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ATMOSPHERIC METHANESULFONIC ACID AND NON-SEA-SALT SULFATE AT FANNING AND AMERICAN SAMOA

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Abstract. Atmospheric concentrations of aerosol methanesulfonic acid (MSA) and non-sea-salt (nss) sulfate were measured in samples collected during one year periods at Fanning and American Samoa Islands in the Pacific Ocean. Mean concentrations were 0.045 ($s=0.011$) $\mu\text{g}/\text{m}^3$ MSA and 0.67 ($s=0.13$) $\mu\text{g}/\text{m}^3$ nss sulfate at Fanning, and 0.026 ($s=0.012$) $\mu\text{g}/\text{m}^3$ MSA and 0.41 (0.19) $\mu\text{g}/\text{m}^3$ nss sulfate at American Samoa. MSA and nss sulfate were significantly correlated at both stations ($r=0.76$), with a mean MSA/nss sulfate ratio of 0.065. The higher mean levels of MSA and nss sulfate at Fanning compared to American Samoa apparently reflect differences in the biological productivity of the surface ocean in the two regions.

Introduction

Emissions of biogenic organosulfur compounds may play a major role in the atmospheric sulfur budget, particularly in remote regions. However, relatively little is known about the biogenic source, including: the biochemical pathways involved, the patterns of spatial and temporal variability, the magnitude of organosulfur emissions, and the nature of their reactions in the atmosphere. The abundance of dimethylsulfide (DMS) in surface seawater suggests that this species may be a major precursor of non-sea-salt sulfate and SO_2 in marine air (Lovelock et al., 1972; Andreae and Raemdonck, 1983). Laboratory studies have demonstrated that methanesulfonic acid (MSA) should be a major oxidation product of DMS in air, via reaction with OH radicals (Hatakeyama and Akimoto, 1983; Niki et al., 1983; Grosjean, 1984). We have undertaken a study of the distribution of MSA in marine air in order to elucidate the reaction pathways of organosulfur compounds, and to investigate the use of MSA as a tracer for organosulfur emissions.

In this paper we present measurements of MSA and nss sulfate in aerosols collected at two atmospheric chemistry sampling stations in the Pacific Ocean network of the Sea Air Exchange (SEAREX) program: Fanning Island (4°N , 159°W) and American Samoa (14°S , 171°W) (Figure 1). These stations were selected for two reasons: because of the contrast between the biologically productive waters of the equatorial divergence zone (Fanning Island) and the low productivity oligotrophic waters (American Samoa); and because these stations are relatively unaffected by long

distance transport of sulfur-containing aerosols from continental areas.

Sampling and Analysis

The sampling periods were not concurrent at the two stations: samples used in this study were collected at Fanning from 4/2/81-8/26/82, and at American Samoa from 3/19/83-8/16/84. The 1982/1983 El Niño occurred between the two sampling periods. Sea surface temperature and meteorological anomalies associated with the El Niño reached a maximum in the central Pacific from December to February of 1983 and then weakened, returning to normal conditions by July (Cane, 1983; Rasmussen and Wallace, 1983). While this phenomenon began after the end of the sampling period at Fanning, anomalous conditions were present during the first few months of sampling at American Samoa.

We analyzed bulk aerosol samples collected over a seven day period on 20 x 25 cm² Whatman 41 filters at air flow rates of about 1 m³/min. The samplers were equipped with wind direction and speed sensors which turned off the pumps when conditions were not favorable for sampling oceanic air (Uematsu et al., 1983). The sampler at Fanning was located on a 25m tower. The American Samoa sampler was located on a 20m tower at the NOAA Global Monitoring for Climate Change (GMCC) station at Cape Matatula. The impact of material derived from local island sources is believed to be minimal at these stations. The total air volumes sampled were about 4,000 m³ at Fanning and 8,000 m³ at American Samoa. The sampling sites have previously been described in detail by Uematsu et al. (1983) and Pszenny et al. (1982).

