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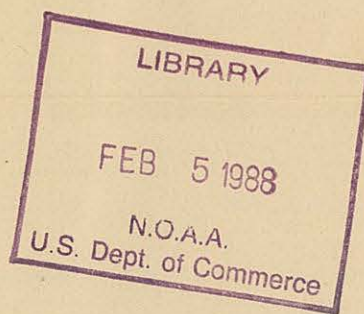
NOAA Technical Report ERL 432-ARL 9



Natural Sulfur Flux From the Gulf of Mexico: Dimethyl Sulfide, Carbonyl Sulfide, and Sulfur Dioxide

Charles C. Van Valin
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Air Resources Laboratory
Geophysical Monitoring for Climatic Change
Air Quality Group
Boulder, Colorado

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Natural Sulfur Flux From the Gulf of Mexico: Dimethyl Sulfide, Carbonyl Sulfide, and Sulfur Dioxide

Charles C. Van Valin, Menachem Luria,* Dennis L. Wellman,
Ruth L. Gunter, and Rudolf F. Pueschel†

ABSTRACT. Atmospheric measurements of natural sulfur compounds were performed over the northern Gulf of Mexico during the late summer months of 1984. Air samples were collected with an instrumented aircraft at elevations of 30-3500 m, during both day and night. Most air samples were representative of the clean maritime atmosphere, although some were from continental contaminated air during periods of offshore flow at the coastline. In all samples, carbonyl sulfide concentrations were within the range of 400-500 pptv. Conversely, the dimethyl sulfide concentrations showed significant variability: during clean atmospheric conditions the average of all measurements was 27 pptv, whereas under polluted conditions the average was 7 pptv. Measurable quantities of dimethyl sulfide (>5 pptv) were not observed above the boundary layer. The average sulfur dioxide concentration measured in the marine (clean) atmosphere was 215 pptv, which is consistent with the oxidation of dimethyl sulfide being its major source.

1. INTRODUCTION

The emission of reduced sulfur (S) compounds into the atmosphere through natural processes has been recognized for a long time. In recent years, however, a growing interest in the magnitude and composition has evolved, mainly because these compounds may make a significant contribution to the atmospheric loading of sulfate (SO_4^{-2}) aerosols. It is difficult to assess accurately the exact emission rate of S-containing compounds into the atmosphere; therefore, variations of 2 orders of magnitude between some estimates are not surprising (Möller, 1984b).

It is widely believed that the primary atmospheric source of natural atmospheric S is dimethyl sulfide (DMS). Andreae and Raemdonck (1983) estimated that the global biogenic emission of S is on the order of 103 Tg yr^{-1} , and about half-- 52 Tg yr^{-1} --is as DMS. Most DMS is emitted from marine sources (~75%), but it is also emitted significantly from continental areas (Adams et al., 1981). Other sources of biogenic S include hydrogen sulfide from biological decay, which was estimated by Adams et al. (1981) to provide $32\text{-}45 \text{ Tg (S) yr}^{-1}$. Khalil and Rasmussen (1984) put the biogenic emission of carbonyl sulfide (COS) and carbon disulfide (CS_2) at about 1 and $1.3 \text{ Tg (S) yr}^{-1}$. Other biogenic S compounds, such as methyl mercaptan, dimethyl

*Permanent address: Environmental Sciences Division, School of Applied Science, The Hebrew University, Jerusalem, Israel.

†Present address: NASA Ames Research Center, Moffett Field, California.

sulfoxide and dimethyl disulfide, are believed to enter into the global S cycle in only a minor way (e.g., Möller, 1984b; Adams et al., 1981; Aneja et al., 1982; Steudler and Peterson, 1984). An additional natural source of atmospheric S is sulfur dioxide (SO_2) from volcanic activity. Cullis and Hirschler (1980) estimated that SO_2 from volcanoes is unlikely to contribute much more than $\sim 5 \text{ Tg (S) yr}^{-1}$; Cadle (1980) estimated as much as $30 \text{ Tg (S) yr}^{-1}$; and other authors (e.g., Möller, 1984b) have placed the value at about 2 Tg (S) yr^{-1} .

