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# Methane Sulfonic Acid in the Marine Atmosphere

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Methane sulfonic acid (MSA) is an oxidation product of the reaction of OH radical with dimethyl sulfide and, hence, should be an important constituent of marine air. MSA concentrations in marine aerosols ranged from 0.009 to 0.075 $\mu g/m^3$ in samples from the Pacific and Indian oceans and Miami, Florida. In the samples from remote areas (Pacific and Indian oceans), MSA levels averaged 6.7% ($S = 1.9$) of the non–sea-salt (nss) $SO_4^=$ values. In the Miami area, ratios were occasionally lower because of the impact of local sulfur emissions (probably pollutant $SO_2$). MSA concentrations in seven rainwater samples collected at Miami, Florida, ranged from 0.001 to 0.034 ppm. Cascade impactor samples from Miami, Florida, and the Gulf of Mexico indicate that MSA occurs primarily in the smaller particles, as does nss $SO_4^=$. In the two samples analyzed, MSA is concentrated on slightly coarser particles than nss $SO_4^=$. The size distributions of both MSA and nss $SO_4^=$ differ markedly from that of sea salt $Na^+$, suggesting that at least the first step in the oxidation of organosulfur compounds is a gas phase reaction. The observed concentrations of MSA in marine air are the result of formation from gas phase reaction of dimethyl sulfide (and other volatile organosulfur compounds) with OH radical and destruction by aqueous phase reaction with OH radical in aerosols. Preliminary experiments indicate that MSA oxidation probably yields $SO_4^=$ under atmospheric conditions. Therefore, MSA destruction is a potentially important pathway for the formation of nss $SO_4^=$ in the marine atmosphere. The magnitude of the fluxes involved in the organosulfur cycle cannot be calculated from the MSA data because of the uncertainty in the free radical chemistry of aerosols.

## INTRODUCTION

The presence of non–sea-salt (nss) sulfate in aerosols throughout the marine troposphere [*Georgii*, 1978; *Mézáros*, 1978] suggests that there is a significant flux of reduced sulfur compounds from the sea surface to the atmosphere. Recent measurements of reduced sulfur compounds in the oceans strongly support these speculations and indicate that the estimated flux of dimethyl sulfide (DMS), the most abundant of these compounds, is sufficient to account for most, if not all, of the background nss sulfate in marine aerosols [*Barnard et al.*, 1982; *Andreae and Raemdonck*, 1983].

Kinetic studies indicate that reaction with OH radical may be a major pathway in the oxidation of DMS. Assuming an OH concentration of $10^6$ molec/$cm^3$, the reported rate constants $8.3 \times 10^{-12}$ [*Kurylo*, 1978] and $1.5 \times 10^{-11}$ [*Cox*, 1975] $cm^3$/molec s yield lifetimes of DMS against destruction by OH of 33.5 and 18.6 hours. Recent experimental studies, *Hatakeyama et al.*, 1982; *Hatakeyama and Akimoto*, 1983; *Grosjean and Lewis*, 1982; *Niki et al.*, 1983] showed that the reaction of OH and DMS resulted in the formation of substantial amounts of both methane sulfonic acid (MSA) and $SO_2$. These studies suggest that MSA should be a major component of the sulfur in the marine troposphere. Methane sulfonic acid has been identified in continental aerosols [*Panter and Penzhorn*, 1980] but has never been measured, to our knowledge, in maritime air masses.

In this report we present measurements of the concentration of methane sulfonic acid in marine aerosols and rain. From this data we assess the importance of this species both in the depositional flux of sulfur to the oceans and as an intermediate oxidation product of DMS in the formation of aerosol sulfate.