The filters were extracted with water and analyzed for sodium by atomic absorption and for sulfate, nitrate and MSA by ion chromatography using techniques previously described (Saltzman et al., 1983). The accuracy of the analyses are $\pm 2\%$ for sodium, and $\pm 5\%$ for the anions. Nss sulfate values were calculated from the Na and sulfate concentrations by assuming that all of the sodium is derived from seawater with a sulfate/sodium ratio of 0.2517. Because a nss sulfate value involves two measurements, its relative error is somewhat larger than that of a MSA measurement and is a function of the sea salt concentration in the sample. For typical values encountered in this study the uncertainty of the nss sulfate values is $\pm 0.1 \mu\text{g}/\text{m}^3$.

The stability of MSA in filter samples and water extracts were tested on an aerosol sample collected at Miami, and analyzed within a week of sampling. After two years, both the original filter extract (stored at 5°C) and a new extract of a portion of the filter were analyzed. All three analyses were within 5% of their mean.

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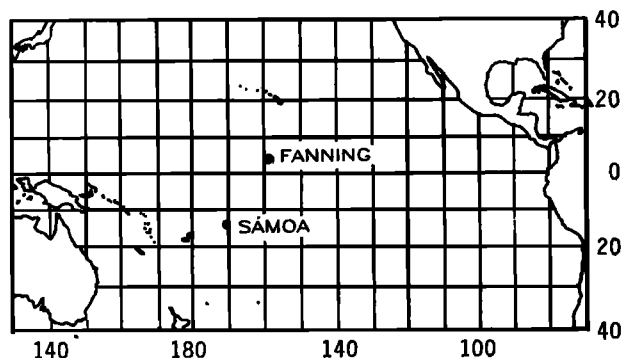


Fig. 1. Locations of the islands on which the samples were collected for this study.

Results

A summary of the Fanning and American Samoa data obtained for Na, nitrate, nss sulfate and MSA is presented in Table 1.

The concentrations of nss sulfate and nitrate were measured in essentially all ($n=72$) samples collected at Fanning from 4/2/81 to 8/26/82 (Figure 2). These have been discussed in detail by Prospero et al. (1985b). MSA concentrations were measured in 28 of these samples. MSA levels ranged from .025 to .068 $\mu\text{g}/\text{m}^3$, with a mean value of 0.045 ($s=0.011$) $\mu\text{g}/\text{m}^3$. Nss sulfate concentrations in the same samples ranged from 0.39 to 0.98 $\mu\text{g}/\text{m}^3$, with a mean value of 0.67 ($s=0.13$) $\mu\text{g}/\text{m}^3$. One Fanning sample exhibited anomalously elevated levels of both nss sulfate (1.6 $\mu\text{g}/\text{m}^3$) and aluminum (52.9 ng/m^3 ; Uematsu et al., 1983). This was presumably the result of contamination by local dust, as the aluminum values for the other samples had a mean of 4 ($s=3$) ng/m^3 (Uematsu et al., 1983). Consequently the data from this sample were rejected. The MSA concentration in this sample was normal (0.05 $\mu\text{g}/\text{m}^3$).

The levels of both MSA and nss sulfate are higher at Fanning than those normally found at open ocean sites (Savoie, 1984; Saltzman et al., 1983; Prospero et al., 1985a,b) and there is no evidence of seasonality in the data. This is attributed to the relatively constant high productivity of the equatorial divergence zone. These MSA levels are comparable to, or slightly less than, those found in coastal waters of the Gulf of Mexico and off the coast of Peru (Saltzman et al., 1984).

Nitrate levels at Fanning ranged from 0.033 to 0.39 $\mu\text{g}/\text{m}^3$, with a pronounced maximum occurring in the fall of 1981 (Prospero et al., 1985a,b). This trend is not present in the sulfur data, suggesting that the increase in nitrate is not related to a change in oceanic productivity.