Because the global natural emission of S is on the same order of magnitude as (Cullis and Hirschler, 1980) or somewhat larger than (Möller, 1984a) the anthropogenic emission, a program to investigate the contribution of natural S to the overall S budget over North America was included in the National Acid Precipitation Assessment Program. This appeared particularly advisable after Reisinger and Crawford (1980) reported SO_4^{-2} fluxes from areas southwest of central Tennessee that were as much as 2.3 times the fluxes of all the other sectors. As a part of this program, the Air Quality Division of the NOAA Air Resources Laboratory conducted a series of research aircraft flights to determine the flux of S compounds into the North American continent from the marine atmosphere and from the zone extending inland as much as a few hundred kilometers. We report here measurements of DMS, COS, and SO_2 made during the late summer of 1984 over the nearshore region of the Gulf of Mexico (Fig. 1).

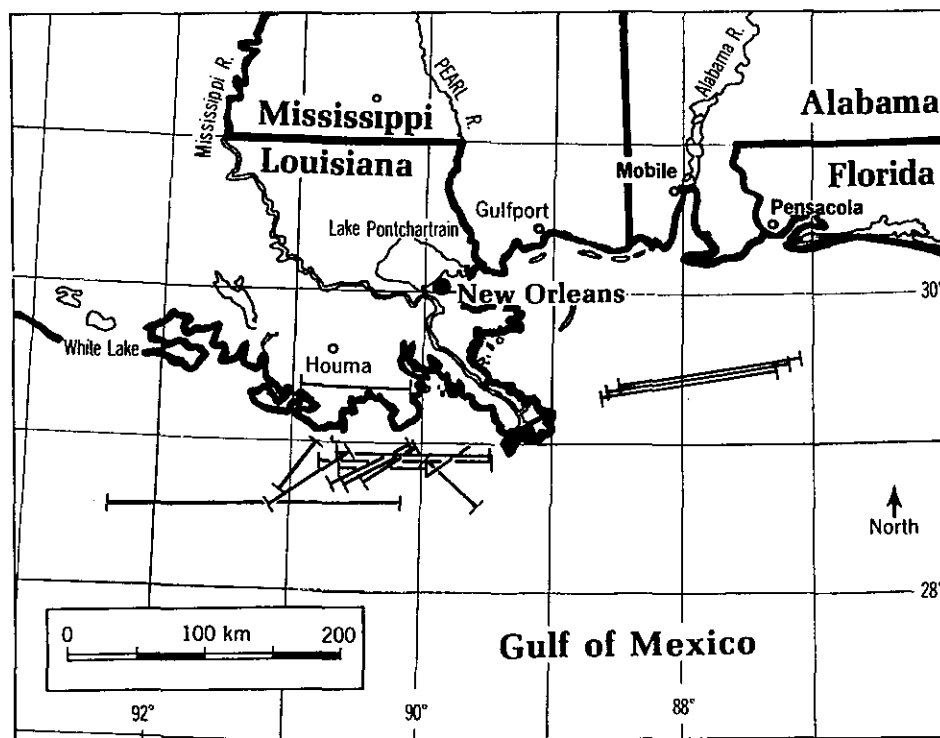


Figure 1.--Locations of NOAA air-sampling flights (—|) during the periods August 10-15 and August 29-September 3, 1984, presented on a map of the southern Gulf states and the northern Gulf of Mexico area.

2. EXPERIMENTAL

Air-sampling flights in the Gulf of Mexico area were carried out in two periods: August 10-15 and August 29-September 3, 1984. In both cases air samples were taken over the water at distances of as much as 80 km from the coast. Flights were performed during daytime at various altitudes from 30 to 3500 m; at night the lowest flight altitude was 300 m. The duration of each flight was 3-4 hours, during which time several "tracks" were flown at a constant elevation for 20 to 40 minutes. The flight headings were orthogonal to the reported (or observed) wind direction. The various flight tracks are shown on Fig. 1. The nine flights of the first period were flown offshore from the Delta region, south of the town of Houma, Louisiana. Of the nine flights of the second period, two were flown near Houma, two offshore south of Houma, and five along the tracks offshore south of Mobile, Alabama. Flight times, altitudes, and locations are listed in Table 1.

