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Journal

Journal of Atmospheric Chemistry, 7(2)

ISSN

0167-7764

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Publication Date

1988-08-01

DOI

10.1007/bf00048046

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Shipboard Measurements of Atmospheric Dimethylsulfide and Hydrogen Sulfide in the Caribbean and Gulf of Mexico

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(Received: 28 December 1987; in revised form: 12 April 1988)

Abstract. Simultaneous shipboard measurements of atmospheric dimethylsulfide and hydrogen sulfide were made on three cruises in the Gulf of Mexico and the Caribbean. The cruise tracks include both oligotrophic and coastal waters and the air masses sampled include both remote marine air and air masses heavily influenced by terrestrial or coastal inputs. Using samples from two north-south Caribbean transects which are thought to represent remote subtropical Atlantic air, mean concentrations of DMS and H₂S were found to be 57 pptv (74 ng S m⁻³, $\sigma = 29$ pptv, $n = 48$) and 8.5 pptv (11 ng S m⁻³, $\sigma = 5.3$ pptv, $n = 36$), respectively. The ranges of measured concentrations for all samples were 0–800 pptv DMS and 0–260 pptv H₂S. Elevated concentrations were found in coastal regions and over some shallow waters. Statistical analysis reveals slight nighttime maxima in the concentrations of both DMS and H₂S in the remote marine atmosphere. The diurnal nature of the H₂S data is only apparent after correcting the measurements for interference due to carbonyl sulfide. Calculations using the measured ratio of H₂S to DMS in remote marine air suggest that the oxidation of H₂S contributes only about 11% to the excess (non-seasalt) sulfate in the marine boundary layer.

Key words. Dimethylsulfide, hydrogen sulfide, sulfur cycle, marine boundary layer.

1. Introduction

Oceanic emissions of reduced sulfur compounds constitute a major flux of sulfur to the atmosphere on a global basis. The atmospheric oxidation of these compounds may account for a significant portion of the sulfur dioxide (SO₂) and sulfate observed in marine air, particularly in highly productive and remote regions of the oceans. Dimethylsulfide (DMS) is known to be the most abundant reduced sulfur gas in surface seawater and its distribution has been studied in many regions of the oceans (Andreae *et al.*, 1986; Bates *et al.*, 1987; Turner *et al.*, 1987). Observations of DMS in the marine troposphere support the concept that DMS emission from the sea surface constitutes a major global flux of sulfur to the atmosphere (Andreae *et al.*, 1985). Model calculations indicate that the magnitude of this flux may be sufficient to account for all of the sulfate in marine air; however, there are large errors associated with such mass balance calculations and other sulfur species may be important.

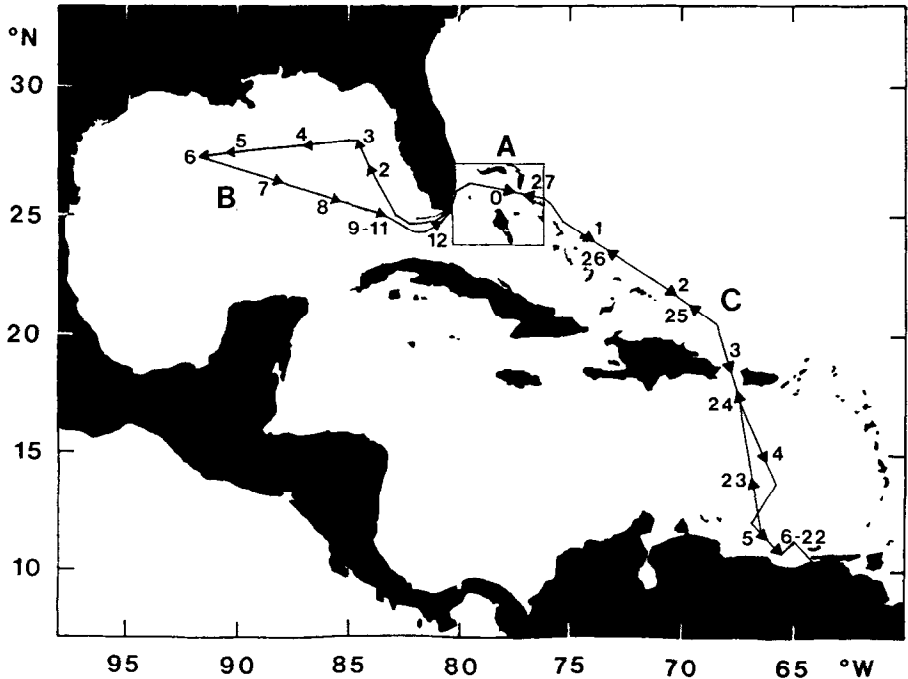
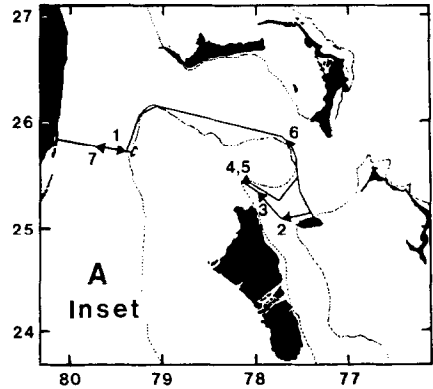
Hydrogen sulfide (H₂S) emissions from shallow coastal waters, exposed coastal muds and salt marshes have been extensively documented, (Jørgensen

and Okholm-Hansen, 1985; de Mello *et al.*, 1987; and references therein), but have not generally been assumed to be a significant oceanic source for two reasons. First, H_2S is thought to be produced solely as a result of anaerobic metabolism in anoxic sediments and, therefore, is unlikely to have a significant source in the open ocean. Second, until recently, it was thought to be rapidly oxidized in oxygenated waters (e.g. Ostlund and Alexander, 1963). However, several factors argue for the possibility that H_2S could be an important sulfur species in the oceans. These include a recent reexamination of the oxidation rate of H_2S supporting a half life of 50 ± 16 hours at 25°C (Millero *et al.*, 1987), and calculations of the rate of hydrolysis of OCS which indicate a potential though quantitatively minor abiotic source (Elliot *et al.*, 1987). The most direct evidence published to date is based on the observations of H_2S in the marine boundary layer, at levels which imply that H_2S must be present in significant concentrations in the surface ocean, and constitute an important sea/air flux of sulfur relative to DMS. Several investigators have observed H_2S in oceanic air. Slatt *et al.* (1978) measured concentrations ranging from 5 to 50 pptv (7 to 65 ng m^{-3}) at Barbados and Sal Island in the North Atlantic. Delmas and Servant (1982) found a mean concentration of 14 pptv (18 ng m^{-3}) in the Gulf of Guinea over productive waters of the west African coastal upwelling area. Herrmann and Jaeschke (1984) reported concentrations ranging from 11 to 118 pptv ($15\text{ to }154\text{ ng m}^{-3}$) over the Atlantic Ocean.

