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Measurements of Atmospheric Dimethyl Sulfide and Carbon Disulfide in the Western Atlantic Boundary Layer

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Abstract. Shipboard measurements of atmospheric dimethyl sulfide were made during two transects along the east coast of the United States and at several stations in the Gulf of Maine. Limited measurements of carbon disulfide and hydrogen sulfide are also reported. The mean DMS mixing ratio was 29 pptv ($\sigma = 25$, $n = 84$, median 19 pptv) during the Atlantic transects, and 101 pptv ($\sigma = 67$, $n = 77$, median 79 pptv) in the Gulf of Maine. Distinct diurnal variations were found in the DMS data from the transects. The meteorology of the study area appears to control day-to-day differences in the magnitude of these diurnal variations, although rapid daytime oxidation is suggested in some cases. Diurnal variations were also evident in near-shore stations in the Gulf of Maine due to nocturnal boundary-layer inversion. Diurnal variation was not evident at other sites in the Gulf due to large scale changes in the atmospheric circulation pattern, which effectively masked any effects due to oxidation processes. Model simulations confirm that the DMS levels and diurnal variation found during the transects are not consistent with atmospheric oxidation processes alone. Atmospheric CS_2 and H_2S mixing ratios were less than 3 pptv during the transects, except for a single period of higher CS_2 mixing ratios (reaching 11 pptv) during advection of continental air. Calculations of the flux of oceanic sulfur to the eastern United States show that the contribution of natural sulfur to the North American sulfur budget is small compared to anthropogenic sources.

Key words: Dimethyl sulfide, natural sulfur, marine boundary layer, diurnal variation.

1. Introduction

The emission of dimethyl sulfide (DMS) from the oceans is believed to account for a large portion of the natural sulfur flux to the atmosphere on a global scale (Love-lock *et al.*, 1972; Barnard *et al.*, 1982; Bates *et al.*, 1987). The most recent gas exchange models predict a sea/air flux of about 22 Tg S/yr (Bates *et al.*, 1987). Shipboard measurements of DMS in the atmosphere have confirmed that DMS is present in the marine boundary layer at mixing ratios spanning a range of zero to more than 1 ppbv (Andreae *et al.*, 1985; Saltzman and Cooper, 1988). The limited aircraft measurements fall at the low end of this range (Ferek *et al.*, 1986; Andreae *et al.*, 1988). These mixing ratios, combined with laboratory reaction rate measurements and product studies, indicate that the oxidation of DMS is the major natural source of atmospheric SO_2 and sulfate over the oceans (Andreae, 1986; Ayers, 1986; Saltzman and Cooper, 1988).

In general, the variability observed in atmospheric mixing ratios of DMS is considerably greater than that observed in sea-surface mixing ratios. This increased variability can be attributed to the effects of (1) variations in the chemical loss rates of DMS, reflecting the distribution and speciation of oxidants, (2) dilution of marine boundary-layer air with either terrestrial or upper level air, and (3) variations in the wind field affecting gas exchange rates. In general, we expect the former two factors to play a significant role in coastal air masses or in oceanic regions heavily impacted by anthropogenic input. Although the available data base is quite limited, this appears to be borne out by the existing atmospheric measurements of DMS. Open ocean data exhibit reasonable diurnal cycles with mixing ratios related to the DMS concentration of the underlying water. Coastal air masses generally exhibit lower mixing ratios without consistent diurnal cycles. The lack of diurnal cycles in some data sets has been interpreted as evidence of nighttime oxidation, implicating the NO_3 radical as a significant sink for DMS (Andreae *et al.*, 1985).

The interpretation of the existing data is complicated by the difficulty of measuring DMS in air with high oxidant concentrations. Analytically, the cotrapping of oxidants or oxidant precursors can result in system losses which yield apparent low DMS mixing ratios. Several studies have indicated the need for effective oxidant removal systems (Ammons, 1980; Andreae *et al.*, 1985; Kuster *et al.* 1986; Saltzman and Cooper, 1989). Because these sampling losses are enhanced in polluted air masses, it is difficult to distinguish *apriori* between analytical and environmental variability with many of the analytical systems employed to date.

