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# Methanesulfonic Acid and Non-Sea-Salt Sulfate in Pacific Air: Regional and Seasonal Variations

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**Abstract.** Concentrations of aerosol methanesulfonic acid (MSA) and non-sea-salt (nss) sulfate were measured at six island stations in the Pacific Ocean to investigate regional and seasonal patterns of organosulfur emissions and the origin of nss sulfate over the Pacific. The mean MSA concentrations, in  $\mu\text{g}/\text{m}^3$ , at the stations were: Shemya,  $0.097 \pm 0.098$ ; Midway,  $0.029 \pm 0.021$ ; Fanning,  $0.044 \pm 0.012$ ; American Samoa,  $0.026 \pm 0.012$ ; New Caledonia,  $0.021 \pm 0.009$ ; Norfolk,  $0.024 \pm 0.019$ . The extremely high MSA levels found at Shemya indicate a major source of organosulfur emissions in the western North Pacific. Significant seasonal trends in MSA were observed, with higher MSA occurring during warm months. The amplitude of the seasonal variation was greatest at higher latitude stations. At Fanning and American Samoa, which have minimal input of continental material, there is a significant positive correlation between MSA and nss sulfate. MSA/nss sulfate ratios at other Pacific stations exhibit greater variability, which may be related to variations in: the input of continentally derived sulfate, the composition of oceanic organosulfur emissions, and atmospheric reaction pathways.

**Key words.** Sulfur cycle, marine atmosphere, marine aerosols.

## 1. Introduction

Volatile biogenic organosulfur compounds are produced by a variety of organisms in both terrestrial and marine environments, and emissions of these compounds play a significant role in the geochemical cycling of sulfur. In order to assess the role of organosulfur emissions in the tropospheric sulfur budget, a better understanding is needed of the factors controlling the spatial and temporal variations of emissions and the transformations of these compounds in the atmosphere. Measurements of dimethylsulfide in ocean surface waters and marine air have led to the suggestion that oceanic emissions of this compound represent a major flux of sulfur to the marine atmosphere (Lovelock *et al.*, 1972; Maroulis and Bandy, 1977; Nguyen *et al.*, 1978; Andreae and Reardonck, 1983; Cline and Bates, 1983). Model calculations based on these measurements suggest that the flux of DMS from the sea surface to the atmosphere could account for a significant fraction of the non-sea-salt (nss) sulfate and  $\text{SO}_2$  in marine air (Andreae *et al.*, 1985).

In the atmosphere, the initial step in the oxidation of organosulfur compounds is reaction with free radicals such as OH or  $\text{NO}_3$  (Atkinson *et al.*, 1984). Subsequent reaction steps are not known, but are likely to be complex due to the large number of possible reaction intermediates or products. One such reaction product, methanesulfonic acid

(MSA), has been found to be a ubiquitous component of marine aerosols (Saltzman *et al.*, 1983). MSA is formed from the oxidation of dimethylsulfide and, possibly, other precursors such as methylmercaptan and dimethyldisulfide.

MSA comprises a relatively small fraction (<10%) of the total mass of non-sea-salt aerosol sulfur and, hence, does not constitute a large depositional flux of sulfur from marine air. However, because there are no other known sources of MSA in marine air, it is a potentially useful tracer for oceanic emissions and atmospheric reaction pathways of organosulfur compounds. The size distribution of aerosol MSA is similar to that of nss sulfate; both are found predominantly on small particles as a result of hydration, nucleation, and coagulation processes (Saltzman *et al.*, 1983; Hatakeyama *et al.*, 1985). Consequently, MSA and nss sulfate will have similar depositional characteristics, and ambient MSA/nss sulfate ratios should reflect the composition of the sulfur source, rather than aerosol removal processes.

A major difficulty in unravelling the marine tropospheric sulfur budget lies in differentiating between the various oceanic and continental sulfur sources which impact upon marine air. We are investigating the chemistry and distribution of MSA over the world oceans as an *in situ* tracer to assess the origin of aerosol nss sulfate and the nature of oceanic sulfur emissions. In this study we present aerosol MSA and nss sulfate data from several island stations in the Pacific Ocean in order to examine large scale regional and seasonal variations (Figure 1). The stations are: Shemya, Midway, New Caledonia, and Norfolk. Data from Fanning and American Samoa have recently been presented in detail elsewhere (Saltzman *et al.*, 1985) and are discussed only briefly in this paper. Samples used in this study were collected during 1981/82 at the North Pacific stations and during 1983/84 at the South Pacific stations.