Recently, Cutter and Oatts (1987) have measured nanomolar concentrations of sulfide in surface seawater. However, the speciation and, hence, volatility of the sulfide has not yet been established. The observations of H_2S in marine air and waters raise interesting questions regarding its origin and relative importance compared to DMS as a precursor of atmospheric SO_2 and non-seasalt sulfate over the open ocean.

In this study we report simultaneous measurements of DMS and H_2S in marine air from three cruises in the Gulf of Mexico and the Caribbean Sea. Cruise tracks are shown in Figure 1. The first of these cruises, to the Tongue of the Ocean, Bahamas, took place during June of 1985 aboard the *R/V Cape Florida*. The second cruise was to the Gulf of Mexico, also aboard the *Cape Florida*, during October 1985. These two cruises were shakedown cruises which resulted in the acquisition of relatively limited data sets. The locations and meteorological conditions were such that they are not representative of open ocean conditions. However the results are of some interest with regard to coastal regions and will be briefly discussed in this paper. The third cruise was from Miami to the Cariaco Trench, off the coast of Venezuela, aboard the *R/V Columbus Iselin* during February and March of 1986. On this cruise a fairly extensive set of measurements was obtained along a north-south transect of the eastern Caribbean Sea, with prevailing winds such that oceanic air masses were sampled much of the time.

Fig. 1. Cruise Tracks. (A, inset) Bahamas, 11–18 June 1985. (B) Gulf of Mexico, 9–22 September 1985. (C) Caribbean Transect, 22 February–24 March 1986. Numbered arrows on the plots indicate the location at the end of each sampling day. The position of the Bahama Banks is indicated by the broken lines shown on the inset.



2. Experimental

2.1. Sampling

All atmospheric samples were collected on the flying bridge of the ships, forward of potential contamination from stack and sewage emissions. Samples were collected only when the relative wind aboard ship was within 90 degrees of the bow. With only a few exceptions, the samples were collected while the ship was underway. In many cases the opportunity for sampling was limited, as these

cruises were primarily run for oceanographic purposes which required long periods of sampling on station.

2.2. Dimethylsulfide

Samples were collected for analysis of DMS by drawing air through cryotrap immersed in liquid oxygen (-183°C). The cryotrap was constructed from Teflon PFA tubing (1/4" OD, 5/32" ID, 16" long) and packed loosely with Teflon wool. The air flow through the trap was controlled and measured using a mass flow controller which was modified to operate in the integrating mode. The flow rate during sampling was initially $500\text{ cm}^3\text{ min}^{-1}$; but decreased as the trap became blocked with ice. Typical air volumes used in this study ranged from 4 to 10 liters depending on the atmospheric DMS concentration. At the end of the sampling period, the level of the liquid oxygen was raised, and the cryotrap was capped with stainless steel end fittings for transfer to the shipboard lab for analysis.

During early tests it was observed that severe losses of DMS and other sulfur compounds occurred in the cryotrap, presumably as a result of the cotrapping of atmospheric oxidants or oxidant precursors such as O_3 or NO_x . This problem was overcome by using Na_2CO_3 prefilters as described by Ammons (1980). Both Ammons (1980) and Andreae *et al.* (1985) have noted a similar difficulty with losses of sulfur compounds trapped on gold foil or gold coated sand. While effective, the prefilters have a relatively limited capacity for oxidant removal. On the Bahamas and Gulf of Mexico cruises we used to prefilters (47 mm diameter) in series in Teflon PFA filter housings. Each pair of prefilters was used for no more than 12 liters of air. On the Cariaco Trench cruise (Caribbean Transect) we used glass tubes packed with Na_2CO_3 coated Chromosorb W/AW (Supelco Inc., Bellefonte, PA) as oxidant scrubbers because of their high capacity compared to the glass fiber filters. Each tube was used for approximately 30 liters of air. These tubes are identical to those used by Ammons (1980). The scrubbers used in the present study were shown to prevent losses of pre-concentrated DMS during sampling of relatively unpolluted marine air. Improved scrubbers have been used in subsequent studies (Cooper and Saltzman, 1988) and will be described in more detail in the future.

DMS samples were analysed by gas chromatography, with flame photometric detection. The column used was $12' \times 1/8''$ Chromosil 330 packed in Teflon (Supelco, Inc. Bellefonte, PA). After sampling, the cryotrap was connected to the gas chromatographic system via a 10-port stainless steel valve (Valco Inc.), purged with dry nitrogen to remove residual oxygen, and the sample injected onto the column by immersing the loop in hot water. The carrier gas was $30\text{ cm}^3\text{ min}^{-1}$ nitrogen, and the column was temperature programmed for an initial hold of two minutes at 25°C followed by heating to 100°C at $25^{\circ}\text{C min}^{-1}$. The analytical system had a detection limit of about 5×10^{-12} moles of sulfur

injected. This corresponds to a detection limit of 12 pptv DMS (16 ng S m⁻³) for a 10 liter air sample.

Calibration of the DMS chromatographic system was performed by injecting 10–200 µl volumes of a liquid standard into a 5 ml glass bubbler containing 1 ml of water. The standard was purged with nitrogen onto a cryotrap and analyzed in the same manner as atmospheric samples. A 60 ppm stock solution of DMS was prepared by diluting the pure liquid in methanol. A dilute working standard was prepared daily by dilution (1 : 1000) of the stock in distilled water. The calibration curves generated during this work were reproducible both within and between cruises. During the first few days of each cruise the detector underwent a gradual increase in sensitivity, then remained constant for the remainder of the cruise. The cause of this phenomenon is not known, but may be related to the loading of the column with high boiling sulfur compounds which slightly raise the background level of sulfur in the detector as they elute from the column.

