 LT) just prior to frontal passage on November 16. Aboard the R/V Bellows the frontal passage was observed at about 2100 LT. Ahead of the front, winds were from the east to northeast (trade winds), and DMS concentrations were quite high in this unpolluted marine air. After the frontal passage, however, the DMS concentration dropped drastically. The low concentrations observed during the night of November 17–18 cannot be explained on the basis of the low initial DMS concentrations in continental air. Air mass trajectory analysis shows that on November 17, 1900 local time, the air sampled on R/V Bellows had spent about 36–48 hours over the ocean since leaving the North American continent. Assuming a boundary layer thickness of 1.5 km and sea-to-air flux of DMS of 10 μg m⁻² h⁻¹ (on the basis of an observed average...
seawater concentration of 84 ng S (DMS) L\(^{-1}\) upwind of the Bellows and a piston velocity of 2.8 m d\(^{-1}\)), we predict that 230–300 ng S (DMS) m\(^{-3}\) had been added to the marine boundary layer since it had left the continent. The observed low concentrations can therefore only be due to very fast oxidation of DMS in the continually influenced air. Similar dramatic decreases of atmospheric DMS concentrations as a result of the advection of continental air masses over the North Atlantic were observed during the R/V Knorr cruise (April–May 1984) and the R/V Cape Hatteras cruise in the Sargasso Sea (June 1984). They are indicated by arrows on Figure 2.

**DISCUSSION**

**Processes Regulating Atmospheric DMS Levels**

DMS in the marine atmosphere was observed to have fairly high concentrations (approximately 100–300 ng S m\(^{-3}\)) except when air of recent continental origin mixed into the marine atmosphere. Measurements over a wide range of marine locations gave remarkably similar average DMS concentrations (Table 1). The data were averaged on a time-weighted basis to eliminate a bias from more frequent sampling during daytime. This similarity of atmospheric DMS concentrations in the different ocean regions is in good agreement with measurements of dissolved DMS in surface waters [Andreae and Raemdonck, 1983] in that its sources (marine phytoplankton) are present in all oceanic areas and average dissolved concentrations do not vary greatly between different open ocean regions. The air concentrations over the remote ocean show less “patchiness” than surface water concentrations, since atmospheric mixing and sampling times (5–30 min) tend to integrate the atmospheric samples over larger areas. It must be emphasized, however, that the high-latitude data (Cape Grim and North Atlantic) are from the season of maximum phytoplankton productivity (spring–summer) and that lower values may be expected during the less productive seasons.

The concentration of DMS in the marine atmosphere is the result of a balance between input and removal processes. The major factor influencing the input of DMS in the remote marine troposphere is the rate of sea-to-air transfer, which is a complex function of wind speed, sea state, dissolved DMS concentration, and phytoplankton productivity in surface water some distance upwind of the air sampling site. At Cape Grim the highest DMS concentrations were measured during periods of sustained high winds and overcast skies. This effect was also observed in the Bahamas data (see Figure 3) prior to frontal passage on November 16. Nguyen et al. [1984] have measured the ocean-to-atmosphere transfer rate of DMS and found that it increases rapidly with increasing wind velocities greater than 3 m s\(^{-1}\), supporting a higher rate of air-to-sea transfer during periods of high winds.

Up to very recently, the reaction of DMS with OH during daylight was believed to be the only significant loss reaction for DMS [Graedel, 1979; Sze and Ko, 1980; Grosjean, 1984]. Model calculations by Graedel [1979] and Bingemer [1984] have predicted a diurnal pattern with a maximum near sunrise and a minimum in the afternoon. Our data show such a diurnal pattern, but the amplitude of the cycle is much lower than amplitudes predicted by these models. On average, the ratio of diurnal maximum to minimum that we have observed is 1.6, compared with 13 and 5 for the models of Graedel and Bingemer, respectively. The diurnal composites we portray on the right in Figure 2 necessarily obscure some diurnal variation, since they average over days with fluctuating DMS sources. Nevertheless, the discrepancy is real. There are a number of factors which may reduce the difference between the predicted minimum and maximum: lower OH concentrations than these authors have suggested would cause a less pronounced afternoon minimum. A somewhat lower rate coefficient than the one used by Bingemer for OH and DMS would have a very similar effect. Nighttime reactions, ignored by both earlier models, would lower the early morning maximum.