## 2. Experimental

Island sampling sites were located on the climatologically determined windward coast. To avoid contamination from local sources, the air samplers were controlled by wind speed and direction sensors that activated the pumps only when the winds blew from the sea at speeds of greater than 5 km/hr (Uematsu *et al.*, 1983). Detailed descriptions of the sites at Shemya, Midway and Fanning were reported by Uematsu *et al.* (1983) and at American Samoa by Pszenny *et al.* (1982). At Norfolk Island, the sampler is located on the southeast coast on the edge of a steep slope, 80 m above sea level. The New Caledonia site is located on the beach near Yate on the east coast. The samplers at Fanning and American Samoa are located on towers that place them at least 20 m above sea level. At Shemya, Midway, and New Caledonia, the samplers are only a few meters above sea level; at these sites, the concentration of sea spray from breaking waves can be quite high.

Bulk aerosol samples were collected on 20 × 25 cm Whatman 41 filters at air flow rates of about 1 m<sup>3</sup>/min. Filters were changed at seven day intervals; hence, no attempt will be made to deduce local or mesoscale processes from the data. The filters were extracted with water and analyzed for sodium by atomic absorption and for sulfate and MSA by ion chromatography. Aluminum and vanadium concentrations were measured

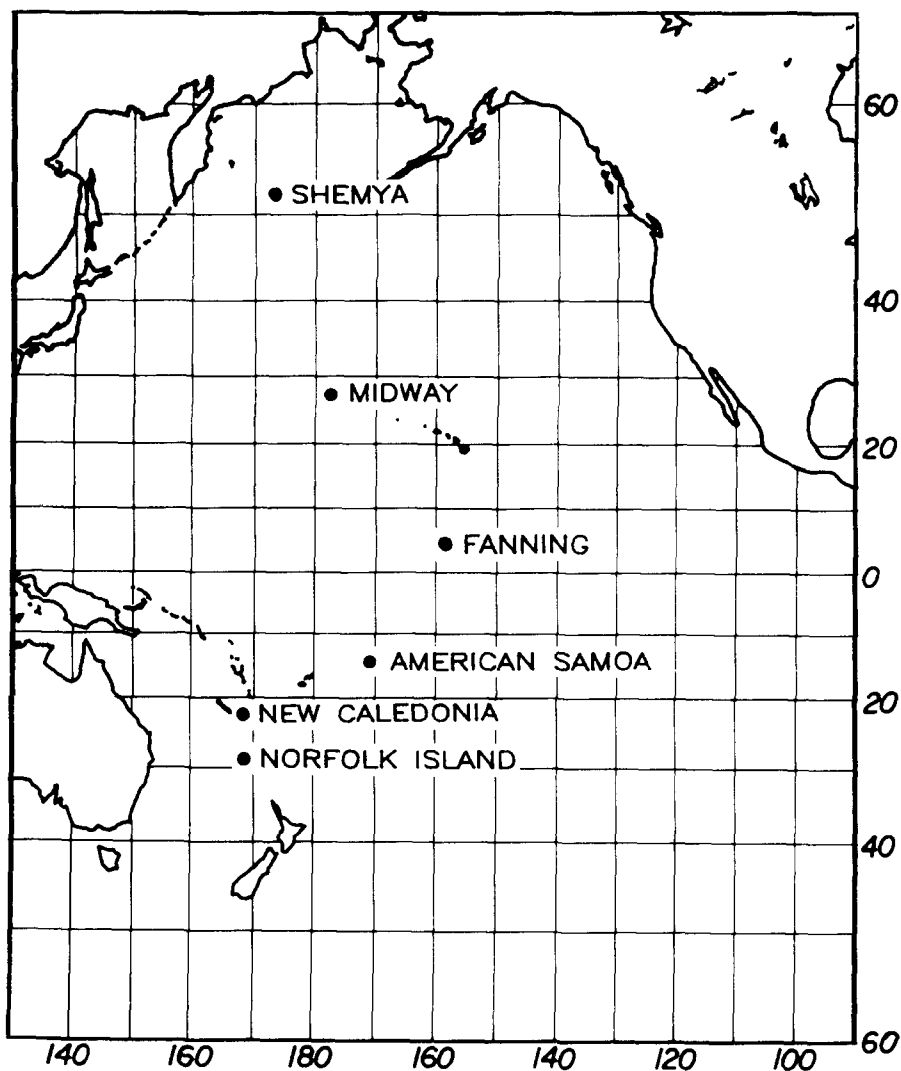


Fig. 1. Location of Pacific island sampling sites used in this study.

on portions of the same filters using instrumental neutron activation; results are reported in detail elsewhere (Uematsu *et al.*, 1983, 1985).

The ion chromatographic system used for the MSA analyses was modified from that described in earlier work by the addition of a guard column system to allow faster throughput of samples. At a preset time after the sample injection the guard column was isolated from the eluent, and rinsed free of slow eluting anions (sulfate and nitrate) with a strong eluent. At the same time, a second guard column was switched into the flow stream to maintain a constant flow through the analyzing column during the run. Samples with high sea-salt contents were pretreated with a Ag-form cation exchange resin to remove chloride before analysis for MSA.

The stability of stored samples was verified by analyzing a portion of a filter sample immediately after collection, and after storage periods of up to two years. No change in the concentration of MSA was detected with time in either stored filters or stored (5°C) extracts. Several experiments were performed to test for possible artifact formation during sampling due to reactions of organosulfur compounds on the filters. Two samplers were operated in parallel at Miami. In one of the samplers, ambient air was spiked with DMS or methylmercaptan from permeation tubes before passing through the filter. The second sampler was operated in the usual manner as a control. In all experiments the concentrations of MSA were identical, within experimental error, in samples with and without added sulfur compounds.