During earlier laboratory and field studies we had obtained good agreement between low rate permeation tubes (GC Industries Inc., Chatsworth, CA), high permeation rate tubes (Kin-Tek Laboratories, Inc., Texas City, TX) and the liquid standards. Our field system was originally designed for use with the low rate, low temperature coefficient permeation tubes. However, during the course of the Bahamas cruise these tubes underwent significant changes in permeation rate and were abandoned in favor of the more reliable liquid standards.

The analytical procedure described above is also suitable for carbon disulfide and dimethyl disulfide. We have made numerous measurements of these compounds in terrestrial wetland environments using the same techniques (Cooper *et al.*, 1987; de Mello *et al.*, 1987). During the present study the system was calibrated for these gases as well as DMS, although they were rarely observed. Particular care was taken to assure that the system was free of CS₂ contamination, as one of our goals was to put at least an upper limit on its abundance in marine air. Standard additions of these compounds to air samples in the field demonstrated that the detection limit of the system was lower than 5 pptv in a 10 liter air sample. The lower detection limit compared to DMS results from the fact that CS₂ and DMDS have two atoms of sulfur per molecule and from the non-linear response of the FPD detector, which varies roughly as the square of the sulfur atom concentration. Other potentially important sulfur compounds such as H₂S, OCS, and mercaptans are not detectable at low levels with this system because of adsorptive losses, and because of quenching of the detector signal due to co-elution of the sulfur compounds with early eluting gases such as CO₂ and/or hydrocarbons. Typical chromatograms of a mixed standard and an atmospheric sample are shown in Figure 2.

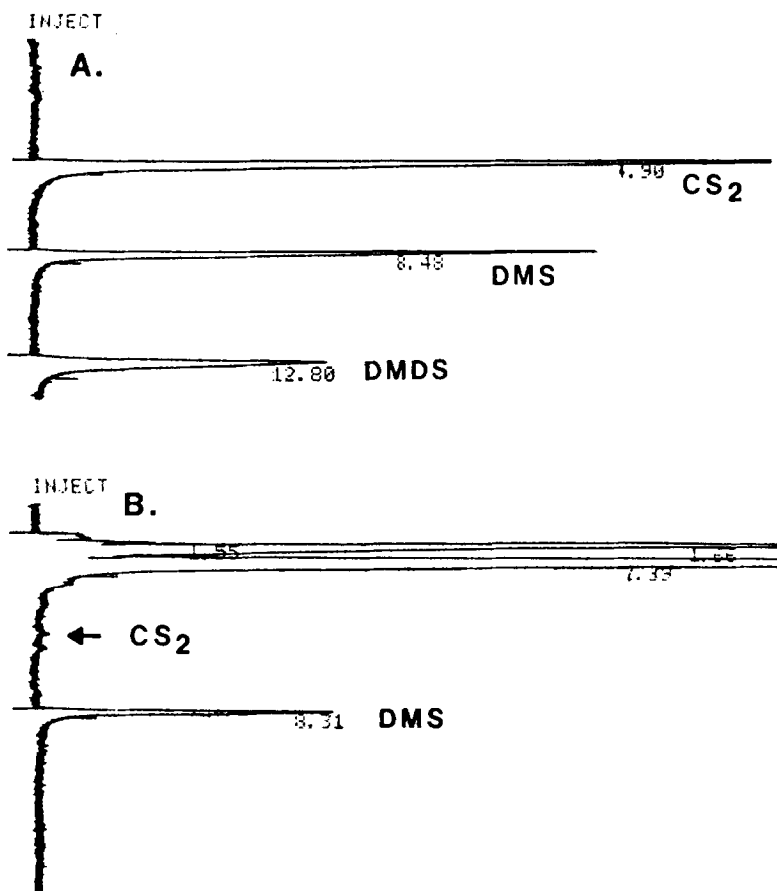


Fig. 2. Typical chromatograms. (A) Mixed DMS, CS_2 and DMDS standard containing 22 pmol DMS. (B) Air sample, 6.8 liters containing 72 ppt (94 ng S m^{-2}) DMS. The early split peak in the sample chromatogram corresponds to OCS, showing the negative interference due to CO_2 and/or hydrocarbons.

2.3. Hydrogen Sulfide

Hydrogen sulfide was collected and analysed using a method similar to that of Natusch *et al.* (1972). An air stream was drawn through a silver nitrate impregnated (Whatman 41) filter in a 47 mm Teflon PFA filter holder. Samples were collected at flow rates of 8 liter min^{-1} for times ranging from 30–100 min depending on the ambient H_2S concentration.

Sulfide was recovered from the silver nitrate filters by washing in 0.1 M NaOH/NaCN solution to a total volume of 20 ml and analysed by the fluorescence quenching of dilute fluorescein mercuric acetate (20 nmol added per sample). A Turner Designs model 10–853 fluorometer was used with a blue lamp and narrow (10 nm) bandpass filters at 500 nm excitation and 520 nm emission wavelengths. The cuvettes were 30 ml capacity and the instrument was

modified to allow rapid mixing of the solution in the cell using a magnetic stirrer.

Calibration was performed by standard addition of fresh sodium sulfide solution to blank filters. A 1 mM stock solution is made in distilled water containing 0.1 N NaOH and 0.1 mM EDTA. The stock solution is diluted (1 : 50) with 0.1 N NaOH/NaCN to make the working standard. The glassware used for preparation of the sulfide standards is conditioned and stored containing sulfide solution. In our experience, the sulfide stock remains intact for a period not exceeding one week. The routine calibration procedure serves primarily to verify that the fluorometer has retained its alignment and sensitivity. We have obtained virtually identical calibration curves over a period of several years. This is probably due to the fact that the sulfide concentration is a function of fluorescence decrease. Since the fluorescence decrease is measured as a percentage of fluorometer full scale, slight changes in the absolute response of the instrument do not affect the calibration. On the Cariaco Trench cruise, we were able to make fresh standards during the cruise using pre-weighed Na₂S crystals, which were stored under nitrogen in sealed glass ampules. The results verified the calibration made at the start of the cruise using the initial sulfide stock solution.