**TABLE 1. DMS Concentrations in the Remote Marine Atmosphere**

<table>
<thead>
<tr>
<th></th>
<th>Time-Weighted Mean</th>
<th>Range</th>
<th>Quartile Range</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Equatorial Pacific</strong></td>
<td>161</td>
<td>68–414</td>
<td>115–196</td>
</tr>
<tr>
<td><strong>Cape Grim</strong></td>
<td>167</td>
<td>34–481</td>
<td>120–223</td>
</tr>
<tr>
<td><strong>Bahamas</strong></td>
<td>122</td>
<td>5–670</td>
<td>66–115</td>
</tr>
<tr>
<td><strong>North Atlantic</strong></td>
<td>97</td>
<td>2–411</td>
<td>35–122</td>
</tr>
<tr>
<td><strong>All points</strong></td>
<td>180</td>
<td>1–1014</td>
<td>49–370</td>
</tr>
</tbody>
</table>

Data are in nanograms of sulfur per cubic meter.

In marine areas influenced by polluted continental air, no systematic diurnal trend of DMS concentrations can be observed. This is probably due to the influence of additional removal reactions which obscure the diurnal effect of the oxidation of DMS by OH. In polluted air, other reactive species become available which can react with DMS faster than OH, and the observed result is a drastic lowering of the atmospheric DMS concentrations and suppression of the diurnal cycle. One likely reactant is nitrate radical (NO\(_3\)), which has been found to exist at night [Platt et al., 1984] in both clean and polluted continental air at concentrations sufficient to react rapidly with the available DMS in marine air [Winer et al., 1984]. Also, the work of Grosjean [1984] and Cox and Sheppard [1980] appears to be consistent with such an additional photooxidation reaction for DMS in the presence of NO\(_3\) and sunlight.

**Model Simulations**

A comparison between the observations of dimethyl sulfide and our current understanding of the chemical and physical processes affecting its concentration was synthesized in a one-box model of the lowest layer of the marine atmosphere. The principal questions addressed by this analysis are as follows: (1) What determines the concentration of DMS? Are the known sinks appropriate? (2) Are the concentrations in reasonable agreement with the estimated emission fluxes? (3) Can the reactions of DMS reasonably account for remote tropospheric SO\(_2\)? (4) Does the non-sea-salt sulfate in remote marine aerosols originate primarily from DMS oxidation? The answers to these questions are strongly interlinked, so that while many parameters and processes remain poorly defined, simulations may constrain the conditions that are in accord with the facts.

As was suggested above, the concentration of DMS in the marine atmosphere appears to be set by the balance of emissions from the ocean and reaction with OH and NO\(_3\) radicals. The appropriate reaction rate coefficients are becoming relatively well measured [Atkinson et al., 1984, and references therein]. Several interesting studies of the mechanism and the intermediate and final products of the reaction have been made in chambers. However, these studies have necessarily
been conducted with high levels of reactants and in reactant ratios not typical of the remote atmosphere [Grosjean, 1984; Hatakeyama et al., 1982; Niki et al., 1983]. In the simulations we discuss below, we assigned the yield of SO2 to be 30% each for the DMS that reacts with either radical, a yield based on the product studies cited above. Since the experimental design of the laboratory experiments does not allow the extrapolation of the SO2 yields obtained in these experiments to the conditions in the remote marine atmosphere, this assumption (H. Niki and D. Grosjean, personal communication, 1984) is rather arbitrary. However, SO2 concentrations in a simulation may easily be reinterpreted if the yield proves to be higher, since the dominant loss processes (solution to the ocean, radical attack, and cloud solution and removal) are very nearly linear in this situation.

The concentration of DMS changes with time as described by the following equation:

$$\frac{dn}{dt} = F_{\text{mix}} - \left(k_{\text{OH}}[\text{OH}] + k_{\text{NO3}}[\text{NO3}]\right)n$$

where $n$ is the number density of DMS, $F$ is the input flux of DMS from the ocean, $F_{\text{mix}}$ is a mixing depth over which DMS remains essentially constant, and $k_{\text{OH}}[\text{OH}]$ and $k_{\text{NO3}}[\text{NO3}]$ are loss processes due to the reaction of DMS with hydroxyl and nitrate radical, respectively ($k_{\text{OH}} = 11 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ [Atkinson et al., 1984]; $k_{\text{NO3}} = 9.9 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ [Atkinson et al., 1984; Tuazon et al., 1984]).