In this paper, we present DMS data from samples that have been collected using neutral aqueous potassium iodide as an oxidant scrubber. This is an extremely efficient scrubber for both ozone (Schechter, 1973) and NO_2 (Lee and Schwartz, 1981), and does not have the limited capacity of most earlier scrubbers (Saltzman and Cooper, 1989). Shipboard measurements of atmospheric DMS were made off the east coast of the U.S. aboard the *R/V Columbus Iselin*. The cruise track includes two transects between Miami, Florida and the Gulf of Maine (Figure 1). This allowed sampling through the pollutant plume off the northeast coast of the United States in the summer of 1987. The object of the work presented here was to characterize the different environmental variables controlling the temporal and spatial variability of DMS. The use of the improved analytical technique with frequent controls should ensure the quality of the DMS data, eliminating much of the uncertainty inherent in interpretation of previous data sets from polluted air masses. The cruise was primarily an oceanographic expedition, with no support measurements of other atmospheric species. The northward transect took place from 27 to 31 July and the southward transect from 14 to 18 August. Data are also presented from several stations in the Gulf of Maine, which were sampled from 2 to 12 August.

Fig. 1. *R/V Columbus Iselin* cruise track, 27 July–18 August 1987. Numbered arrows refer to the position at the end of each day during the transects. Letters refer to the sampling station locations in the Gulf of Maine.

2. Methods

All atmospheric samples were collected from the flying bridge level of the ship, at a height of approximately 10 m above the sea surface. The sampling apparatus was attached to an open construction platform that protruded forward of the superstructure to the forward mast (about 3 m). This platform was constructed in order to minimize disturbance of the sampled air by ship-related turbulence and emissions.

DMS and CS₂ were collected cryogenically using a Teflon loop (1/4" OD × 5/32" ID × 16" long) packed with Teflon wool and immersed in liquid oxygen (−183 °C). The loops were fitted with Teflon-lined stainless steel Swagelok fittings. Sample flow rates and volumes were monitored using a mass flow controller/integrator (Sierra Instrument Co.). Flow rates ranged from 0.2 to 0.5 liter min^{−1}, and sample volumes were generally in the range of 5–8 liters.

Oxidants were removed from the sample stream before the cryogenic trap using aqueous potassium iodide solution (2%) buffered at pH 7.0 with 0.05 M KH₂PO₄ and 0.05 M Na₂HPO₄ phosphate buffers (Schechter, 1973). A 250 ml glass fritted bubbler containing 60 ml of KI solution was used. The air stream was drawn through the glass frit at the base of the bubbler at 500 cm³ min^{−1}. The bubbler was

kept in an ice bath to lower the water vapor content of the sampled air stream. Residual water in the sample stream was removed by passage through an open Teflon loop in an alcohol bath at -20°C .

Two independent sampling channels were operated at all times, allowing either the collection of duplicate samples or monitoring of the recovery of standard additions to either sample stream. This procedure had been adopted during methods development as a practical way of verifying the efficiency of the scrubbers, thus ensuring the quality of the DMS data.

Samples were analysed immediately after collection by a GC/FPD method. The sample loops were disconnected from the scrubber/drier after raising the level of the cryogen and connected to the GC system via a 10 port Valco valve. The loops were then momentarily purged with N_2 to remove residual atmospheric oxygen, and the sample injected onto the column by immersion in hot water. Separation of DMS from other sulfur compounds was achieved using a 2 or 3 m Chromosil 330 column (Supelco, Inc., Bellefonte, PA), with N_2 carrier gas at $30\text{ cm}^3/\text{min}$. The 3 m column was used on the return leg in order to achieve separation between OCS and CS_2 . The oven was temperature programmed from 20 to 70°C with an initial hold of 4 min, a 3 min ramp, and a final hold of 8 min.

Calibration of the GC/FPD system was performed by purging dilute liquid standards onto a sample loop and injecting into the GC column as a normal sample. The preparation of these standards was described by Saltzman and Cooper (1988). The relative standard deviation of both replicate DMS standards and atmospheric samples is better than $\pm 6\%$. The detection limit of the detector is approximately 1 pmol sulfur, which corresponds to 3 pptv DMS and less than 2 pptv CS_2 in a ten liter sample.

Aqueous DMS concentrations in seawater samples were also measured periodically during the cruise by purging 5 cm^3 of seawater onto a sample loop using $150\text{ cm}^3\text{ min}^{-1}$ of N_2 for 10 min. The purge sample was then analysed in the same manner as air samples.