The data from American Samoa consist of seven day samples collected from 3/19/83 to 8/16/84 (Figure 3; Prospero et al., 1985a). MSA concentrations, measured in 22 of these samples, ranged from 0.010 to 0.045 $\mu\text{g}/\text{m}^3$, with a mean of 0.026 ($s=0.012$) $\mu\text{g}/\text{m}^3$. Nss sulfate ranged from 0.14 to 0.74 $\mu\text{g}/\text{m}^3$, with a mean of 0.41 ($s=0.19$) $\mu\text{g}/\text{m}^3$. There appears to be a seasonal trend to the nss sulfate data, with higher values in the southern hemisphere spring and fall months. This trend is not as pronounced in the MSA data.

Unfortunately, few data are available for the summer months. The 1984 fall nss sulfate maximum (April) was not present in 1983. The low 1983 levels may be a result of anomalously high sea surface temperatures in the central Pacific during the 1982/1983 El Niño (Cane, 1983; Rasmussen and Wallace, 1983). Nitrate values at American Samoa ranged from 0.05 to 0.25 $\mu\text{g}/\text{m}^3$ and, in contrast to the nss sulfate data, no seasonality is evident in the data. Seasonal trends in MSA and nss sulfate have been found at a number of other marine stations and will be the focus of another study (Saltzman et al., in prep.).

Discussion

The levels of MSA and nss sulfate observed in this study are consistent with the general pattern of biological productivity in the central Pacific Ocean. High values of both nss sulfate and MSA were found at Fanning Island, which is located in the highly productive equatorial divergence zone. DMS concentrations of 300-425 ng/L were reported for this region (Cline and Bates, 1983; Andreae and Raemdonck, 1983). These elevated DMS levels, which are several fold higher than the mean ocean levels, are confined to a narrow belt bordering the equator. Northward of this zone DMS levels drop off sharply to below 100 ng/L by 8°N. No measurements of DMS have been made south of 4°S, but the general pattern of productivity should be similar to that in the northern hemisphere, with productivity decreasing with distance from the equatorial divergence zone. This is supported by the data from American Samoa, where the average concentrations of MSA and nss sulfate were considerably lower than those found at Fanning.

One surprising feature of the data is the fact that the higher end of the MSA and nss sulfate concentrations at American Samoa are comparable to the average levels at Fanning. This suggests that either there is some strong local source of organosulfur compounds in the region of American Samoa, or that transport of MSA and nss sulfate has modified the distributions of these sulfur species relative to their sources. Measurements of DMS in the South Pacific surface ocean are needed.

The data from the two stations exhibit a positive correlation ($r=0.76$) between MSA and nss

TABLE 1. Summary of the aerosol concentrations in all samples analysed for MSA from American Samoa and Fanning.

Station	Na ⁺	NO ₃ ⁻	nss SO ₄ ⁼	MSA	MSA/nss SO ₄ ⁼
			($\mu\text{g}/\text{m}^3$)		
Fanning (n=27)					
x	4.2	0.194	0.67	0.045	0.068
(s)	1.4	0.089	0.13	0.011	0.016
American Samoa (n=22)					
x	5.6	0.118	0.41	0.026	0.066
(s)	1.5	0.049	0.19	0.012	0.019