Figures 5 through 7 show the results of calculations for a box model conceived to describe an idealized situation: a maritime mixed layer 1 km thick with a constant sea surface emission rate of DMS: 0.1 g S (DMS) m$^{-2}$ yr$^{-1}$. This rate corresponds to a global sea-to-air DMS flux of 37 Tg yr$^{-1}$ and is based on data presented in a previous paper [Andreae and Raemdonck, 1983]. No venting to the free troposphere was included in this box model; the effects of vertical transport on the atmospheric distribution of DMS will be discussed briefly below but will be addressed in detail in a separate paper based on aircraft data (R. J. Ferek et al., manuscript in preparation, 1985). A mixed layer thickness of 1 km was chosen as a compromise to allow comparison between cases with different chemical reactions included. For the cloudless cases (Figures 5 and 6) a 500-m boundary layer might be more realistic, whereas in the cloudy case (Figure 7) a thicker boundary layer (≈1.5 km) might be more applicable. Constant values of the important parameters which control the levels of OH and NO3 were also assumed. These are indeed idealizations: for example, the data of Figure 2 and our previous discussion of sea-to-air transfer of DMS [Andreae and Raemdonck, 1983] suggest that the input flux is not constant. Nevertheless, the composited diurnal variations shown in Figure 2 do suggest that an average picture is instructive. Specifically, our working assumption is that the model with a constant diurnally repeating behavior adequately describes the ensemble-mean behavior of DMS in the remote marine atmosphere for our present purposes.

The diurnal course of OH and NO3 concentrations was obtained from a simulation of the CO-O3-NOx chemistry of the remote oceanic troposphere, using the chemistry described by Chatfield and Crutzen [1984] and Baulch et al. [1982]. The kinetics equations were integrated by an exponential technique described by Hessavfelt et al. [1978].
The parameters described do allow for considerable latitude in fitting the data; nevertheless, there are limits in the fitting. Table 2 describes some limits to the parameters of the equation above that appear appropriate in defining the role of DMS in the sulfur cycle. We simulated OH concentrations that were consistent with photolysis rates when the sun is at equinox at 30°N with 290 m atm cm⁻³. Total reactive nitrogen (essentially NO + NO₂ during daytime) was maintained at 100 pptv. These are conditions that allow relatively high values of OH. Other important parameters determining the radical concentrations were varied according to the limits set in Table 2. Three simulations appeared particularly informative, and their results are shown in Figures 5 through 7. The conditions and consequent behavior of DMS for these simulations were these:

**High OH, no NO₃ reaction (Figure 5).** CO was maintained at 130 ppbv, and this CO concentration was considered to partially represent nonmethane hydrocarbons. Photolysis rates for a cloudless sky produced an OH concentration of 1.1 x 10⁷ molecule cm⁻³ at noon. No NO₃ reaction with DMS was simulated. In consequence, the DMS exhibited the large diurnal variation shown in Figure 5. NO₃ concentrations were calculated and, with essentially no sinks during the night, reached levels one-half those of daytime NO₃, much as in the model of Logan et al. [1981]. Since under these conditions there is no strong influence of NO₃ chemistry on the concentrations of OH in our model, the results from this simulation are also applicable to the remote atmosphere with very low NO₃ levels.

**High OH, with NO₃ reaction (Figure 6).** Conditions similar to those described above were maintained, but NO₃ was allowed to react with DMS. The rate of Atkinson et al. [1984], multiplied by 1.8 as the work of Tuazon et al. [1984] suggests may be reasonable, gave a rate coefficient only about a factor of 10 slower than that for OH. As Figure 6 shows, the mean level of DMS was lowered, and the apparent diurnal variations of DMS diminished even more. DMS was the major sink for NO₃, and the maximum levels of the latter dropped to around 20 x 10⁶ molecules cm⁻³. This case study indicates that the NO₃ reaction has a secondary effect on mean DMS concentrations but may have important effects upon the diurnal variation.

**Low OH, with NO₃ reaction (Figure 7).** In order to simulate lower OH concentrations, we simulated an atmosphere in which CO was raised to 200 ppbv, and clouds were allowed to diminish photolysis rates. Interpreting the work of Stephens [1978], which describes visible irradiances, we reduced the photolysis rates for Figure 6 by a factor of 2 cos² ζ times the transmissions Stephens quotes for representative low clouds exposed to solar radiation when cos ζ = 0.8 (ζ represents the zenith angle of the sun). This crude interpretation of Stephens' results produced OH levels 35% as high as in Figures 5 and 6 (Figure 7). The resulting DMS concentrations were much higher, similar to those observed under cloudy conditions in the Bahamas region (Figures 2 and 3), but the diurnal variation was even more reduced. This reduction was limited by an interesting indirect effect: lower OH values produced larger DMS concentrations, which in turn depressed nighttime NO₃ levels. This simulation illustrates the limited possible effect of NO₃ in situations where the total amount of NO₃ remains fixed. Under cloudy conditions the DMS would be likely to mix upwards to about 1500 m. Such mixing would reduce the mean concentration of DMS by factors of approximately 1.5. The diurnal variation would be slightly lower owing to the nonproportionality (so-called "nonlinearity") of the DMS-NO₃ chemistry.