Several samples were also taken for atmospheric H_2S using the AgNO_3 filter method, modified according to Saltzman and Cooper (1988). These were collected as duplicate samples with back-up filters to correct for OCS interference (Cooper and Saltzman, 1987). This method has a detection limit of 2–3 pptv. H_2S samples were only collected while the ship was underway, with a relative wind direction less than $\pm 90^{\circ}$ to the bow.

The laboratory studies described here were carried out in a rooftop laboratory on Virginia Key, a barrier island east of Miami, Florida.

3. Results and Discussion

3.1. Analytical Considerations

The effectiveness of the aqueous neutral KI oxidant scrubber was evaluated in a

series of standard additions experiments carried out using ambient air both at sea and on the roof of our laboratory. A variety of meteorological conditions were encountered during the rooftop study, resulting in air masses ranging from unpolluted trade wind air with ozone mixing ratios less than 30 ppbv to post frontal continental air with ozone mixing ratios up to 140 ppbv. Two air samples were collected simultaneously in each experiment. One of these samples was spiked at the beginning of collection with an injection of aqueous DMS standard into the KI bubbler. The results of these experiments are shown in Figure 2. Within the analytical uncertainty, the DMS spike was quantitatively recovered in all samples, thereby demonstrating that sampling losses were not occurring.

During the shipboard work presented here, apparent low and variable recoveries were observed when the spike was injected into the inlet of the sampling train rather than into the bubbler itself. The 'missing' DMS appeared as carryover in the subsequent sample. This problem was attributed to insufficient gas transfer from the droplets to the sample air stream, and was avoided in subsequent experiments by injecting the standard (made up in the buffered KI solution) onto a plug of glass or Teflon wool in the inlet tubing. The thin liquid film produced on the surface of the wool provides for a more effective gas transfer. This procedure resulted in quantitative recoveries of spikes injected at the inlet, confirming that the earlier laboratory results were also applicable under the more arduous conditions encountered during the field study.

Fig. 2. Recovery of DMS standard additions to air samples.

3.2. Atmospheric DMS Concentrations

3.2.1. North-South Transects. The atmospheric DMS measurements are plotted in Figure 3. The mixing ratio during the northward and southward transects ranged from 1–110 pptv with a mean of 29 pptv ($\sigma = 25$, $n = 84$), and a median of 19 pptv. These data fall within the range of the limited previous DMS measurements made in polluted or continentally influenced North Atlantic boundary-layer air. Andreae *et al.* (1985) reported a mean mixing ratio of 59 pptv during a shipboard study from the Azores to the northeastern United States. Van Valin *et al.* (1985) reported mixing ratios ranging from 0.5 to 18 pptv in samples collected aboard aircraft in the vicinity of Boston.

Sorting the data diurnally into 2 hour intervals yields a striking diurnal cycle in the DMS mixing ratio with an afternoon minimum and a nighttime maximum of 14 and 51 pptv, respectively (Figure 4). The magnitude of this variation, a factor of 3.7, is significantly greater than reported in previous studies of marine air. Using similar data analysis, a factor of 1.4–1.7 has been found in more remote marine air (Andreae and Raemdonck, 1983; Andreae *et al.*, 1985; Berresheim, 1987; Saltzman and Cooper, 1988). Diurnal changes have not been evident in continentally influenced air masses (Andreae *et al.*, 1985; Luria *et al.*, 1986; Van Valin *et al.*, 1987).

The concentration of DMS in surface seawater samples taken during the transects ranged from 0.6 to 2.4 nM, with a mean of 1.5 nM ($\sigma = 0.7$), $n = 8$). This mean is almost identical to the concentration measured previously in a remote ocean study (1.4 nM; Saltzman and Cooper, 1988), where the atmospheric mixing ratio ranged diurnally from 38–58 pptv. The lower atmospheric levels found during the present study suggest either that the atmospheric oxidation processes are occurring more rapidly here or that the source term is lower. A lower source could be due to a somewhat lower mean wind speed (5.4 m/sec compared to 7.6 m/sec over the Caribbean) or possibly to the 'dilution' or periodic replacement of marine air with continental air.