## SAMPLING AND ANALYSIS

Bulk aerosol samples were collected on 20 × 25 cm Whatman 41 filters at an air flow rate of about 1 $m^3$/min. For the

Miami and Indian Ocean samples, sampling periods were nominally 1 day in length with sampled volumes on the order of 1,500 $m^3$. At Fanning Island and Midway Island, samples were collected over weekly intervals with total sampled volumes of about 10,000 $m^3$. Daily cascade impactor samples were collected with a modified Weather Measure Corp. model 235 High Volume Cascade Impactor operated at 0.86 $m^3$/min with polycarbonate sheets as impaction surfaces and a 20 × 25 cm Whatman 41 filter as the backup [*Savoie and Prospero*, 1982a]. Assuming a particle density of 1.2 g/$cm^3$ (sea salt at 80% relative humidity), the 50% cutoff diameters for stages 1–6 were 16.7, 8.4, 4.2, 2.1, 1.0, and 0.5 microns, respectively. Rainwater samples were collected on an event basis by using an automatic wet-dry collector; the wet-side collection bucket was exposed only when it was raining.

For analysis, quarter sections of the Whatman 41 filters were extracted with 20 ml of Milli-Q water (16 Mohm cm). The entire polycarbonate impaction sheets were extracted ultrasonically in 25 ml of Milli-Q water. All the extracts were filtered through pre-washed 0.45 $\mu$m filters and, along with the rainwater samples, were maintained at 5°C until analyzed. In addition to MSA, aerosol extracts and rainwaters were analyzed for sodium, nitrate, and sulfate: sodium to ±2% by atomic absorption spectrometry and nitrate and sulfate to ±5% by ion chromatography [*Savoie and Prospero*, 1982a]. Nss $SO_4^=$ values were calculated from $Na^+$ and $SO_4^=$ concentrations by assuming that $Na^+$ is derived exclusively from seawater, which has a $SO_4^=/Na^+$ of 0.2517.

Previous measurements of MSA have involved esterification to the methyl ester ($CH_3SO_3CH_3$), which was then detected and quantified by using a gas chromatograph with a flame photometric detector and/or a mass spectrometer [*Penzhorn and Filby*, 1976]. Because MSA is a relatively strong acid and, thus, conductive in aqueous solutions, ion chromatography appeared to be a simple and viable alternative; this proved to be the case. MSA was determined by using a Dionex model 10 Ion Chromatograph with a 0.8 ml sample volume, 3 ml/min flow rate, and 0.0003 M $NaHCO_3$ eluent. Calibration curves were prepared as concentration versus the peak areas as mea-

## Standard



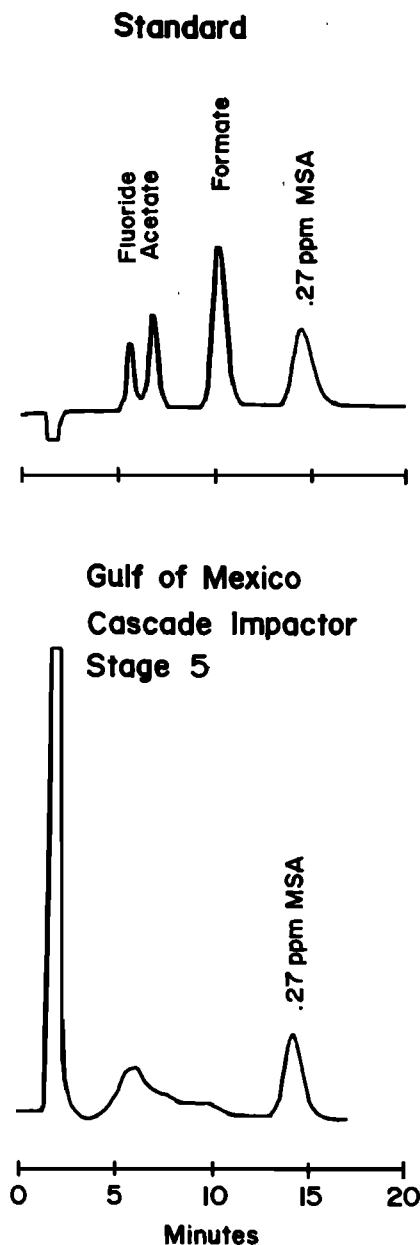## Gulf of Mexico
## Cascade Impactor
## Stage 5



Fig. 1. Ion chromatographic analyses of MSA in a standard and an aerosol sample.

sured by a Hewlett-Packard 3390A integrator. In this configuration, the detection limit was about 1 ppb with standard errors of ±5%. With these parameters, good separation was achieved between MSA and possible interferents such as low molecular weight organic acids (primarily formate and acetate) and fluoride (see Figure 1). No MSA was observed in filter blanks.