The lower limit of detection of the method is limited by the variability of filter blanks. Individual batches of filters had blanks ranging from 0–200 pmol S²⁻ per filter (Cooper, 1986), but variability within each batch was never greater than about 40 pmol. This gave a practical detection limit of about 10⁻¹⁰ moles H₂S per filter which is equivalent to 3 pptv for a 100 min sample.

Contamination of the filters and the analytical glassware was a major problem on the Bahamas cruise, primarily because of a leak in the ships plumbing which vented some H₂S into the ships lab late in the cruise. For the subsequent cruises the sulfur analyses were relocated into a van which was bolted onto the deck of the ship, and was thus removed from the plumbing system. We also modified the sample preparation procedures. To minimize sample handling, the filters were extracted in sealed scintillation vials, rather than a Buchner funnel that had been used previously. The NaOH/NaCN washing solution was stored in and delivered from a glass repipet. No further contamination problems were encountered during the laboratory procedures as demonstrated by regular analysis of blank filters.

Laboratory and field tests have demonstrated that a single silver nitrate filter is >98% efficient for H₂S removal under the sampling conditions used for terrestrial environments (Cooper, 1986). However, aboard ship, where longer sampling times were necessary to detect background levels of H₂S, we consistently observed a signal on back-up filters. This artifact sulfide has been attributed to the retention and subsequent hydrolysis of carbonyl sulfide on the basis of subsequent laboratory experiments. A temperature dependance of the artifact generation is evidenced by the diurnal nature of the signal found on the

back-up filters (Cooper and Saltzman, 1987). The total concentration of sulfide measured on the front filter is assumed to include an artifact equivalent to that on the back-up filter. The measured sulfide is corrected by subtracting the sulfide content of the back-up filter, as discussed in our earlier paper.

Back-up filters were only used during the Cariaco Trench cruise, where the mean sulfide concentration of these back-ups was found to be 4.9 pptv (6.4 ng S m⁻³) and to be independent of that on the front filters. Hydrogen sulfide data obtained on the Bahamas and Gulf of Mexico cruises, where only single stage filters were used, are probably overestimated by a similar amount.

The question of contamination of the air by H₂S released by the ship is a critical one which is difficult to dismiss out of hand. We have attempted to minimize this problem by sampling only when the ship was underway, and by monitoring the relative wind speed and direction to assure headwinds during sampling. Perhaps the most convincing evidence that the measurements represent the composition of marine air is the data itself. With the exception of very few samples, large atmospheric H₂S concentrations were normally only observed downwind of shallow waters or exposed mudflats. When sampling oceanic trajectories the H₂S concentrations invariably decreased markedly. No differences in H₂S levels were observed between samples collected on the bow of the ship and those collected on the flying bridge. There is no evidence to suggest that the measurements do not reflect the composition of the ambient marine air sampled.

3. Results

3.1. *Bahamas Cruise*

The Bahamas cruise track was from Miami to the Tongue of the Ocean, an elongate, deep basin which intrudes into the Bahamas platform (Figure 1, inset). Wind directions during the cruise ranged from southeasterly to southwesterly (120 to 250 degrees) during the first four days, after which southeasterly winds predominated. The predominant trajectory appeared to be down the axis of the Tongue of the Ocean, however, several shifts in wind direction brought air which had passed over Andros Island or portions of the Bahama Banks.

The concentrations of DMS and H₂S ranged from 25–300 pptv (33–392 ng S m⁻³) and 10–260 pptv (13–340 ng S m⁻³) respectively on this cruise (Figure 3). The two large peaks in H₂S on days 2 and 4 coincided with slight changes in the wind direction which shifted from along the length of the Tongue of the Ocean to trajectories skirting Andros (day 3) and the northeastern Great Bahama Bank (day 5). A similar effect appears in the DMS data, with the peak concentration on day 6 accompanying a brief change from southeasterly winds to almost northerly winds, from the northeastern Bahama Bank. Interestingly, the changes in the DMS and H₂S concentrations on days 5 and 6 did not occur simultan-