3.2.2. Gulf of Maine Stations. The atmospheric DMS mixing ratio measured over the Gulf of Maine ranged from 11–335 pptv with a mean of 101 pptv ($\sigma = 67$, $n = 77$), and a median of 79 pptv. This range is similar to that reported previously for 'unpolluted' air over the North Atlantic Ocean (mean 138 pptv; Andreae *et al.*, 1985). The higher levels in the Gulf compared to our data from the transects probably reflect the higher concentration of aqueous DMS in the productive coastal waters in the Gulf of Maine (Keller *et al.*, 1989). Seawater samples from the Gulf had DMS levels averaging 3.7 nM (range 1.2 to 5.9 nM, $\sigma = 1.9$, $n = 5$).

The Gulf of Maine data show considerably more random variability than the data from the transects (Figure 3). Strong diurnal changes in DMS are evident at the nearshore sampling sites (stations D–H, days 11–14) due to the presence of nocturnal surface layer inversions, characterized by extremely low wind speeds.

Fig. 3. Atmospheric DMS mixing ratios. The upper scale on the abscissa shows days from 27 July 1987. The lower scale refers to the sampling stations shown in Figure 1.

Fig. 4. Diurnal variation in atmospheric DMS during the east coast transects. The data are averaged into two hour mean mixing ratios with standard errors shown as vertical bars.

Fig. 5. Diurnal variation in atmospheric DMS at in the Gulf of Maine. The data are averaged into two hour mean mixing ratios except for the data from midnight to 06:00, which is averaged into a single point. Standard errors of the mean are shown as vertical bars.

Individual features in the DMS data from the remainder of the stations are all related to large scale features in the circulation patterns. The periods of high concentration correspond to wind trajectories from the central north Atlantic, whereas the low concentrations (days 8–9, and 16) correspond to post-frontal air masses

with northerly or northwesterly winds. Similar results were observed by Andreae *et al.* (1985) during frontal passage in the region of the Bahamas/Sargasso Sea. The post-frontal air masses probably contain residual continental pollutants from the northeastern United States and may not be in equilibrium with the seawater DMS due to their relatively short transport time over the ocean.

As a consequence of the greater overall variability, neither the data from the off-shore stations or the combined nearshore/offshore data show significant diurnal variations after sorting and averaging into two hour intervals (Figure 5). The large day-to-day variability is evident from the magnitude of the standard errors associated with the individual data points. It is not possible to discern any diurnal effects due to oxidation processes in this data set.

3.3. Atmospheric CS₂ and H₂S Concentrations

CS₂ was routinely observed in samples after the 3 m chromatographic column was installed. The mixing ratios during the southward transect ranged from 1–11 pptv (Figure 6), with a mean of 2.7 pptv ($\sigma = 2.5$, $n = 46$). This is similar to the limited data of Saltzman and Cooper (2.2 pptv, 1988) from close to the Bahamas. Elevated mixing ratios (up to 11 pptv) were found on day 21 and presumably indicate advection of continental air. Strong westerly air flow was occurring at a time when the ship was relatively close to the coast. If these points are excluded, a mean of 1.8

Fig. 6. Wind velocity, wind direction, DMS and CS₂ measurements made during the southward transect.

pptv ($\sigma = 0.7$, $n = 40$) is obtained, similar to the data of Kim and Andreae (1.3 pptv, 1987) over the open Atlantic Ocean.

Unlike the DMS data, sorting and averaging the CS_2 data set into 4 h mean concentrations does not yield a statistically significant diurnal cycle. This is not surprising, as the diurnal amplitude expected (approximately 0.2 pptv) is within the analytical uncertainty.

Several samples were taken for atmospheric H_2S during the north-south transects, using the AgNO_3 filter method (Saltzman and Cooper, 1988). These yielded values that were not statistically higher than the method blanks (equivalent to 2–3 pptv). The observation of H_2S mixing ratios at or below our detection limit is likely to be real, as no negative interferences are known for this method. The method is more prone to positive interference from contaminant H_2S in the ship's plume.

The low levels of atmospheric H_2S are interesting in light of the fact that sulfide has been observed at nanomolar concentrations in North Atlantic surface waters (Cutter and Oatts, 1987; Luther and Tsamakis, 1989). The latter study suggests that the sulfide may be mostly complexed, which may be a major factor controlling its sea/air exchange rate. In an earlier study, we observed mixing ratios of atmospheric H_2S ranging from 7–11 pptv in remote marine air over the Caribbean. If we assume a similar sea/air flux in this region, i.e. a similar aqueous concentration with similar complexation, then the upper limit of 2–3 pptv H_2S obtained during this cruise is consistent with severalfold faster daytime oxidation processes in the air masses sampled here.