Table 1.--Research aircraft flight times, altitudes, and locations in 1984

Date	Time (CDT)	Altitude (m)	Location*
Period 1			
Aug. 9	1024-1208	300-1650	D
Aug. 10	0946-1111	450-1700†	D
Aug. 10	1539-1745	450-1700†	D
Aug. 11	0749-0835	300	D
Aug. 11	0930-1230	30-3000†	D
Aug. 13	0654-0937	150-3500†	D
Aug. 15	0707-0951	30-3000†	D
Aug. 15	1320-1619	30-600	D
Aug. 16	0657-0910	300-3000	D
Period 2			
Aug. 29	0938-1013	---	---
Aug. 29	2219-0130	300-2100	D → H
Aug. 30	2212-0031	300-2100	D
Aug. 31	2031-2254	300-2100†	D
Sept. 1	0126-0327	300-2100†	H
Sept. 1	1532-1850	100-2000	M
Sept. 2	0944-1302	100-3000†	M
Sept. 2	2307-0244	300-3000†	M
Sept. 3	1314-1635	300-3000†	M

*Location D is offshore south of the Mississippi Delta region, M is offshore south of Mobile, Alabama, and H is near Houma, Louisiana.

†Flask sampling flights.

Table 2.--Aircraft instrumentation and quantities measured

Quantity	Instrument	Analytical method	Detection limit	Time
O ₃	AID/560	Chemiluminescence	2 ppbv	10 s
Aerosols, SO ₂	Tandem filter pack*	Series filtration, ion chromatography	0.1 µg m ⁻³	20 min
SO ₄ ⁻² , Cl ⁻	Front: 1-µm Millipore/Fluoropore			
NO ₃ ⁻	Middle: NaCl-treated Whatman 41			
SO ₂	Back: Glycerol- and K ₂ CO ₃ -treated Whatman 41			
COS	Flasks†	GC-mass spectroscopy	5 pptv	2 min
DMS	Flasks‡	GC-flame photometry	5 pptv	2 min
CO, hydrocarbons	Flasks†	GC-flame ionization	10 pptv	2 min

*Forrest et al. (1979).

†Rasmussen et al. (1982a).

‡R.A. Rasmussen; Oregon Graduate Center; private communication, 1984.

A turboprop, twin-engine, Beechcraft King Air C-90 was used as a platform for measuring the quantities given in Table 2, as well as others. Flask air samples were collected during both study periods with a system developed and reported by Rasmussen et al. (1982a,b), and were later analyzed in his laboratory for the concentrations of hydrocarbons, COS, and CO by methods described in the same reports. DMS concentrations were also determined from the flask samples, within 72 h of the time of collection, using a gas chromatographic-flame photometric method (R.A. Rasmussen; Oregon Graduate Center; private communication, 1984). A test of the stability of the DMS in a flask sample collected near Barbados on June 21, 1984, showed (R. Ferek; University of Washington; private communication, 1985) that 96% of the DMS was recoverable after 7 days, when analyzed by the method described by Andreae et al. (1985).

O₃ was measured continuously by a chemiluminescent monitor but only during the second period. SO₂ and SO₄⁻² concentrations were determined during both periods using 47-mm series filter packs (Forrest et al., 1979), where SO₄⁻² was collected on a 1-µm-pore-size Millipore/Fluoropore filter and SO₂ was trapped on a Whatman 41 filter pretreated with K₂CO₃ and glycerol. The SO₄⁻² analysis was by ion chromatography; the SO₂ trapped on the filter was oxidized to SO₄⁻², which was then analyzed by ion chromatography. The SO₄⁻² data, and the interpretation of its importance to the North American S budget, were previously reported (Luria et al., 1986).

The westward extension of the subtropical Bermuda High dominated weather over the northern Gulf of Mexico during the first period, August 9-16, 1984. However, a weak surface trough was situated across southeast Louisiana, extending northeast-southwest, during August 12-14; the movement and position of

this trough were due, in part, to thunderstorms that developed near the trough. Low-level flow was determined by the position of the Bermuda High, but the wind field was weak because of a weak pressure gradient. In general, flow over the northern Gulf east of the trough was southerly. Flow over the coastal zone was chaotic because of vigorous convective activity.

Airflow during the second period, August 28-September 4, 1984, was similar. Flow over the northern Gulf was southeasterly in response to high pressure along the Atlantic coast. As was the case during the previous period, high surface temperatures and a very weak pressure gradient led to much convective activity and a chaotic wind field along and immediately inland from the shore.