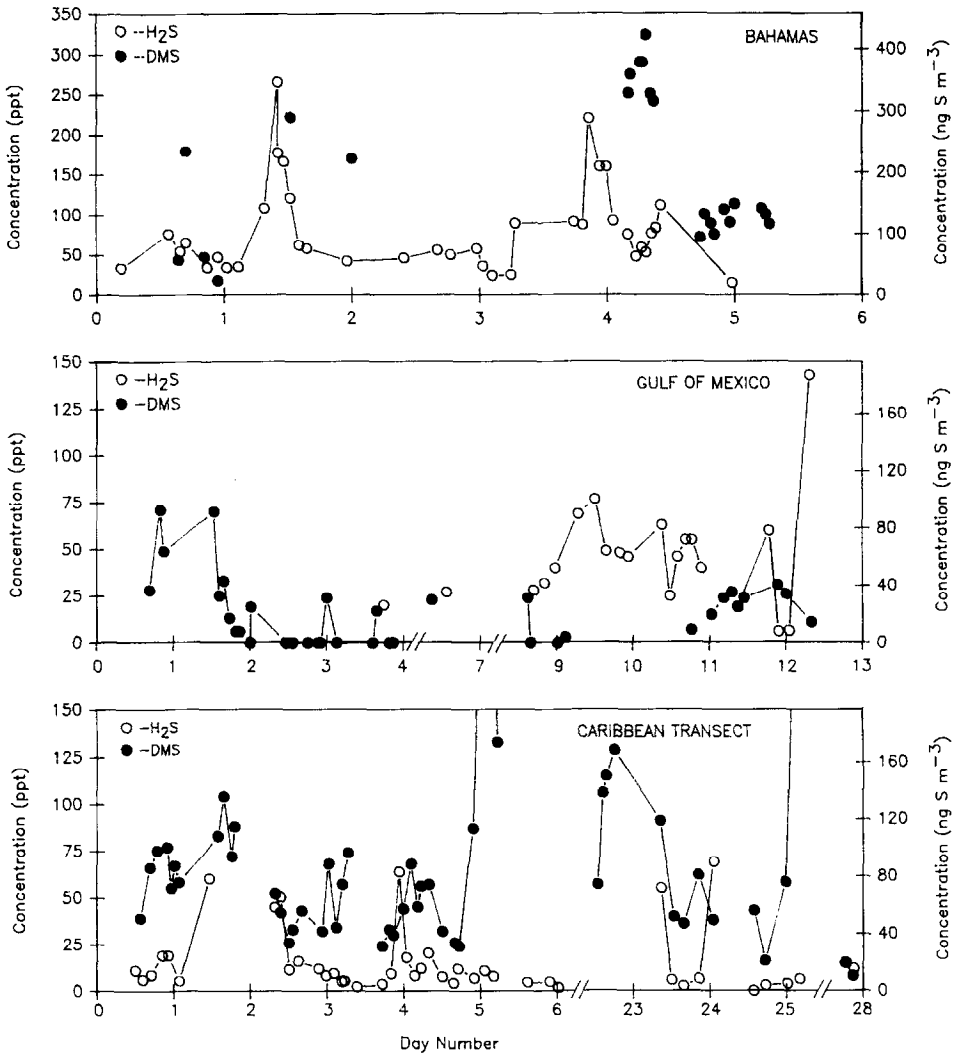


Fig. 3. Atmospheric DMS (●) and H₂S (○) measurements. (a) Bahamas Cruise, 11-17 June 1985; (b) Gulf of Mexico Cruise, 10-22 September 1985 (c) Caribbean Transect, 24 February-23 March 1986. Day numbers correspond to locations shown in Figure 1. Zero concentrations in (b) indicate samples below the limit of detection.

ously, suggesting that their sources are geographically or temporally different. This is in agreement with results from numerous emissions studies of various coastal environments (Jørgensen and Okholm-Hansen, 1985; de Mello *et al.*, 1987; and references therein).

The data from this cruise is, therefore, not representative of 'background' marine conditions. It does, however, clearly demonstrate the significance of island effects on the ambient reduced sulfur levels in this region. On the last night of the cruise, measurements were made in the Gulf Stream with southerly

winds. These winds should have brought air from south of the Bahamas platform, and, hence, provided an environment more representative of true marine conditions. Both DMS and H₂S dropped to values similar to those measured in more remote locations.

3.2. *Gulf of Mexico Cruise*

During the first portion of this cruise, data was obtained only for DMS. Concentrations ranging from 25–70 pptv (33–91 ng S m⁻³, Figure 3b) were measured as the ship steamed from Miami southwest offshore of the Florida keys and then northwest along the western shelf of Florida in the Gulf of Mexico. On the shelf, DMS concentrations were low, with more than half the samples below the detection limit, and a range from 5–25 pptv (7–33 ng S m⁻³) in the remainder. The low concentrations probably reflect the influence of continental air. Aerosol data collected simultaneously on this cruise show a threefold increase in nitrate and a tenfold increase in non-seasalt sulfate over remote oceanic values during this time. Weather patterns during the period indicate that the pollutant sources of oxidized sulfur are probably the industrialized areas on the west coast of Florida. The influence of continental air has been previously shown to decrease the measured DMS concentrations. This may be a result of increased oxidant generation in the polluted air (Andreae *et al.*, 1985), and/or failure of the oxidant scrubbers under these conditions (Cooper and Saltzman, 1988).

Atmospheric sampling was interrupted during the middle portion of this cruise while the ship was on station for water column studies and because of following winds and severe weather. Towards the end of the cruise several days were spent at anchor off the Dry Tortugas. Atmospheric sampling was possible because of steady southeasterly winds. DMS concentrations were very low, often below the limit of detection (indicated by the zero concentrations in Figure 3b). In order to verify that the analytical technique was functioning properly, some measurements were made by difference, using standard additions of DMS to air samples. The results indicate that the analysis was functioning properly, and that DMS concentrations were as low as 3 pptv. The cause of these low values is not known, but slightly elevated aerosol nitrate and non-seasalt sulfate values indicate that a continental component to the sampled air may still have been present. H₂S concentrations were consistently greater than those of DMS at this station, ranging from 30–90 pptv (39–118 ng S m⁻³). The source of this H₂S was presumably the shallow muds and tidal flats of nearby Florida Bay and the Florida Keys. H₂S concentrations of up to 24 ppb (31 μg m⁻³) have been measured in a mangrove habitat in this region (Cooper, 1986).

3.3. *Cariaco Trench Cruise (Caribbean Transect)*

The Cariaco Trench cruise consisted of two transects obtained while the ship

was underway from Miami to the coast of Venezuela and back to Miami (Figure 1, track C). No atmospheric measurements were made during the two week period in which the ship was on station at the Trench. East to northeasterly winds predominated for the duration of the cruise. Data from this cruise (Figure 3c) are therefore representative of true marine background conditions, except for three notable periods. The concentration of DMS was markedly higher during passage over shallow waters at the still of the Cariaco Basin (days 5–6 and 23) and also during transit near the Turks and Caicos Islands (day 26). Hydrogen sulfide concentrations were not noticeably affected at these times, but several small 'spikes' in the H₂S data may be a result of ship contamination at times of low relative wind speed.

DMS concentrations were found to be consistently higher than H₂S during this cruise, with ranges of 16–104 pptv (21–136 ng S m⁻³) and 0–20 pptv (0–26 ng S m⁻³), respectively, excluding the anomalously high values mentioned above. CS₂ was above the detection limit (approximately 1.5 pptv) in only a few samples, taken on day 28 over shallow waters in the vicinity of the Bahamas. The concentration range of 1.5–2.6 pptv (mean 2.2 pptv, 5.7 ng S m⁻³) is in good agreement with the results of Kim and Andreae (1987) and our own subsequent data (Cooper and Saltzman, 1988).