Comparison of these simulations with the data of Figure 2 shows that there is reasonable correspondence between our current understanding of physical and chemical phenomena as represented by the model and the observed concentrations. For meteorological and oceanographic reasons, the diurnal composites portrayed on the right side of Figure 2 undoubt-
The diurnal variations are frequently small, and this suggests that some process depleting DMS operates at night. The NOx concentrations and the calculated NO3 concentrations are perhaps at the upper limit of what might be considered typical of remote marine mixed layer [Helas and Warneck, 1981]. Consequently, there is the possibility of other diurnally varying behavior, such as a diurnal variation of mixed layer depth, or another nighttime sink. On the other hand, there is no evidence for a diurnal variability of the source flux of DMS from the ocean surface: the concentration of DMS in the surface ocean shows no detectable diurnal change [Andreae et al., 1983; Andreae, 1985b].

Examination of the diurnal behavior of DMS on a day-to-day basis in the time series diagrams (Figure 2) shows a substantial amount of variability which is superimposed on the "average" diurnal behavior. Such variability may result in periods where no clear diurnal trends are distinguishable or where even daytime maxima and nighttime minima are observed. Such variability must be expected, since transport processes (especially air mass advection) which are not considered in the steady state box model used here play a large role in determining the concentration of a relatively short-lived species like DMS at any given place and time. Only by averaging over a relatively large number of individual cases can the effect of such variability be removed; these averaged data can then be compared in a valid fashion with the results of the steady state model. We consider the disagreements between the averaged data and the model predictions not to be major; the differences might be attributed to sampling variation or to as yet unrecorded phenomena, for example, additional sink processes. Further measurements are required in either case.

The model used here to explore the atmospheric chemical behavior of DMS considers only processes within a well-mixed layer of 1-km thickness without vertical exchange with the free troposphere. However, we know from aircraft data (R. J. Ferek et al., manuscript in preparation, 1985) that DMS decreases with altitude above the mixed layer; therefore such vertical exchange may have significant effects. To approximate these effects, we have applied the tropospheric model of Chatfield and Crutzen [1984]. In fair weather with few clouds, general tropospheric subsidence of the air through the capping inversion proceeds at rates of about 20 mbar d^-1. We modeled this as an introduction of DMS-free air into the boundary layer but did not simulate transport of other species. The model predicts that under these conditions the removal of DMS by reaction with OH is much faster than the loss due to ventilation and that ventilation has only a minor effect on DMS mean concentrations and diurnal variation (<10%). However, simulation of a cloud-covered mixed layer like that shown in Figure 7 gave different results. For these meteorological conditions a 50 mbar d^-1 ventilation rate appeared more appropriate, reflecting the activity of deeper clouds and forced subsidence in more convective regions [Chatfield and Crutzen, 1984]. The simulation reduced the DMS concentrations by about 40% but produced little change in the diurnal variation of DMS, which is already small in the presence of cloud cover because of the low concentration of OH radical. The real atmosphere can of course provide even stronger exchange than was assumed here, but since this will lead to increasing DMS levels in the free troposphere, more DMS will be returned with the downwelling air back into the mixed layer, reducing the effect of ventilation on the concentration of DMS in the mixed layer.

The SO2 concentrations in our simulations are all within reasonable limits. Figures 5 through 7 show a small diurnal variation of SO2 at levels of 50–80 pptv, despite the assumption of a substantial sink by solution to the sea surface and other heterogeneous processes, which we represented by a bulk deposition velocity of 0.8 cm s^-1. Higher deposition velocities, which would be applicable under conditions of significant cloud cycling and deposition, would simply be reflected in a proportional decrease in the SO2 concentrations. The model predictions agree quite well with the SO2 levels observed in the remote marine atmosphere [Nguyen et al., 1983; Maroulis et al., 1980; Herrmann and Jaeschke, 1984]. This suggests that DMS is present in sufficient quantity to provide most of the SO2 observed in the marine lower atmosphere. The simulations assume that only 30% of the DMS oxidized produces SO2; however, models which assume more rapid transport and reaction in low clouds would require higher SO2 yields to produce agreement with observations.