3.4. Processes Controlling Diurnal Variations in Atmospheric DMS

3.4.1. Chemical Process. The source of DMS to the atmosphere is emission from the sea surface, where it has been shown that the aqueous DMS concentration does not vary diurnally (Andreae 1986; Berresheim, 1987). The generally assumed sinks of DMS in the atmosphere are oxidation by photochemically produced OH radicals during the day, and by NO_3 radicals at night (for a review see Plane, 1989). Diurnal variation in the DMS mixing ratio due to these chemical processes can therefore be attributed to the relative magnitude of these two pathways.

In a previous report (Saltzman and Cooper, 1989), we have applied a simple box model to simulate the diurnal variation in the DMS mixing ratio over the remote oceans. This is similar to the model used by Andreae *et al.* (1985). A sinusoidal source term is used for the OH concentration, with a specified maximum at solar midday. The boundary-layer mixing depth is fixed at 1 km. The source of DMS to the atmosphere is calculated using the measured aqueous DMS concentration and by assuming one of the experimentally derived relationships between exchange coefficient (k) and wind speed (Smethie *et al.*, 1985; Wanninkhof *et al.*, 1985). Reasonable agreement was obtained between model predictions and remote oceanic field data when using (1) daytime oxidation alone and (2) the lower estimates of k .

During the present study, the average wind speeds measured during the transects and in the Gulf of Maine were 5.4 and 4.3 m/sec, respectively. Based on these values, the average value of k is predicted as 1.3 or 1.6 m/day during the transects and 0.8 or 0.9 m/day in the Gulf. Model runs using these conditions and an OH concentration of 5×10^6 molecules/cm³ are shown in Figure 7. These model runs predict a DMS minimum at approximately 16:40 and a maximum at 07:00. The DMS mixing ratio predicted for the transects (average 59–73 pptv) is about a factor of two higher than the field data, whereas the model prediction for the Gulf of Maine (average 89–100 pptv) is in fair agreement with the field data. The diurnal cycle predicted in all cases varies by a factor of 1.6 in maximum/minimum mixing ratio. This is a factor of two smaller than found in the field data from the transects.

Any nighttime oxidation by NO₃ radicals should have the effect of preventing or slowing the overnight accumulation of DMS. Inclusion of nighttime NO₃ in the model therefore has the effect of making the predicted diurnal variation even smaller in magnitude. In the averaged DMS data from the transects (Figure 4) there is not a steady nighttime increase in DMS levels, in contrast to the earlier data from the remote atmosphere (Andreae and Raemdonck, 1983; Saltzman and Cooper, 1988). The DMS mixing ratio here remains low for several hours after sunset and rises rapidly in the late evening to peak several hours before dawn. The evening increase in DMS levels is too rapid to be explained by a steady sea surface source term, and the decrease before dawn occurs at a time when NO₃ levels should be at a minimum.

The field data are modelled more accurately by increasing the OH concentra-

Fig. 7. Model predictions of atmospheric DMS. Units of k are m/day. A midday OH concentration of 5×10^6 molecules/cm³ and a mixing depth of 1 km are specified.

Fig. 8. Model predictions of atmospheric DMS. Units of k are m/day. Units of midday OH concentration are 10^6 molecules/cm³. A mixing depth of 1 km is specified.

tion to greater than 10^7 molecule/cm³, however both the phase and the rate of change in the predicted diurnal variation are not in good agreement with the field data (Figure 8). It is clear that the observed diurnal variation cannot be explained satisfactorily from a chemical viewpoint alone, but that daytime oxidation may be faster than in the remote air studied previously. As in the earlier data, there is no evidence for nighttime removal processes.

3.4.2. Meteorological Effects. There are three major ways in which meteorological effects could theoretically influence either the levels or diurnal variation of atmospheric DMS. First, diurnal changes could be a consequence of variation in the mixing height of the planetary boundary layer. This effect has previously been documented over land masses (Cooper, 1986), but has not been evident over the open ocean. Theoretically the depth of the boundary layer is linearly related to the surface wind speed (Yu, 1988), which should lead to a negative correlation between the wind speed and the mixing ratio of any species with a sea surface source. Second, and somewhat conversely, the exchange coefficient (piston velocity, k), and hence the emission rate, of gases from the sea surface is related linearly to the surface wind speed (Merlivat and Memery, 1983; Smethie *et al.*, 1985). Lastly, the meteorology controls the transport time and distance of an air mass over the ocean to the sampling site. Atmospheric DMS levels are dependent on the surface source strength, which is not uniform over large geographic areas. The equilibration time is on the order of days. A trajectory that passes over land during that time will result in lowered DMS levels, whereas a trajectory that passes over productive waters (e.g. along a coastal area) may result in elevated DMS levels.