The measured concentrations of CO, hydrocarbons, and aerosols indicated that air sampled within the boundary layer on the latter 3 days of the second field period were contaminated with anthropogenic emissions. Although the synoptic airflow was southerly during most of both field periods, the shore zone windfield was quite variable. The offshore-onshore diurnal cycle can produce further confusion of airflow in the coastal zone. We can assume, however, that all samples collected before September 1 had a long history over water and were relatively nonpolluted. This assumption was verified by measured background concentrations of CO and O₃.

Seventy-four flask samples were collected and analyzed for trace atmospheric gases during the course of this study; 37 samples were taken inside (IBL) and 37 above (ABL) the atmospheric boundary layer. Sixty-two samples were taken during the daylight hours and 12 during night hours. Although measurements of the depth of the boundary layer were not available in advance of the flights, it was assumed to extend to 1000 m.

3. RESULTS

Figure 2 shows the concentrations of DMS, COS, and CO as a function of altitude. The upper part shows the data collected during southerly air flows (marine air) and the lower part during the opposite flow (continental air). A statistical summary of the DMS, COS, and CO concentrations, divided into IBL and ABL measurements, is given in Table 3. The SO₂ data are presented in Fig. 3 and Table 3.

O₃ concentrations were available only during the second series of flights. Nevertheless, the O₃ data, presented in Fig. 4 as a function of altitude, include measurements performed under southerly and northerly airflows.

4. DISCUSSION

The CO data presented with the DMS and COS data in Fig. 2 were introduced to demonstrate the differences between the two situations observed in this study. During the first part of the study (Fig. 2, top), CO concentrations