The presence of MSA in environmental samples was independently verified by esterification with diazomethane and detection of the resultant methyl sulfonate by GC-MS.

### STABILITY OF MSA SAMPLES

A simple experiment was performed to test the stability of MSA on the filters during sampling. Air was drawn through two pump and filter systems which were run simultaneously. In one system the filter was changed at intervals of 1–3 days. In the other, the filter was left in place for 8 days. If MSA was

produced or destroyed on the filters by some component in the air, the effect should be most pronounced on the continuous sample, as it was exposed to a considerably greater volume of air than the other samples. The results, Table 1, indicate no significant difference between the average MSA and nss $SO_4^=$ contents of the short interval samples (weighted by air volume) and that of the 8 day sample. No changes in MSA concentration with time were observed in aerosol sample extracts or rainwater samples (stored (5°C) over a period of approximately 6 months).

### SAMPLES

Bulk aerosol samples were collected at Miami, Florida, and at Fanning (4°N, 159°W) and Midway (8°N, 177°W) islands in the mid-Pacific as part of the Sea-Air Exchange (SEAREX) program [Uematsu et al., 1983]. Bulk aerosol samples were also collected off the coast of Somalia in the western Indian Ocean aboard the research vessels Salernum, Researcher, and Columbus Iselin during the GARP Global Weather Experiment (GWE). Cascade impactor samples were collected at the Cape Florida State Recreation Area on Key Biscayne, Miami, Florida, and in the eastern Gulf of Mexico aboard the R/V Researcher. Rain samples were obtained at the Rosenstiel School of Marine and Atmospheric Science campus, University of Miami, on Virginia Key, Miami, Florida.

### RESULTS

#### Bulk Aerosols

The atmospheric concentrations of MSA and nss $SO_4^=$ as determined from the bulk aerosol samples are listed in Table 2. In the Pacific Ocean, the Fanning and Midway islands samples yielded similar results with MSA concentrations of 0.042 $\mu g/m^3$ ($s = 0.010$) and 0.035 $\mu g/m^3$ ($s = 0.027$), respectively. Nss $SO_4^=$ levels were 0.63 $\mu g/m^3$ ($s = 0.15$) at Fanning Island and 0.52 $\mu g/m^3$ ($s = 0.32$) at Midway Island, values which are typical of remote oceanic areas [Prospero et al., 1982; Savoie and Prospero, 1982b]. At these stations, MSA concentrations ranged from 4 to 10% of the nss $SO_4^=$ concentrations.

In the Indian Ocean, off the coast of Somalia, MSA concentrations were slightly lower than in the Pacific with a mean of 0.020 $\mu g/m^3$ ($s = 0.013$). The nss $SO_4^=$ concentrations were again typical oceanic values, 0.56 $\mu g/m^3$ ($s = 0.24$). MSA ranged from 1 to 11% of the excess $SO_4^=$ in individual samples. The last four samples overlapped with the onset of the summer monsoon [Schott and Fernandez-Partagas, 1981]. During mid and late May there were two pulses of southerly winds, accompanied by a lowering of sea surface temperature, which indicates that some upwelling had occurred. The in-

TABLE 1. Stability Test of MSA During Sampling

|  | MSA, $\mu g/m^3$ | NSS $SO_4^=$, $\mu g/m^3$ |
| --- | --- | --- |
| Sample Interval |  |  |
| July 12–13 | 0.031 | 0.90 |
| July 13–14 | 0.038 | 1.03 |
| July 14–15 | 0.030 | 0.80 |
| July 15–16 | 0.024 | 0.68 |
| July 16–19 | 0.033 | 1.21 |
| July 19–20 | 0.043 | 0.99 |
| Weighted mean | 0.033 | 0.98 |
| July 12–20 | 0.033 | 1.02 |