The wind speed data taken from the shipboard meteorological system during the present study do not show any indication of strong repeating diurnal cycles during this cruise. It therefore follows that variations in the boundary layer height or the sea/air exchange rate should not be important here. However, we observe an apparent positive correlation between the wind speed and the measured DMS mixing ratio. This correlation can be explained by the observation that the higher wind speeds encountered during the transects were generally associated with easterly winds and, hence, air masses more representative of an oceanic atmosphere. Conversely, the low wind speeds were associated with westerly (or offshore) winds.

The meteorological and chemical data from the southward transect are plotted together in Figure 6. This clearly shows the relationship between wind speed and wind direction. It also shows that there were few prolonged periods of steady meteorological conditions, and that periodic changes in either wind speed or direction were sometimes extremely abrupt. There are, however, obvious diurnal cycles in the DMS mixing ratio, whose magnitude varies from day to day. All exhibit a daytime minimum and a nighttime maximum. This appears to be mostly fortuitous, however, as all the individual features can be explained through the meteorology. The only period with a steady wind direction occurred on day 19, with easterly flow. This resulted in the observation of high DMS levels from the oceanic air. A daytime minimum occurs at approximately 16:00, which could be the result of daytime oxidation processes. DMS levels then decreased dramatically during the night (into day 20) as the ship moved into weak westerly air flow close to the coast of North Carolina. The levels began to rise again after the ship moved into long-shore flow off South Carolina late in day 20. In the morning of day 21, the DMS levels fell and the CS₂ levels rose dramatically as offshore winds were again encountered off South Carolina and Georgia. Finally, strong easterly flow was established during day 22 off the Florida coast, accompanied by rising DMS and low CS₂ levels.

In more general analysis, there are two major periods with a westerly component to the air flow, in the mornings of days 20 and 21. In both cases, a switch to more easterly flow occurs in the afternoon, possibly being a result of seabreeze circulation. It is likely, therefore, that the daytime minimum in the data of Figure 4 reflects not only daytime oxidation, but a low DMS mixing ratio resulting from this westerly flow pattern. Meteorological effects therefore appear to be the dominating factor in controlling the temporal variation of DMS during the transects. Clearly, caution is necessary in the interpretation of data from coastal regions, as the magnitude of the observed diurnal cycle depends strongly on the meteorology of the area being studied.

3.5. The Flux of Oceanic DMS to the Eastern United States

Balancing the North American sulfur budget requires knowledge of the transport of biogenic sulfur to the eastern United States. Since DMS is the major component

of the oceanic sulfur emission, the flux should be due almost entirely to this compound and its oxidation products.

Atmospheric DMS levels during the transects were highest on day 19, averaging 67 pptv over the 24 hour period. With steady easterly winds averaging 7.2 m/sec over the same period, the flux of DMS in the oceanic air advecting the continental United States during that time is calculated to be 22 nmol/m²/sec. Additionally, the flux of DMS oxidation products should be considered as a component of the natural sulfur sources. SO₂ should be at a low steady-state concentration due to its rapid deposition or conversion to sulfate. Aerosol sulfate is present at a background concentration of approximately 0.7 µg/m³ (Savoie, 1984) which results in a flux of 50 nmol/m²/sec.

During westerly flow at approximately the same location, the fluxes of SO₂ and SO₄²⁻ away from the United States were calculated to be 750 and 200 nmol/m²/sec, respectively (Thornton and Bandy, 1987; Whelpdale *et al.*, 1987). It is clear, therefore that the flux of natural sulfur (DMS + SO₂ + SO₄²⁻) to the United States during easterly flow is less than 10% of the transport of anthropogenic sulfur in the reverse direction during westerly flow.