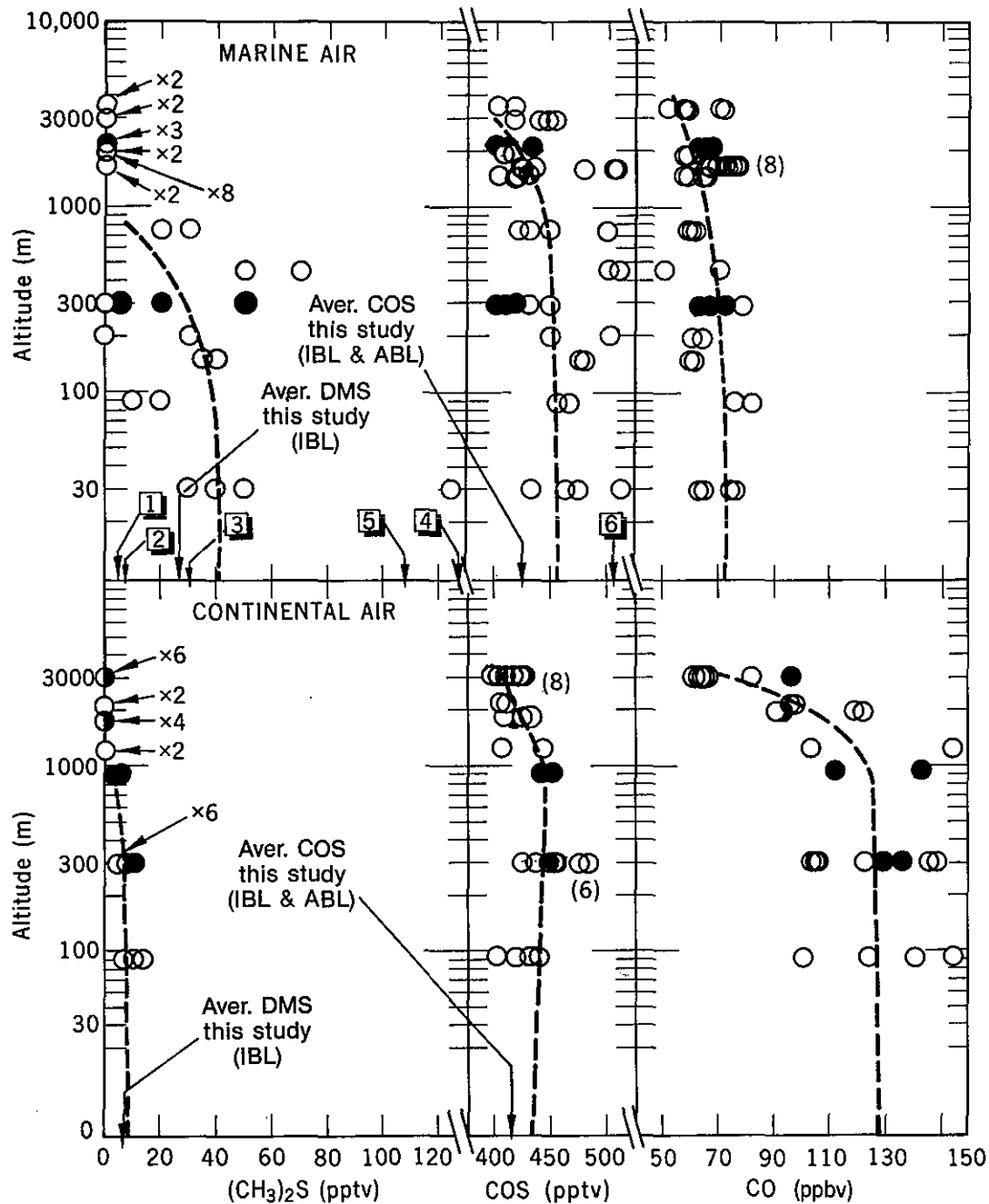


Figure 2.--DMS, COS, and CO as functions of altitude. The upper part of this figure shows data collected during southerly winds (marine air), and the lower part shows data collected from continental (polluted) air masses. The open and dark circles represent measurements performed during daytime and nighttime, respectively. IBL and ABL mean inside the boundary layer and above the boundary layer for this study. The dashed lines show the best linear fit for the data as given in Table 3. The arrows numbered 1-4 point to Andreae and Raemdonck (1983) DMS averages for the Atlantic Ocean, Gulf of Mexico, Peru Shelf, and remote Pacific Ocean, respectively. Arrow number 5 indicates the average of all values reported by Andreae et al. (1985). Arrow number 6 points to the worldwide average COS as determined by Torres et al. (1980).

Table 3.--CO, COS, DMS, and SO₂ data summary

	CO (ppbv)	COS (pptv)	DMS (pptv)	SO ₂ (pptv)
<u>In the boundary layer</u>				
Marine air samples*				
Aver. concentration	69 ± 8	456 ± 31	27 ± 30	215 ± 130
Linear fit (n=23)†	71 - 5.6h	467 - 24h	42 - 43h	---
Continental air samples#				
Aver. concentration	127 ± 18	443 ± 21	7 ± 3	3150 ± 2700
Linear fit (n=14)†	128 - 2h	435 + 25h	8.8 - 5.2h	---
<u>Above the boundary layer</u>				
Marine air samples*				
Aver. concentration	64 ± 7	434 ± 30	<5	105 ± 103
Linear fit (n=23)†	70 - 2.6h	453 - 9h	---	---
Continental air samples#				
Aver. concentration	94 ± 26	416 ± 12	<5	140 ± 100
Linear fit (n=14)†	162 - 30h	429 - 6h	---	---

*Samples taken on August 10, 11, 13, 15, and 31, 1984.

†h is the altitude in kilometers.

#Samples taken on September 1, 2, and 3, 1984.

averaged 69 ppbv IBL and 64 ppbv ABL. In fact, within the standard deviation, the CO concentration was constant throughout the boundary layer (Table 3) and the free troposphere. CO concentrations observed during this part of the study were similar to those reported by Seiler and Fishman (1981) for the remote clean atmosphere. The CO levels measured in the second part of the study (Fig. 2, bottom) clearly indicate that the air mass sampled was contaminated. The IBL average CO levels were twice as high as the ABL levels, and a significant increase was noticed in the free troposphere (above 1000 m).

The continental contamination of the air mass sampled in the second part of the study was further confirmed by a parallel increase in nonmethane hydrocarbons, which increased in some cases by a factor of 10. The effect of the continental air mass is also noticeable in the O₃ data (Fig. 4). On August 29 and 30, when the area was affected by marine air, the O₃ average background concentration was about 40 ppbv and the standard deviation was minimal; during the second part of the study, the standard deviation of the O₃ level was, as expected, significantly larger, since O₃ levels typically increase in the polluted atmosphere because of photochemical reactions but can also decrease in an NO-rich atmosphere.