TABLE 2. NSS $SO_4^=$ and MSA Aerosol Measurements

|  | NSS $SO_4^=$, $\mu g/m^3$ | MSA, $\mu g/m^3$ | (MSA/NSS $SO_4^=$) × 100, % |
|---|---|---|---|
| *Pacific Ocean* | | | |
| Fanning Island | | | |
| May 21–29, 1981 | 0.71 | 0.046 | 6.5 |
| Aug. 8–13, 1981 | 0.60 | 0.037 | 6.2 |
| Oct. 1–8, 1981 | 0.62 | 0.032 | 5.1 |
| Oct. 29 to Nov. 5, 1981 | 0.86 | 0.044 | 5.1 |
| Jan. 14–21, 1982 | 0.39 | 0.036 | 9.2 |
| March 4–11, 1982 | 0.59 | 0.059 | 10.0 |
| $\bar{x}$ | 0.63 | 0.042 | |
| $s$ | 0.15 | 0.027 | |
| Midway Island | | | |
| Feb. 26 to March 5, 1981 | 0.35 | 0.022 | 6.3 |
| May 7–14, 1981 | 1.02 | 0.075 | 7.4 |
| July 2–9, 1981 | 0.66 | 0.031 | 4.7 |
| Sept. 3–10, 1981 | 0.66 | 0.060 | 9.0 |
| Nov. 12–19, 1981 | 0.20 | 0.014 | 7.0 |
| Dec. 24–31, 1981 | 0.20 | 0.009 | 4.4 |
| $\bar{x}$ | 0.517 | 0.035 | |
| $s$ | 0.323 | 0.027 | |
| *Indian Ocean* | | | |
| Somalia Coast | | | |
| Feb. 2–3, 1979* | 0.52 | 0.012 | 2.3 |
| March 11–12, 1979† | 0.84 | 0.020 | 2.4 |
| April 30 to May 1, 1979‡ | 0.43 | 0.009 | 2.1 |
| May 3–4, 1979‡ | 0.58 | 0.025 | 4.3 |
| May 6–7, 1979‡ | 0.053 | 0.006 | 11.6 |
| May 15–16, 1979‡ | 0.77 | 0.007 | 0.9 |
| May 21–22, 1979‡ | 0.44 | 0.024 | 5.5 |
| May 27–28, 1979‡ | 0.76 | 0.037 | 4.9 |
| May 31 to June 1, 1979‡ | 0.64 | 0.040 | 6.3 |
| $\bar{x}$ | 0.56 | 0.020 | |
| $s$ | 0.24 | 0.013 | |
| *South Florida* | | | |
| Miami, Grosvenor Roof | | | |
| Aug. 21–22, 1978 | 0.84 | 0.022 | 2.6 |
| May 9–11, 1979 | 1.22 | 0.066 | 5.4 |
| May 18–21, 1979 | 7.7 | 0.045 | 0.6 |
| June 21–22, 1979 | 9.9 | 0.053 | 0.5 |
| June 28–29, 1979 | 0.88 | 0.029 | 3.4 |
| July 12–20, 1979 | 1.02 | 0.033 | 3.2 |
| Cape Florida | | | |
| Aug. 12, 1981 | 0.96 | 0.038 | 4.0 |
| $\bar{x}$ | 3.2 | 0.041 | |
| $s$ | 3.9 | 0.051 | |

*R/V *Salernum*.
†R/V *Columbus Iselin*.
‡R/V *Researcher*.

crease in MSA concentrations in the last three samples may reflect this change in oceanographic and meteorological conditions. Unfortunately, no samples were available from after the onset of steady monsoonal conditions which occurred in early June.

In Miami, MSA concentrations were 0.041 $\mu g/m^3$ ($s = 0.015$), which is quite similar to those observed in the other, more remote sampling locations. The nss $SO_4^=$ concentrations in the same samples vary over an order of magnitude from 0.84 to 9.9 $\mu g/m^3$ [*Savoie*, 1983]. Previous aerosol studies at Miami have shown that the low values correlate with steady easterly winds and represent normal marine conditions, while the higher values occur during disturbed conditions that bring air from the nearby city to the sampling site. The fact that samples with high nss $SO_4^=$ do not contain large amounts of MSA is additional evidence that local $SO_4^=$ is due primarily to urban sulfur sources (presumably $SO_2$) rather than to DMS emitted from local biological sources

such as Biscayne Bay or the Everglades. However, it does not eliminate biogenic $H_2S$ as a potential sulfur source.