4. Summary

Shipboard measurements of atmospheric DMS were made during two transects along the east coast of the United States and at several stations in the Gulf of Maine. Improved analytical methods were used with frequent controls, eliminating much of the uncertainty associated with earlier measurements made in polluted air masses. The mean DMS mixing ratio was 29 pptv ($\sigma = 25$, $n = 84$) during the transects, and 101 pptv ($\sigma = 67$, $n = 77$) in the Gulf of Maine. The difference between the two data sets is consistent with higher seawater DMS concentrations in the Gulf.

Distinct diurnal cycles were found in the DMS data from the transects, with an amplitude of 14–51 pptv. Diurnal cycles were evident at nearshore stations in the Gulf of Maine, reflecting nocturnal boundary-layer inversion. None were evident from offshore stations in the Gulf. The diurnal variation found during the transects has a greater amplitude than in previous studies, and can be explained in part by oxidation processes and in part by meteorological effects. The lack of diurnal variation in the DMS data from the Gulf of Maine results from large-scale changes in the atmospheric circulation pattern, which masked any diurnal effects due to oxidation processes.

Limited measurements of CS₂ and H₂S during the transects showed that the mixing ratios of these gases were generally less than 3 pptv. A peak of 11 pptv CS₂ was measured during advection of continental air. The low H₂S levels compared to earlier work may indicate faster atmospheric oxidation processes here.

The flux of oceanic sulfur to the eastern United States at a time of steady easterly air flow is calculated to be approximately 72 nmol/m²/sec, indicating that the

contribution of natural sulfur to the North American sulfur budget is small compared to anthropogenic sulfur sources.

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References

- Ammons, J. M., Preconcentration methods for the determination of gaseous sulfur compounds in air, PhD dissertation, University of South Florida, Tampa.
- Andreae, M. O., 1986, The ocean as a source of atmospheric sulfur compounds, in P. Buat-Menrad (ed.), *The Role of Air-Sea Exchange in Geochemical Cycling*, D. Reidel, Dordrecht, pp. 3311–3362.
- Andreae, M. O. and Raemdonck, H., 1983, Dimethyl sulfide in the surface ocean and the marine atmosphere, *Science* **221**, 74–747.
- Andreae, M. O., Ferek, R. O., Bermond, F., Byrd, K. P., Engstrom, R. T., Hardin, S., Houmère, P. D., LeMarrec, F., Raemdonck, H., and Chatfield, R. B., 1985, Dimethyl sulfide in the marine atmosphere, *J. Geophys. Res.* **90**, 12891–12900.
- Andreae, M. O., Berresheim, H., Andreae, T. W., Kritz, M. A., Bates, T. S., and Merrill, J. T., 1988, Vertical distribution of dimethyl sulfide, sulfur dioxide, aerosol ions, and radon over the northeast Pacific Ocean, *J. Atmos. Chem.* **7**, 149–173.
- Ayers, G. P., Ivey, J. P., and Goodman, H. S., 1986, Sulfate and methanesulfonate in the maritime aerosol at Cape Grim, Tasmania, *J. Atmos. Chem.* **4**, 173–185.
- Barnard, W. R., Andreae, M. O., Watkins, W. E., Bingemer, H., and Georgii, H.-W., 1982, The flux of dimethyl sulfide from the oceans to the atmosphere, *J. Geophys. Res.* **87**, 8787–8793.
- Bates, T. S., Cline, J. D., Gammon, R. H., and Kelly-Hansen, S. R., 1987, Regional and seasonal variations in the flux of oceanic dimethyl sulfide to the atmosphere, *J. Geophys. Res.* **92**, 2930–2938.
- Berresheim, H., 1987, Biogenic sulfur emissions from the subantarctic and Antarctic oceans, *J. Geophys. Res.* **92**, 13245–13262.
- Cooper, D. J., 1986, Variability in biogenic hydrogen sulfide emissions from selected florida ecosystems. MS thesis, University of Miami.
- Cooper, D. J. and Saltzman, E. S., 1987, Uptake of carbonyl sulfide by silver nitrate impregnated filters: Implications for the measurement of low level atmospheric H₂S, *Geophys. Res. Lett.* **14**, 206–209.
- Cutter, G. A. and Oatts, T. J., 1987, Determination of sulfide and sedimentary sulfur speciation using gas chromatography-photoionization detection, *Anal. Chem.* **59**, 717–721.
- Ferek, R. O., Chatfield, R. B., and Andreae, M. O., 1986, Vertical distribution of dimethyl sulfide in the marine atmosphere, *Nature* **320**, 514–516.
- Keller, M. D., Bellows, W. K., and Guillard, R. R. L., 1989, Dimethyl sulfide production in marine phytoplankton, in W. J. Cooper and E. S. Saltzman (eds.), *Biogenic Sulfur in the Environment*, ACS Symposium Series 393, American Chemical Society, Washington, D.C., pp. 167–182.
- Kim, K.-H. and Andreae, M. O., 1987, Carbon disulfide in seawater and the marine atmosphere over the North Atlantic, *J. Geophys. Res.* **92**, 14733–14738.
- Kuster, W. C., Goldan, P. D., and Albritton, D. L., 1986, Ozone interference with ambient dimethyl sulfide measurements: The problem and a solution, *Eos* **67**, 887.