COS levels observed in this study under all conditions are within the standard deviation of the values reported by Torres et al. (1980), but the

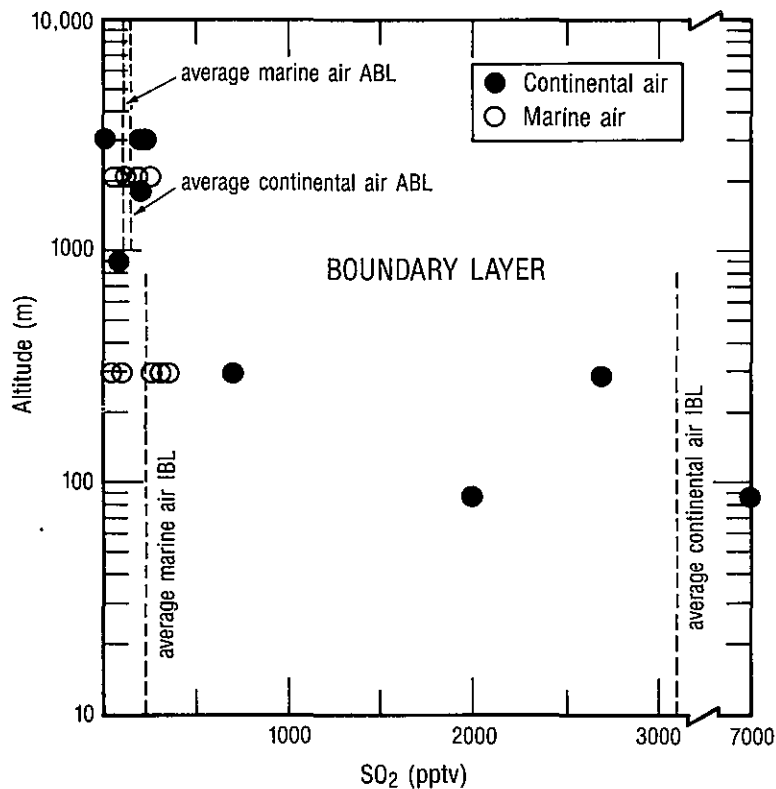


Figure 3.--SO₂ as a function of altitude. The open and filled circles represent data obtained during onshore (marine air) and offshore (continental air) air flows, respectively.

average values are lower by nearly 10%. No meaningful difference was observed between the data collected during the two parts of the study (Table 3). However, the data suggest (but do not prove) that COS levels inside the boundary layer were higher than those observed in the free troposphere. This observation can be explained by the fact that atmospheric COS results from two sources: direct emission and atmospheric oxidation of CS₂. Although COS and CS₂ are emitted at similar rates (Khalil and Rasmussen, 1984), their atmospheric lifetimes differ significantly. The major atmospheric sink for both compounds is oxidation by HO free radicals:



The rate coefficients for these reactions are $k_1 = 2 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ (Jones et al., 1983) and $k_2 < 8.8 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ (Ravishankara et al., 1980). Therefore, if one assumes an average HO concentration of $3 \times 10^6 \text{ molec cm}^{-3}$, COS and CS₂ atmospheric lifetimes can be estimated to be 440 and 1.9 days, respectively. Hence, the oxidation of CS₂ is expected to take place mostly IBL, and is probably responsible for the apparent increase of the COS in this layer.