## Particle Size Distribution

The concentrations of MSA, nss $SO_4^=$, and $Na^+$ as a function of particle size are shown in Figure 2 for the Key Biscayne, Florida, and Gulf of Mexico samples. The total concentrations of 0.038 $\mu g/m^3$ MSA and 0.960 $\mu g/m^3$ nss $SO_4^=$ in the Key Biscayne sample are consistent with those of the Miami bulk aerosol samples. Although the MSA concentration of 0.069 $\mu g/m^3$ in the Gulf of Mexico sample is near expected levels, the nss $SO_4^=$, 2.2 $\mu g/m^3$, is considerably higher than the normal marine background [*Savoie*, 1983] probably due to the advection of polluted continental air from Florida into the sampling regions. The synoptic conditions during the sampling period favored such transport. In the two samples studied, nss $SO_4^=$ was concentrated primarily in the smaller particles, while $Na^+$ was found primarily in the coar-
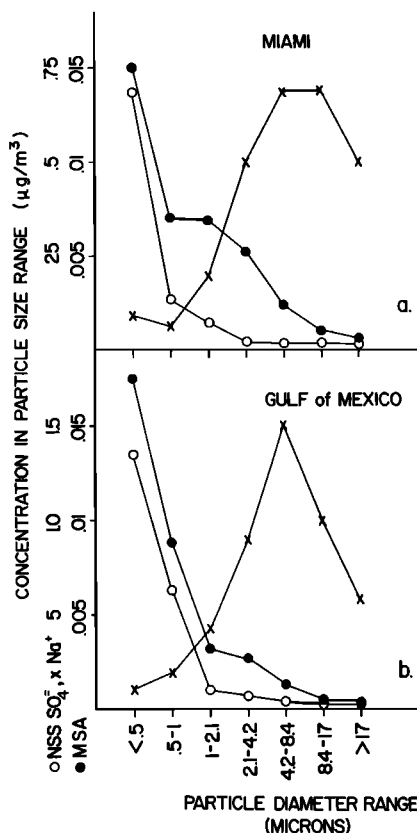
Fig. 2. Particle size distribution of MSA, nss $SO_4^=$, and $Na^+$ in cascade impactor samples from Miami, Florida, and the Gulf of Mexico.

ser particles. This difference has been noted by numerous authors previously and is explained by a sea-salt origin for $Na^+$ versus a "gas to particle conversion" origin for nss $SO_4^=$. Size distribution data have been used to argue against a heterogeneous origin for nss $SO_4^=$, as this would lead to a correlation between nss $SO_4^=$ and particle surface area, which is not observed.

MSA, like nss $SO_4^=$, is concentrated near the lower end of the size spectrum. However, in detail there appear to be significant differences between their size distributions. In the Key Biscayne sample, the MSA mass distribution is accurately (within analytical error) defined by a single peak with a log-normal distribution that has mass median diameter of 0.7 $\mu$m and a standard geometric deviation of 4.2. In contrast, the MSA distribution in the Gulf of Mexico sample appears to be bimodal. While a log-normal distribution similar to that found in Miami holds for the larger particle size portion, there is, in addition, a definite peak in the smallest size fractions.

If both MSA and nss $SO_4^=$ are formed by homogeneous

gas phase reactions, the observed differences in their size distributions is somewhat surprising. The physical processes of particle formation and coagulation must be similar for the two species because they have very similar physical properties. Chemically, however, there is a significant difference; $SO_4^=$ is stable in the aerosol, while MSA is not. In a subsequent section of this paper we discuss evidence for the atmospheric destruction of MSA via reaction with OH radical. We expect the rate of MSA oxidation to vary with particle size primarily because of the concentration of $CO_3^=$ and $Cl^-$ in the coarser sea-salt particles. These species react rapidly with OH, lowering the OH concentration and therefore slowing the rate of MSA oxidation in the larger particles. This stabilization process would tend to shift the MSA peak to the coarser end of the size spectrum.