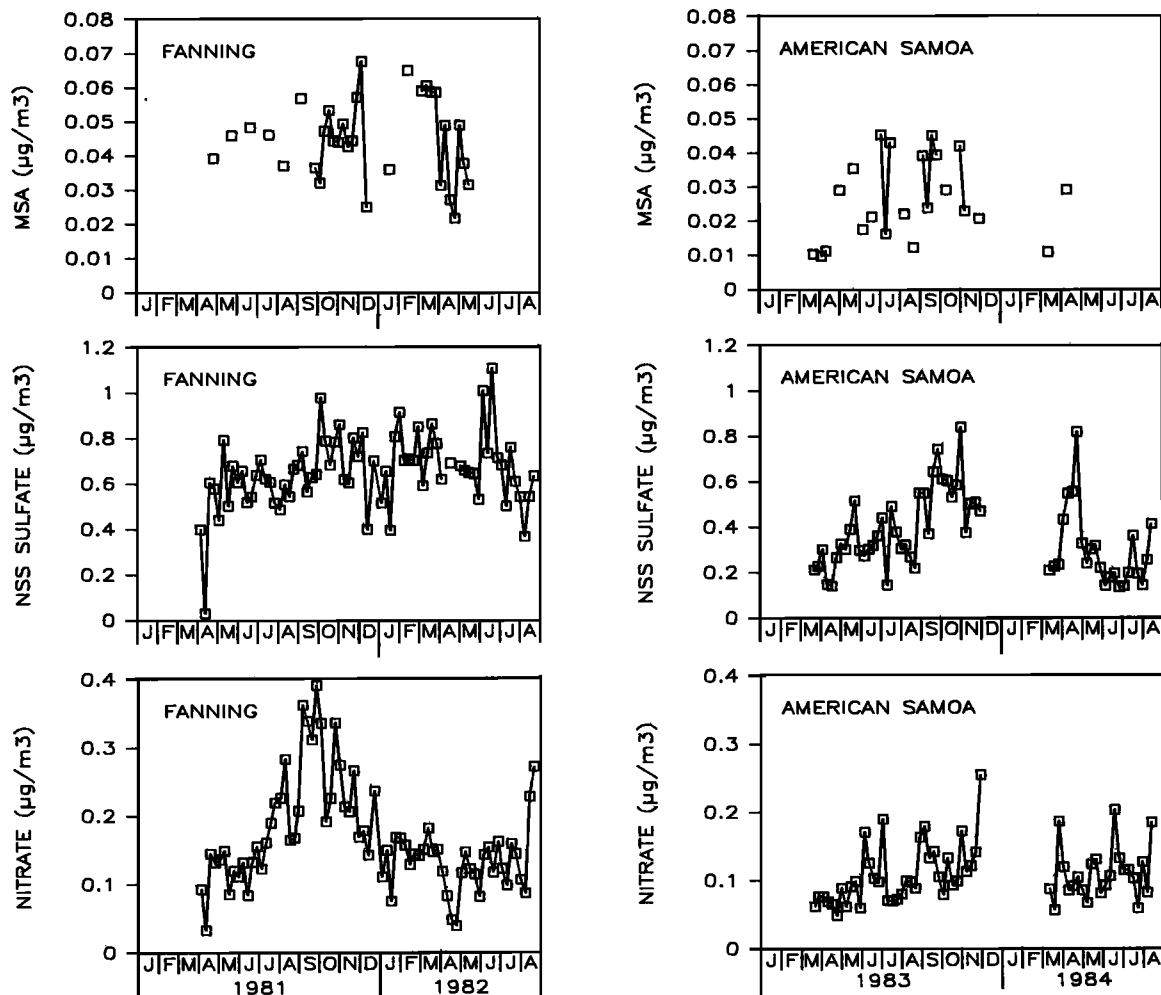


Fig. 2. Concentrations of MSA, nss sulfate and nitrate in aerosol samples from Fanning and American Samoa. Tie lines connect adjacent samples, and indicate continuous sampling.

sulfate (Figure 3). A linear fit of the data (MSA vs nss sulfate) gives a slope of .065. In all samples from this study the ratio of MSA to nss sulfate varies by less than a factor of three, with 90% of the data between .044 and .103. The regression line of MSA vs nss sulfate has a y-intercept which is not significantly different from zero.