Consequences of DMS-NO3 Reaction

The model results presented can be extended to several other reasonable assumptions in a linear manner. Parameters exerting a linearly proportional effect are marked in Table 2. NO3 is the compound that exhibits the most nonlinear effects in the model. If DMS provides the only sink for NO3 at night, the removal rate of DMS from the system numerically equals the production rate of NO3. Higher DMS values simply depress the NO3 concentration. More generally, the nighttime removal rate of DMS should be approximately linearly proportional to the levels of NO3 present in the system, which may explain the low levels of DMS in air of recent continental origin transported over the ocean.

Some support for the importance of NO3 chemistry for the fate of DMS in the marine atmosphere can be derived from the aerosol data obtained during the Bahamas cruise (M. O. Andreae et al., manuscript in preparation, 1985). The aerosol nitrate concentration increased from 9.7 to 26.4 nmol m^-3 following the frontal passage on November 16. Since this increase in nitrate was accompanied by only moderate increases in soot carbon and other continental aerosols, we assume that the nitrate aerosol is not advected from the continent, but formed from gaseous nitric acid by reaction with the marine aerosol. The presence of the nitrate in the same size fraction as the sea-salt aerosol and a chloride deficit of comparable magnitude (30 nmol m^-3) to the amount of nitrate present support this view. Assuming that most of the formation of HNO3 took place during the two days while the air was over the ocean before arriving at the research vessel, the amount of nitrate found corresponds to the conversion of about 400 pptv of NO3 to HNO3 and suggests that the NO3 levels in the post-frontal air mass were high enough to cause a significant nighttime oxidation of DMS by NO3. In addition, model calculations predict increased daytime OH concentrations as a consequence of the elevated NO3 levels and consequently enhanced daytime DMS oxidation by OH.

The consequences of the DMS-NO3 reaction for the nitrogen chemistry in the marine boundary layer depend strongly on the as yet unknown mechanism for this reaction. If NO3 abstracts a hydrogen atom from DMS, nitric acid is formed, which will be removed by deposition and provide an efficient sink for NO3 in the remote marine troposphere. If, on
the other hand, oxygen is transferred to form NO$_2$ and dimethyl sulfoxide (DMSO). NO$_3$ acts only as a catalyst for the ozone-DMS reaction:

$$\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$$
$$\text{NO}_3 + \text{DMS} \rightarrow \text{DMSO} + \text{NO}_2$$
$$\text{DMS} + \text{O}_3 \rightarrow \text{DMSO} + \text{O}_2$$

In this case the reaction with DMS would be controlling NO$_3$ concentrations but would not provide a NO$_2$ sink. Since there is no known reaction producing SO$_2$ from DMSO, this reaction would also lead to a low SO$_2$ yield from DMS oxidation. While DMSO has been found in the marine atmosphere [Andreae, 1980], its presence is not diagnostic for the pathway which is followed in the DMS-NO$_3$ reaction, since it may also be produced in the oxidation of DMS by OH [Grosjean, 1984].

CONCLUSIONS

In agreement with previous studies, which showed relatively small variations in the DMS concentrations in surface seawater between different oceanic regions [e.g., Andreae and Raemdonck, 1983], we have found the average concentrations of DMS in the marine atmosphere from five oceanic regions also to be remarkably similar. The fluctuation in the atmospheric DMS levels in each region could be explained on the basis of meteorological phenomena and of the processes which control the oxidation of DMS in the atmosphere, i.e., the reactions with OH and probably also NO$_3$. Model simulations were able to reproduce both the observed DMS concentrations and their diurnal variation in the marine atmosphere within reasonable limits. These calculations suggest that the observed levels of DMS in the marine atmosphere are consistent with a biogenic DMS flux from the oceans of about 40 ± 20 Tg S yr$^{-1}$.

Acknowledgments. We thank the masters and crews of the research vessels Conrad, Bellows, Knorr, and Cape Hatteras for their collaboration. We gratefully acknowledge the permission of the Australian Department of Science and Technology to work at the Australian Baseline Station at Cape Grim and thank the station staff for their help. We thank M. Dancy for help in the preparation of the manuscript and figures. This research was supported by the National Science Foundation under grants ATM-8017574, OCE-8315733, and ATM-8407137 and by the Belgian National Fonds voor Wetenschappelijk Onderzoek.

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(Received March 11, 1985; revised June 19, 1985; accepted July 8, 1985.)