In terms of this process, the Miami sample is clearly more evolved than that of the Gulf of Mexico sample. In the Gulf of Mexico sample the higher MSA concentration and the presence of an MSA peak in the smaller particles suggest either that the sample was taken close to the dimethyl sulfide source or that the OH concentrations were low. The extent to which aerosols exhibit the MSA shift to larger particles is probably a function of those chemical and meteorological factors that control the oxidation rate of MSA and its precursors and the residence time of aerosols in a given air mass.

Because only two sample sets have been analyzed, the above discussion is clearly speculative. Further field measurements and laboratory experiments are needed to confirm the observed distributions and to test the hypothesis.

### Rainwater

Concentrations of $Na^+$, $Cl^-$, $NO_3^-$, total $SO_4^=$, nss $SO_4^=$, and MSA in seven Miami rainwater samples are listed in Table 3. MSA is present in all samples at concentrations ranging from 1 to 34 ppb. The MSA/nss $SO_4^=$ ratio ranged from 0.4 to 2.1%, values similar to those in the Miami aerosol data previously discussed. Therefore, the origin of both the MSA and nss $SO_4^=$ in these samples may be the scavenging of aerosols within and below the clouds. If droplet uptake of gaseous species is important, we would expect to see lower MSA/nss $SO_4^=$ ratios in rainwater than in aerosols, due to the more rapid dissolution and oxidation of $SO_2$ than of DMS. However, the variability of the nss $SO_4^=$ in Miami aerosols is large and may obscure the signal from such reactions.

### DISCUSSION

### Atmospheric Destruction of Methane Sulfonic Acid

The results of this study show that MSA is present in remote marine aerosols at levels approximately 5% that of nss

TABLE 3. Miami Rainwater

|  | $Na^+$ | $Cl^-$ | $NO_3^-$ | $SO_4^=$ | nss $SO_4^=$ | MSA | (MSA/nss $SO_4^=$) × 100, % |
|---|---|---|---|---|---|---|---|
| Nov. 15, 1982 | 8.0 | 14.4 | 3.4 | 5.6 | 3.6 | 0.017 | 0.4 |
| Jan. 21, 1983 | 17.5 | 31.0 | 0.44 | 5.0 | 0.58 | 0.003 | 0.5 |
| Feb. 8, 1983 | 6.4 | 12.2 | 2.8 | 7.3 | 5.7 | 0.022 | 0.4 |
| Feb. 21, 1983 | 4.0 | 7.0 | 3.4 | 6.7 | 5.7 | 0.031 | 0.5 |
| Feb. 23, 1983 | 10.4 | 19.2 | 1.63 | 4.3 | 1.65 | 0.034 | 2.1 |
| Feb. 28, 1983 | 1.95 | 3.8 | 0.128 | 0.74 | 0.25 | 0.001* | 0.4* |
| March 8, 1983 | 0.98 | 2.0 | 0.40 | 1.17 | 0.99 | 0.011 | 1.1 |

Concentrations in ppm.
*Approximate value only, close to limit of detection.

$SO_4^=$. Thus, MSA represents a relatively minor flux of sulfur to the sea surface. However, MSA is not stable under atmospheric conditions, as assumed by previous workers. In this section we discuss the reactivity of MSA and its possible role as an intermediate oxidation state of sulfur in the conversion of DMS to $SO_4^=$.

We have performed some preliminary experiments that suggest that reaction with OH radical in aerosols and cloud droplets is probably the major atmospheric pathway for the destruction of atmospheric MSA. No detectable reaction occurred between MSA and $H_2O_2$ or $O_3$ in aqueous solution. In concentrated $O_3$ solutions a small amount of $SO_4^=$ was produced from MSA; we attribute the production of $SO_4^=$ in this case to the reaction of MSA with OH radicals generated by $O_3$ decomposition.

*Lind and Eriksen* [1975] have reported a rate constant of $k = 1.39 \times 10^9$ l mol$^{-1}$ s for the reaction of MSA with OH radical in aqueous solution. From pulse radiolysis-conductance data, they concluded that the reaction proceeds by H abstraction from the sulfonic acid producing the $CH_2SO_3^=$ radical.