4. Discussion

4.1. Processes Regulating Atmospheric DMS and H₂S Concentrations

Marine air representing three distinct sets of boundary layer conditions has been sampled in this study. These are (1) coastal regions and shallow waters, (2) continentally influenced marine air, and (3) background marine air. Each of these environments may have different factors controlling the ambient reduced sulfur gas concentrations.

The highest levels of DMS and H₂S were measured over shallow and coastal waters, but did not occur simultaneously. Concentrations of up to 300 pptv (392 ng S m⁻³) DMS and 260 pptv (340 ng S m⁻³) H₂S measured on the Bahamas cruise can be attributed to the proximity of productive shelf waters. Extremely high DMS concentrations over shallow waters on the Cariaco Trench Cruise (up to 800 pptv, 1045 ng S m⁻³) were measured simultaneously with background H₂S concentrations (4–11 pptv, 6–14 ng S m⁻³). The difference in spatial and temporal emissions of DMS and H₂S probably reflects their different biological production processes. DMS appears to be a product of healthy aerobic algal metabolism and zooplankton grazing (Dacey and Wakeham, 1986). In contrast, H₂S is formed primarily in anoxic environments, via either bacterial sulfate reduction or degradation of organic matter.

The lowest concentrations of DMS were measured in continentally influenced air. This trend is most evident during the Gulf of Mexico cruise when

19 samples were found to be below the limit of detection. Similarly, Andreae *et al.* (1985), in the Bahamas and North Atlantic, found their lowest DMS concentrations during the passage of continental air associated with cold fronts. They attributed the low DMS levels to its rapid removal because of the enhanced concentration of oxidants in the continental air mass. It should be noted that sampling losses may also contribute to an apparent decrease in the DMS concentrations (Saltzman and Cooper, 1987).

It is not clear from our data whether the destruction rate of atmospheric H₂S is enhanced because of the increased oxidant levels. The only H₂S measurements made where the influence of continental air was evident showed the reverse effect, with a much higher concentrations of H₂S (28–77 pptv, 37–101 ng S m⁻³). However, these high levels probably reflect the presence of H₂S from the coastal areas discussed in the previous section.

Remote marine conditions were only encountered during the Cariaco Trench cruise (Caribbean Transect) and are most apparent from the consistently low H₂S concentrations. Although sharp peaks in DMS concentration were found during passage over shallow waters, no DMS samples were below the limit of detection.

4.2. Background Levels of DMS and H₂S in Marine Air

Results from the statistical analysis of all the shipboard data are presented in Table I. The concentrations shown as representing 'background' conditions are calculated from the DMS and H₂S data sets of the Caribbean Transect, after excluding all data points which fell outside the range of the mean \pm one standard deviation. These modified means are in excellent agreement with the median values of the unmodified DMS and H₂S data sets. Both statistical treatments eliminate bias in averaging due to (1) the extremely high DMS concentrations

Table I. Statistical analysis of shipboard reduced sulfur measurements. Concentrations units are pptv

Cruise	Dimethylsulfide				Hydrogen Sulfide			
	Median	Mean	σ	<i>n</i>	Median	Mean	σ	<i>n</i>
Bahamas	108	154	93	23	59	82	56	38
Gulf of Mexico	24 ^a	25	17	24	46	45	30	21
Caribbean Transect	57	83	116	52	8.5	15	18	44
All cruises	57 ^a	86	105	99	34	46	48	103
'Background' data ^b	na	57	29	48	na	8.5	5.3	36

^a Median does not include 19 measurements below the detection limit, which are assumed to result from continental influence (see text).

^b Calculated from the Caribbean Transect data after discarding all values greater than one standard deviation different from the mean concentration.

na Not applicable.

measured over shallow waters, and (2) spikes in the H₂S data, which may be the result of ship contamination. Average background concentrations of 57 pptv (74 ng S m⁻³) DMS and 8.5 pptv (11 ng S m⁻³) H₂S are calculated using both of these statistical procedures.

Our DMS data are in reasonable agreement with previous reports. In extensive studies of the marine atmosphere, Andreae *et al.* (1985) reported a mean DMS concentration of 107 pptv (140 ng S m⁻³), slightly higher than our mean for all cruises of 86 pptv (112 ng S m⁻³). However, our median estimate of 57 pptv (74 ng S m⁻³) for the 'background' DMS concentration is significantly lower than their mean value. The difference may be due, at least in part, to the fact that many of their measurements were made over biologically productive waters and during the season of maximum phytoplankton productivity.

Our estimate of 8.5 pptv (11 ng S m⁻³) 'background' H₂S concentration falls within the range reported by Slatt *et al.* (1978) for remote environments (medians 2–10 pptv). Delmas and Servant (1982) measured a mean concentration of 15 pptv (20 ng S m⁻³) over the Gulf of Guinea; this value is identical to our unadjusted mean. The most extensive data set previously reported for H₂S in the marine atmosphere is that of Herrmann and Jaeschke (1984). They reported a mean concentration of 31 pptv (40 ng H₂S m⁻³) from a data set of 39 samples judged to be representative of background conditions over the Atlantic Ocean. However, the detection limit of their method was 11 pptv (15 ng S m⁻³), and they applied this value to all of the samples which had undetectable levels. The greater sensitivity of our H₂S method allowed the measurement of H₂S concentrations as low as 3 pptv. The majority of the samples considered representative of background conditions in our study had concentrations lower than the detection limit quoted by Herrmann and Jaeschke in their study.

Preliminary analysis of our H₂S data revealed that OCS interferes in the determination of low concentrations (Cooper and Saltzman, 1987). The background data presented here have been corrected for this effect. It is impossible to assess the magnitude of this artifact in the earlier studies because of its temperature dependence, but it is probable that the previously reported concentrations of atmospheric H₂S have included a similar artifact component.

4.3. Diurnal Cycles of Atmospheric DMS and H₂S

To discern any diurnal cycles in the ambient concentrations of DMS and H₂S, the scatter in the data necessitates the use of an averaging technique. Figure 4 shows the data from the Caribbean Transect after grouping the points into four-hour intervals and calculating the mean concentration in each grouping. Anomalous data points, as discussed above, have been discarded for the purpose of this calculation. This treatment reveals a slightly higher concentration of DMS during the night, similar to that observed by Andreae *et al.* (1985) in remote marine air.