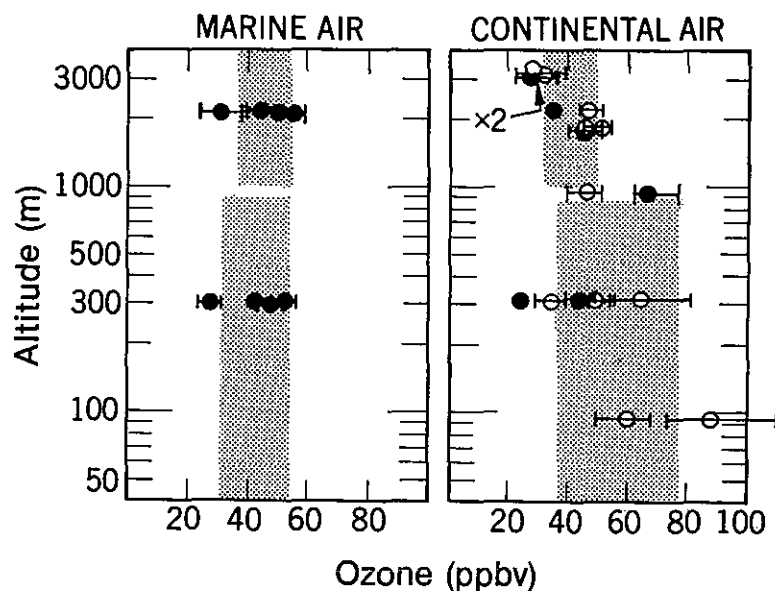


Figure 4.--O₃ as a function of altitude. Open and dark circles represent daytime and nighttime data, respectively. The shaded area represents the standard deviation of the data.

Despite the fact that the atmospheric concentration of COS is relatively high, its contribution to the atmospheric load of S aerosols has been calculated to be rather small (Chatfield and Crutzen, 1984). However, the COS measurements did serve a useful function in the sense that since the DMS and COS measurements were made on the same flask sample, and by similar methods, they provided an assurance regarding the correctness of the sampling procedure (Fig. 2).

None of the samples taken ABL (~1000 m) contained any measurable (>5 pptv) quantity of DMS. This observation is consistent with the relatively short (~9 h) atmospheric lifetime of DMS compared with the long tropospheric mixing time (Chatfield and Crutzen, 1984), especially under the meteorological conditions prevalent during the study. The difference between DMS concentrations above and within the boundary layer clearly justifies the separation into two data sets. Although most (88%) IBL measurements show measurable levels of DMS (Fig. 2), the average DMS concentration measured during the first part of the study is larger by a factor of about 4 than the average during the second part (Table 3). Another interesting feature in the data is the finding that under both sets of meteorological conditions daytime and nighttime values do not deviate from each other. This suggests a destruction mechanism of DMS that is independent of photochemistry.

The most comprehensive measurements made so far of DMS over marine sources have been by Andreae and his coworkers (Andreae and Raemdonck, 1983; Andreae et al., 1985.) These measurements were performed aboard ship in widely dispersed marine locations, including the Atlantic and Pacific Oceans, the Gulf of Mexico, the Tasman Sea, and the Peru Shelf. The DMS concentrations in air samples from the clean marine atmosphere were approximately 3 times greater than in air with a continental history; in specific instances

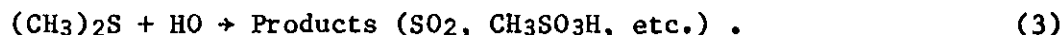
the difference was much greater. We compared these values from Andreae and his coworkers with the values from our samples collected by aircraft and found that our measured DMS concentrations IBL during demonstrably polluted conditions are very close to their values for continental air masses, whereas most of our other values are between their values for continental and marine sources. It is worth noting that our samples were collected during periods of low to moderate wind velocities, when the exchange rate between water and atmosphere is presumed to have been low, as was found by Andreae et al. (1985), and when photochemical activity was relatively high. One data point observed during the first part of this study deviates significantly from the rest of the points and is close to the values reported for the remote oceans. This suggests that the DMS concentration can be much higher under certain atmospheric conditions, that is, free of continental influence to the same degree as in the remote Pacific atmosphere, and it can be concluded that the present observations provide direct evidence for the strong inverse relationship between DMS levels and trace atmospheric pollutants.

This study presents vertical distributions of DMS that are in essential agreement with results reported by Ferek et al. (1986) for the tropical marine atmosphere. Although the data are scattered, a statistical analysis of the concentration as a function of elevation (Table 4) indicates that DMS concentration decreases as a function of elevation, under both marine and continental conditions. Furthermore, whenever measurements were made within the boundary layer at different altitudes during the same flight, the DMS concentration was always an inverse function of altitude, as can be seen from the data presented in Table 4. This observation suggests that the DMS is generated by the sea and that its atmospheric lifetime is of the same order as the boundary layer mixing time.