To identify the end products, we studied this reaction in an $O_2$ saturated solution containing MSA and $H_2O_2$ in a 2:1 molar ratio. This solution was irradiated to generate OH radicals by photolysis of $H_2O_2$. In this experiment a 25% decrease in the concentration of MSA was observed, accompanied by the appearance of an equimolar quantity of $SO_4^=$. As a control experiment we irradiated a similar solution of MSA without $H_2O_2$. In this case, no change in the MSA concentration was observed, demonstrating that the light source used did not affect the MSA directly. While further work on the mechanism of MSA oxidation is certainly needed, the data suggest that in the atmosphere the rate limiting step is reaction with OH and that the end product is $SO_4^=$. Details of this work and of other experimental studies currently in progress will be reported elsewhere.

Scavenging of gas phase MSA by aerosols and cloud droplets must be extremely rapid due to its low vapor pressure and hygroscopic nature. A rough estimate of the $SO_4^=$ formed from MSA can therefore be obtained simply from the observed MSA levels if we can estimate OH radical concentrations in these solutions.

Model calculations for 5, 12, and 35 $\mu$m radius cloud droplets [*Chameides and Davis*, 1982] yield OH concentrations that ranged from $2 \times 10^{-14}$ to $1 \times 10^{-12}$ m/l. By using these values for OH, the lifetime of MSA in cloud droplets can be calculated as follows:

$$\tau = \frac{MSA}{d\ MSA/dt} = \frac{1}{k\{OH\}}$$

$$= 2.1 - 10.7 \text{ hours}$$

The residence time of droplets in raining clouds is extremely short, on the order of a few minutes; consequently, the amount of $SO_4^=$ derived from MSA in rain is probably not important. However, nonraining clouds persist for longer periods of time, 10 min to 1 hour [*Pruppacker and Klett*, 1978]. The in-cloud destruction of MSA and subsequent production of $SO_4^=$ aerosol appears to be a potentially important process at the higher end of the model OH concentration range where the lifetime of MSA may be shorter than its residence time in the cloud.

Hydroxyl radical concentrations in aerosol particles have not yet been modeled, so it is not possible to calculate MSA lifetimes directly. However, we can use the MSA data to calculate the OH concentration needed in order for MSA destruction to be a significant pathway for $SO_4^=$ formation. Assume that aerosol particles have a mean residence time of 6 days in the troposphere ($\tau_{dep} = 10^{5.7}$ s, $k_{dep} = 1/\tau = 10^{-5.7}$ s$^{-1}$) and that both MSA and excess $SO_4^=$ are in steady state over the oceans. While the conversion of MSA to $SO_4^=$ is undoubtedly a multi-step process, we will assume that the rate limiting step is the initial reaction of OH radical with MSA. The amount of $SO_4^=$ derived from MSA can then be expressed as follows:

$$[SO_4^=] = \frac{k[MSA][OH]}{k_{dep}}$$

We can then calculate the OH concentration required for all of the nss $SO_4^=$ in marine air to have been produced from MSA by inserting the measured values of MSA and nss $SO_4^=$ and the appropriate rate constants.

$$[OH] = \frac{k_{dep}}{k} \frac{[SO_4^=]}{[MSA]} = \frac{10^{-5.7}}{1.3 \times 10^9} \times 20 = 3.1 \times 10^{-14} \text{ M/l}$$

This simple calculation places an upper limit on the aerosol OH concentrations since $SO_2$ oxidation must account for some of the nss $SO_4^=$ [*Bonsang et al.*, 1980].

The preceding calculations are presented to demonstrate that the reactivity of MSA may be an important factor controlling ambient MSA levels and that $SO_4^=$ formation via MSA may be a significant process in the marine atmosphere. A direct calculation of the fluxes involved will require independent assessments (model or measured) of aerosol OH concentrations and models that incorporate gas phase, cloud water, and aerosol-free radical chemistry.