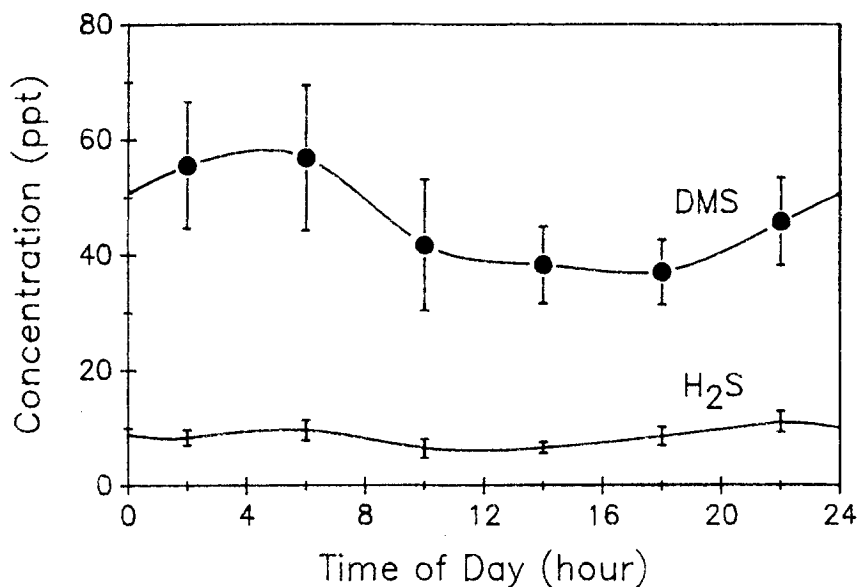


Fig. 4. Diurnal variation in atmospheric DMS and H₂S. Data points are four hour mean concentrations, with the standard errors of the mean plotted as vertical bars.

Our hydrogen sulfide data also exhibit a slight diurnal cycle, with the highest concentration at night. Previously, this effect had only been found in coastal or terrestrial environments (Herrmann and Jaeschke, 1984; Cooper, 1986). The diurnal cycle in H₂S in the remote marine atmosphere only becomes apparent after the data are corrected for the analytical artifact from OCS hydrolysis. The magnitude of this artifact is at a maximum during the daytime (Figure 5). The sulfide concentrations measured on both front and back-up filters are grouped into four-hour mean values, shown along with the resultant corrected means (of Figure 4) obtained by simple subtraction of the back-up filter sulfide from the front filter sulfide. It is clear in Figure 5 that the uncorrected data show an anomalous daytime maximum in H₂S, and that the artifact component is greater than the actual concentration at this time. The uncorrected data are similar to those of Delmas and Servant (1982), suggesting that their results may include a similar artifact component.

The magnitude of the diurnal cycles in both H₂S and DMS are smaller than predicted in photochemical models of their atmospheric oxidation (e.g. Graedel, 1979). The models assume removal to be due solely to photochemically generated OH and, hence, predict a large nocturnal accumulation. Andreae *et al.* (1985) showed in a model that the nighttime reaction of DMS with NO₃, as suggested by Winer *et al.* (1984), could explain the small diurnal changes in ambient DMS. In contrast, NO₃ is not thought to be of importance in the oxidation of H₂S since the rate constant is less than $5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ (Dlugokencky and Howard, 1988). Hence, an alternative explanation for the

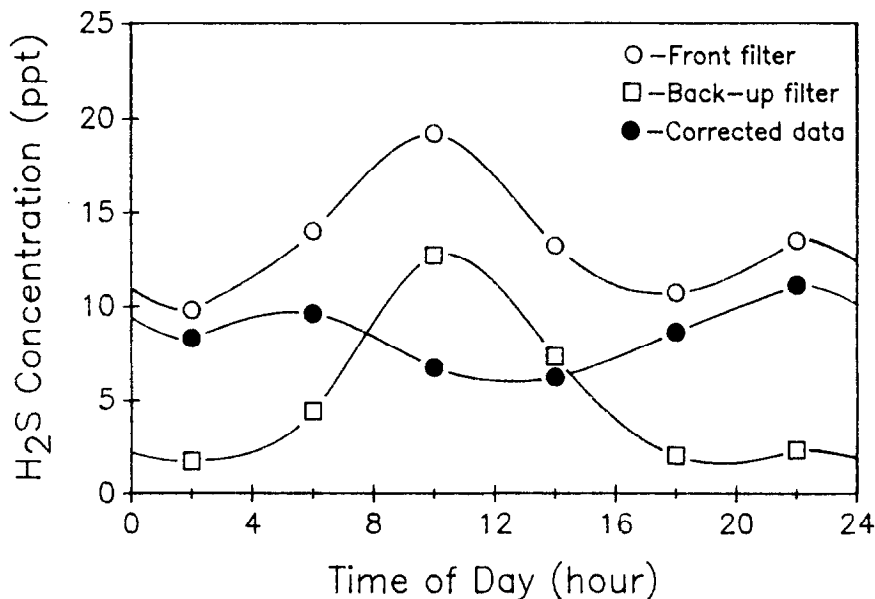


Fig. 5. Diurnal variation in the interference of carbonyl sulfide to hydrogen sulfide analysis. The corrected data are the concentrations calculated by subtraction of the artifact sulfide (back-up filters) from the total sulfide collected (front filters).

relatively small diurnal change in H₂S should be sought. It is possible that diurnal variations in the sea surface concentration of H₂S may result in a corresponding diurnal variation in the flux of H₂S to the atmosphere.

4.4. *Origin of H₂S in the Marine Boundary Layer*

The data presented here sheds little light on the source of hydrogen sulfide over the surface ocean. In nearshore environments, as in the Bahamas, H₂S emissions are dominated by coastal emissions presumably from anoxic intertidal and/or subtidal muds. Over oligotrophic waters, our data suggest that there is a marine source; however, the magnitude of this source is smaller than previously thought. The possibility certainly exists that unknown positive artifacts continue to contribute to our 'corrected' signal. The development of methods with higher selectivity is desirable, and we are currently working in this direction. During the Bahamas cruise, we made several attempts to directly measure the sea/air flux of H₂S using a Teflon lined floating chamber (Cooper, 1986). No emissions were ever detected, yielding an upper limit of 0.3 mg S m⁻² yr⁻¹ for the H₂S flux. This result, although the experiment has not been repeated, adds to our conviction that the oceanic H₂S flux is not large.