- Lee, Y.-N. and Schwartz, S. E., 1981, Evaluation of the rate of uptake of nitrogen dioxide by atmospheric and surface liquid water, *J. Geophys. Res.* **86**, 11971.
- Lovelock, J. E., Maggs, R. J., and Rasmussen, R. A., 1972, Atmospheric dimethyl sulfide and the natural sulfur cycle, *Nature* **237**, 452–453.
- Luria, M., Van Valin, C. C., Wellman, D. L., and Pueschel, R. F., 1986, Contribution of Gulf area natural sulfur to the North American sulfur budget, *Environ. Sci. Technol.* **20**, 91–95.
- Luther, G. W. and Tsamakis, E., 1989, Concentration and form of dissolved sulfide in the oxic water column of the ocean, *Marine Chem.* **27**, 165–177.
- Merlivat, L. and Memery, L., 1983, Gas exchange across an air-water interface: Experimental results and modelling of bubble contribution to transfer, *J. Geophys. Res.* **88**, 707–724.
- Plane, J. M. C., 1989, Laboratory studies of the gas-phase atmospheric oxidation of biogenic sulfur compounds: A review, in E. S. Saltzman and W. J. Cooper (eds.), *Biogenic Sulfur in the Environment*, ACS Symposium Series 393, American Chemical Society, Washington, D.C.
- Saltzman E. S. and Cooper, D. J., 1988, Shipboard measurements of atmospheric dimethyl sulfide and hydrogen sulfide in the Caribbean and Gulf of Mexico, *J. Atmos. Chem.* **6**, 191–209.
- Saltzman, E. S. and Cooper, D. J., 1989, Dimethyl sulfide and hydrogen sulfide in marine air, in W. J. Cooper and E. S. Saltzman (eds.), *Biogenic Sulfur in the Environment*, ACS Symposium Series 393, American Chemical Society, Washington, D.C., pp. 330–351.
- Savoie, D. L., 1984, Nitrate and non-sea-salt sulfate aerosols over major regions of the world ocean: Concentrations, sources, and fluxes, PhD dissertation, University of Miami.
- Schechter, H., 1973, Spectrophotometric method for determination of ozone in aqueous solutions, *Water Res.* **7**, 729–739.
- Smethie, W. M., Jr., Takahashi, T., Chipman, D. W., and Ledwell, J. R., 1985, Gas exchange and CO₂ flux in the tropical Atlantic Ocean determined from ²²²Rn and pCO₂ measurements, *J. Geophys. Res.* **90**, 7005–7022.
- Thornton, D. C., Bandy, A. R., and Driedger, A. R., III, 1987, Sulfur Dioxide over the Western Atlantic Ocean, *Global Biogeochem. Cycles* **1**, 317–328.
- Wanninkhof, R., Ledwell, R. R., and Broecker, W. S., 1985, Gas exchange – wind speed relation measured with sulfur hexafluoride on a lake, *Science* **227**, 1224–1226.
- Whelpdale, D. M., Keene, W. C., Hansen, A. D. A., and Boatman, J., 1987, Aircraft measurements of sulfur, nitrogen, and carbon speciation during WATOX-86. *Global Biogeochem. Cycles* **1**, 357–380.
- Van Valin, C. C., Berresheim, H., Andreae, M. O., and Luria, M., 1987, Dimethyl sulfide over the western Atlantic Ocean, *Geophys. Res. Lett.* **14**, 715–718.
- Yu, T.-W., 1988, A method for determining equivalent depths of the atmospheric boundary layer over the oceans, *J. Geophys. Res.* **93**, 3655–3661.