*Implications for the Origin of*
*Maritime $SO_2$ and nss $SO_4^=$*

Do the observed MSA concentrations over the oceans support the idea that DMS is the major source of background nss sulfur compounds in marine air? One way to test this hypothesis is to compare the ambient ratio of MSA to $SO_2$ to the ratio obtained by experimental oxidation of DMS by OH radical.

We estimate the marine background molar ratio of MSA to $SO_2$ to be roughly 1:3.7 assuming a mean MSA concentration of 0.04 $\mu$g/m$^3$ and a mean $SO_2$ concentration of 0.1 $\mu$g/m$^3$ [*Bonsang, et al.*, 1980]. This ratio may be increased slightly if we consider that at least some of the $SO_2$ is derived from the background $CS_2$ and COS. The lifetimes of these compounds are sufficiently long that they are uniformly distributed in the troposphere, and their source may be both biological (terrestrial and marine) and anthropogenic. *Bandy and Maroulis* [1980] estimated that the oxidation of these compounds could account for roughly 30% of the marine background $SO_2$. Subtracting this amount from the total leaves 0.067 $\mu$g/m$^3$ $SO_2$ and an ambient MSA to $SO_2$ ratio of 1:2.5.

*Hatekeyama et al.* [1982] found that the gas phase reaction of OH with DMS produced more than 50% MSA and only 21% $SO_2$, giving a MSA to $SO_2$ source ratio greater than 2.5:1. If we assume that this source ratio is correct for the marine atmosphere, then MSA must be removed at least 6 times faster than $SO_2$ in order to maintain the low ambient ratio. Is this a reasonable proposition? At the present time our

knowledge of aerosol chemistry and depositional processes is insufficient to answer this question. However, if the above proposition is valid, then the data is consistent with the idea that DMS is the ultimate origin of marine background $SO_2$, MSA, and aerosol nss $SO_4^=$. This is consistent with measurements of surface seawater samples from a variety of environments where it was found that DMS was by far the most abundant volatile sulfur compound present [Barnard et al., 1982; W. J. Cooper et al., unpublished data, 1982]. In this case, $DMS \rightarrow MSA \rightarrow SO_4^=$ must be a major pathway for the formation of marine aerosol $SO_4^=$. If not, then either the experimentally determined source ratio is not correct for marine air or additional sources (either marine or long distance transport from continents) are required to account for at least some of the background sulfur in the marine atmosphere.

It is clear from this discussion that the relationship between MSA levels and organosulfur emissions is not necessarily a simple one. While MSA is a potentially useful tracer for organosulfur emissions in both continental and marine environments, its application is subject to considerable uncertainty at the present time.

## SUMMARY

1. Methane sulfonic acid concentrations in marine aerosols ranged from 0.009 to 0.075 $\mu g/m^3$ in samples from the Pacific and Indian oceans and Miami, Florida. In the samples from remote areas (Pacific and Indian oceans) MSA levels averaged 6.7% ($s = 1.9$) of the nss $SO_4^=$ values. Local sulfur emissions in the Miami area (probably $SO_2$ pollution) resulted in lower ratios in some samples.

2. MSA concentrations in seven rainwater samples collected at Miami, Florida, ranged from 0.001 to 0.034 ppm.

3. Cascade impactor samples from Miami, Florida, and the Gulf of Mexico indicate that MSA is concentrated primarily in the smaller particles, as is nss $SO_4^=$. In the two samples analyzed, MSA is concentrated on slightly coarser particles than nss $SO_4^=$. The size distributions of both sulfur compounds differ markedly from that of sea salt $Na^+$ which is concentrated on the coarsest particles.

4. The observed concentrations of MSA in marine air result from formation from the reaction of DMS with OH radical and destruction by aqueous phase reaction with OH radical in the aerosols. Preliminary experiments indicate that MSA oxidation probably yields $SO_4^=$ under atmospheric conditions. Therefore, MSA destruction is a potentially important pathway for the formation of nss $SO_4^=$ in the marine atmosphere. The magnitude of the fluxes involved in the organosulfur cycle cannot be calculated from the MSA data because of the uncertainty in the free radical chemistry of aerosols.

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