4.5. *Implications for the Origin of Non-seasalt Sulfate*

The relative contributions of DMS and H₂S to SO₂ and nonseasalt sulfate in the

remote marine atmosphere can be assessed by comparing calculated oxidation rates for the two species using our estimated background concentrations of DMS (57 pptv) and H₂S (8.5 pptv) from the Caribbean Transects. The major oxidation pathway of DMS in unpolluted air is via reaction with OH radical. This reaction yields primarily SO₂, which is then further oxidized by both homogeneous and heterogeneous pathways to sulfate. DMS also has an oxidation pathway to methanesulfonic acid; however, the branching ratio of MSA to SO₂ formed from DMS has been the subject of some controversy. It now appears that the high yields of MSA (>50%) observed by some workers (Hatakeyama and Akimoto, 1983; Hatakeyama *et al.*, 1985) resulted from the presence of nitrogen oxides in some laboratory experiments, and that the value at marine NO_x levels is quite low (<10%; Grosjean, 1984b; Barnes *et al.*, 1987). This conclusion is in general agreement with both kinetic studies (Hynes *et al.*, 1986) and field measurements of the ambient ratio of MSA to non-seasalt sulfate (Saltzman *et al.*, 1983). For the purpose of this calculation, we use a rate constant of $6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Hynes *et al.*, 1986) and assume an SO₂ yield of 95% from the oxidation of DMS by OH. A rate constant of $5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Barnes *et al.*, 1986, and references therein) is used for the oxidation of H₂S by OH and assume that the reaction product is entirely SO₂. Using these rate constants and the background concentrations above, the relative contributions of DMS and H₂S to the production of SO₂ over the oceans are 87 and 11%, respectively.

Two other oxidants have been proposed as potentially significant in DMS oxidation: NO₃ (Winer *et al.*, 1984) and IO (Barnes *et al.*, 1987). If operative, either mechanism for DMS oxidation would further decrease the relative contribution of H₂S to the atmospheric sulfate. It is unlikely that either of these oxidants would react sufficiently rapidly to compete with OH in H₂S removal. An upper estimate of $5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the rate constant of the reaction between NO₃ and H₂S has been reported by Dlugokencky and Howard (1988). The reaction of IO with DMS probably proceeds via a stabilized (conjugated) intermediate which breaks down to yield DMSO + I (Barnes *et al.*, 1987). A similar stabilized intermediate does not exist for the IO + H₂S reaction. It is not likely that either mechanism is particularly important in the removal of DMS from the remote marine atmosphere. NO₃ radicals are associated with polluted air masses and are probably not present at sufficient concentration to significantly affect DMS levels in clean marine air (Winer *et al.*, 1984). IO radicals are generated from the photolysis of methyl iodide. This may be released from the sea surface in highly productive coastal regions with abundant planktonic and macro-algae, but is not likely to be significant in oligotrophic oceanic regimes.

A summary of the relative contributions of the various sulfur species present in background marine air to the background sulfate over the remote oceans is given in Table II. Oxidation of carbonyl sulfide, the most abundant reduced

Table II. The relative contribution of various sulfur containing species to background (non-sea-salt) sulfate over the oceans. Rate constant units are $\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. See text for references

Species	Concentration (pptv)	Rate Constant	Contribution (%)
DMS	57	6.0×10^{-12}	87
H ₂ S	8.5	5.0×10^{-12}	11
CS ₂	2.2	1.5×10^{-12}	1.8
OCS	500	2.0×10^{-15}	0.3

sulfur gas in the atmosphere, accounts for less than 1% of the non-seasalt sulfate, based on a concentration of 500 pptv (Khalil and Rasmussen, 1984) and a rate constant of $2 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Wahner and Ravishankara, 1987). The oxidation pathway of CS₂ is not clear at this time, and OCS may be produced in addition to SO₂. A rate constant of $1.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ has been reported for the reaction of CS₂ with OH (Hynes and Wine, 1987). Using this value, and assuming complete oxidation to SO₂ of our measured concentration of 2.2 pptv CS₂ (a probable upper limit) gives a contribution of less than 2% to the total non-seasalt sulfate.

5. Summary and Conclusions

Measurements of atmospheric DMS and H₂S were made on three cruises in the Gulf of Mexico and the Caribbean. The ranges of measured concentrations were 0–800 pptv (0–1045 ng S m⁻³) DMS and 0–260 pptv (0–340 ng S m⁻³) H₂S, with the highest concentrations found in coastal regions and over shallow waters. The lowest DMS concentrations were found in a continentally influenced air mass, whereas the lowest H₂S concentrations were found in remote marine air. Concentrations of 57 pptv DMS (74 ng S m⁻³) and 8.5 pptv H₂S (11 ng S m⁻³) are calculated for conditions representing the remote marine boundary layer. These concentrations suggest that oxidation of DMS and H₂S contribute approximately 87 and 11%, respectively, of the non-seasalt sulfate in the marine boundary layer.

Diurnal cycles were found in the atmospheric concentrations of DMS and H₂S in background marine conditions, exhibiting slight nighttime elevations of both compounds. The small magnitude of these variations cannot be fully explained.

Acknowledgements

We wish to acknowledge the considerable efforts of William Zamboni de Mello and Dennis L. Savoie in both methods development and field work. The work was also made possible through the expert technical assistance of Dave Odum

and Tom Snowdon. Thanks are also due to the crew of the *R/V Cape Florida* and the *R/V Columbus Iselin*, and to Paul Lundgren and Ron Hutchinson of the RSMAS Marine Department. We are also grateful to Rod Zika for the use of his fluorometer, to Ken Mopper and Ollie Zafiriou for their efforts as chief scientists of the cruises, and to John Plane for helpful discussions. The work was supported by grants ATM 84-05921 and ATM 87-09802 from the National Science Foundation.

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