The high degree of correlation between MSA and nss sulfate at Fanning and American Samoa suggests that organosulfur emissions are a major source of nss sulfate at these sites. The data also suggest that the proportions of the various reduced sulfur compounds in oceanic emissions remains roughly constant, while the magnitude of the emissions may vary by more than a factor of ten. Analytical uncertainty in the nss sulfate values accounts for roughly half of the variance of the data about the regression line. The remainder of the scatter represents real variability in the MSA/nss sulfate ratio. Changes in the ratio may reflect fluctuations in the proportion of organosulfur compounds relative to inorganic reduced sulfur species in sea surface emissions. This scatter could also be due to variations in the oxidation pathway of organosulfur compounds and, consequently, in the

yield of MSA. The latter is expected to be a minor effect at these remote sites.

The data do not rule out the possible importance of inorganic sulfur emissions, such as H_2S and CS_2 . However, it does suggest that all of the emitted reduced sulfur compounds that are converted to nss sulfate in the troposphere covary with the emissions of organosulfur compounds. The constancy of the MSA/nss sulfate ratio in marine air also suggests that this ratio may be a sensitive indicator with which to assess the impact of continental sources (i.e. anthropogenic SO_2 and sulfate) on the nss sulfate concentration at oceanic sites (Saltzman et al., 1983).

A number of recent studies have demonstrated that MSA and SO_2 are major products of the gas phase reaction of DMS with OH radicals, which is thought to be the primary pathway for the oxidation of alkyl sulfides in marine air. If the yield of MSA from this reaction was known, the oceanic flux of DMS could be calculated directly from the concentration of MSA in air. This would provide an independent estimate for comparison with fluxes calculated from sea surface DMS concentrations using the thin film model. However, the mechanism of DMS oxidation and the factors which control the yields of

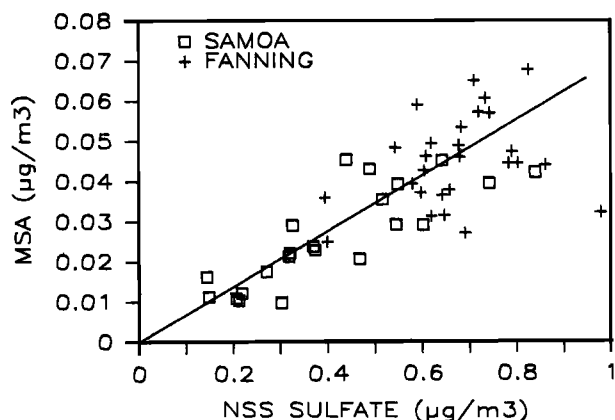


Fig. 3. Concentrations of MSA vs. those of nss sulfate at Fanning and American Samoa.

various oxidation products are not well understood. The reaction has been studied only in systems with elevated levels of NO or alkyl nitrites, which have been shown to influence the reaction mechanism (Hatakeyama and Akimoto, 1982; Grosjean, 1984; Niki et al., 1983). It is not clear that either the mechanisms or the product yields obtained in those studies apply to the remote marine atmosphere. We feel that this uncertainty must be resolved before the experimental results can be used to calculate oceanic DMS emissions from the MSA data.

Summary

1. Mean aerosol concentrations of MSA and nss sulfate at Fanning Island were 0.045 ug/m^3 and 0.67 ug/m^3 , respectively. At American Samoa, the levels were 0.026 ug/m^3 of MSA and 0.41 ug/m^3 of nss sulfate.
2. The relative concentrations of MSA and nss sulfate at Fanning and American Samoa are consistent with the patterns of biological productivity and previous observations of DMS in the equatorial Pacific surface ocean.
3. There is a significant positive correlation between MSA and nss sulfate at these stations. On a plot of MSA vs nss sulfate the correlation line has a slope of 0.065 and passes through the origin. This relationship supports the idea that organosulfur emissions are a major source of aerosol nss sulfate and make up a relatively constant proportion of the total reduced sulfur emissions from the sea surface at these sites.

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