Table 4.--DMS as a function of altitude for the various flights within the boundary layer

Date	Altitude (m)	No. of samples	Average DMS (pptv)
Aug. 10	460	2	60
	760	2	28
Aug. 11	30	2	35
	90	2	15
Aug. 13	150	2	38
	760	2	<5
Aug. 15	30	2	68
	210	2	15
Sept. 1	90	2	9
	300	2	5
Sept. 2	90	2	11
	300	2	5

The major atmospheric removal mechanism of DMS, at least during the daytime, is by means of its reaction with hydroxyl free radicals; that is,



The rate coefficient for this reaction is close to $10^{-11} \text{ cm}^3 \text{ s}^{-1}$ according to Kurylo (1978), Atkinson et al. (1978), and Cox and Sheppard (1980) [although the value given by Wine et al. (1981) is lower by 50%]. If we assume an average HO concentration of $3 \times 10^6 \text{ molec cm}^{-3}$ for the clean atmosphere (Chatfield and Crutzen, 1984) and an average boundary layer depth of 1000 m, a simple steady state calculation suggests that the Gulf-area emission of DMS is approximately $100 \mu\text{g (S) m}^{-2} \text{ day}^{-1}$. This value is one-third of the estimate made by Andreae and Raemdonck (1983) for the remote oceans. The difference between the two estimates can be explained by the different methods used for flux estimate (Andreae and Raemdonck based their estimate on the concentration gradient between the aqueous and gas phases), by the fact that DMS production is not uniform oceanwide, and/or by the fact that the average removal rate for DMS in the atmosphere over the Gulf area is still faster than in the clean, remote oceanic atmosphere.

The occurrence of markedly lower DMS concentrations during the latter part of this study has already been attributed to the presence of atmospheric pollutants from continental sources. Under these polluted conditions the HO steady-state concentration can increase by a factor of 3-4 to a level of approximately $1.0 \times 10^7 \text{ molec cm}^{-3}$ (Calvert et al., 1978), thus reducing DMS levels accordingly. However, HO radicals, which are directly associated with photochemical activity, cannot be responsible for the nighttime reduction of DMS. This can probably be explained by the rapid dark reaction,



for which a rate coefficient of $1.0 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ was estimated by Atkinson et al. (1984). Hence, $1.0 \times 10^8 \text{ molec cm}^{-3}$ (4 pptv) of NO_3 would be as important a sink for DMS as $1.0 \times 10^7 \text{ molec cm}^{-3}$ of HO. NO_3 concentrations of this order and higher have been observed in moderately polluted areas during nighttime hours (Platt et al., 1984).

During the times when measurements were made in the marine (clean) atmosphere, the average SO_2 concentration was 215 pptv (Table 3). Under the same conditions, DMS averaged 27 pptv, giving a concentration ratio of approximately 8 to 1. This ratio is very close to the ratio between the rate constants of the reactions of SO_2 and DMS with the HO radical, which is 9.6. Since the reaction of SO_2 and DMS with HO is considered to be the major atmospheric removal mechanism for both compounds, the similarity between the ratios is consistent with the oxidation of DMS being the major source of SO_2 in the marine atmosphere.

Although a diurnal cycle for DMS is expected, it was observed only in the remote oceanic measurements of Andreae et al. (1985) and Andreae and Raemdonck (1983). Their data showed approximately a 60% change between minimum and

maximum values. This variation is indicative of a daytime atmospheric lifetime of about 8 to 10 hours and no nighttime destruction. The data available from the clean samples taken during this study are insufficient to draw a conclusion, positive or negative, regarding a diurnal cycle.

5. CONCLUSIONS

Although there may be a large experimental uncertainty in the DMS measurements, the results of this study suggest that atmospheric DMS is surface derived, has a half-life commensurate with the boundary layer mixing time, and is extremely sensitive to the presence of trace atmospheric pollutants. Under relatively clean atmospheric conditions in marine air masses, DMS concentrations over the Gulf of Mexico approached those typical of remote oceanic areas. A reduction in DMS by a factor of 4 was observed when the Gulf air was displaced by continental air.

There was no demonstrable diurnal cycle for DMS during the study; any possible diurnal cycle is buried in the noise level of the data. The very low concentrations at night, when admixture of continental air is suggested, support the importance of the recently proposed dark reaction between DMS and NO_3 .

COS concentrations were slightly higher IBL than ABL.

The ratios between the concentrations of DMS and SO_2 , and their reaction rates with HO, suggest that the oxidation of DMS is the principal source of SO_2 in the marine atmosphere.

6. ACKNOWLEDGMENTS

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