The accuracy of the analyses are  $\pm 2\%$  for Na and  $\pm 5\%$  for sulfate and MSA. Nss sulfate values were calculated from the Na and sulfate concentrations by assuming that all of the Na is derived from seawater with a sulfate/Na ratio of 0.2517. Because each nss sulfate value involves two measurements, its relative error is somewhat larger than that of an MSA determination, which requires only one measurement. The uncertainty of an nss sulfate value is a function of the sea-salt concentration; for the samples used in this study, the uncertainty of the nss sulfate values is on the order of  $\pm 0.1 \mu\text{g}/\text{m}^3$ .

A number of samples from Shemya had negative nss sulfate values. To some extent, these negative nss sulfates may be explained by the large analytical uncertainty caused by extremely high sea-salt concentrations. However, some nss sulfate values were significantly negative. At present, these results are problematical. The negative nss sulfate values cannot be explained by addition of non-sea-salt sodium from continental dust to the aerosols because the sodium/chloride ratios of the samples with negative nss sulfate values were about 1.8, which is close to that of seawater. Until the cause of the anomalous use sulfate data is determined, the sulfate data from Shemya cannot be interpreted and are not presented in this paper. Three samples from Midway also had slightly negative nss sulfate values, only one of which is significantly negative. With the exception of this one sample, the nss sulfate data from Midway are consistent with regional patterns and are assumed to be valid.

### 3. Results

#### 3.1. *Fanning and American Samoa*

MSA and nss sulfate data from Fanning (4°N, 159°W) and American Samoa (14°S, 170°W) have recently been reported (Saltzman *et al.*, 1985) and are only briefly summarized here. Because these sites are relatively unaffected by transport of material from continental sources, they represent 'clean' marine air and form a basis for comparison with the other sites in this study, all of which are affected to some extent by advection of continental material. The mean concentrations of MSA and nss sulfate at Fanning were  $0.044 \pm 0.012$  and  $0.63 \pm 0.18 \mu\text{g}/\text{m}^3$ , respectively. At American Samoa mean concentrations of MSA and nss sulfate were  $0.026 \pm 0.012$  and  $0.39 \pm 0.16 \mu\text{g}/\text{m}^3$ . The concentrations of MSA and nss sulfate at Fanning are significantly higher than marine background

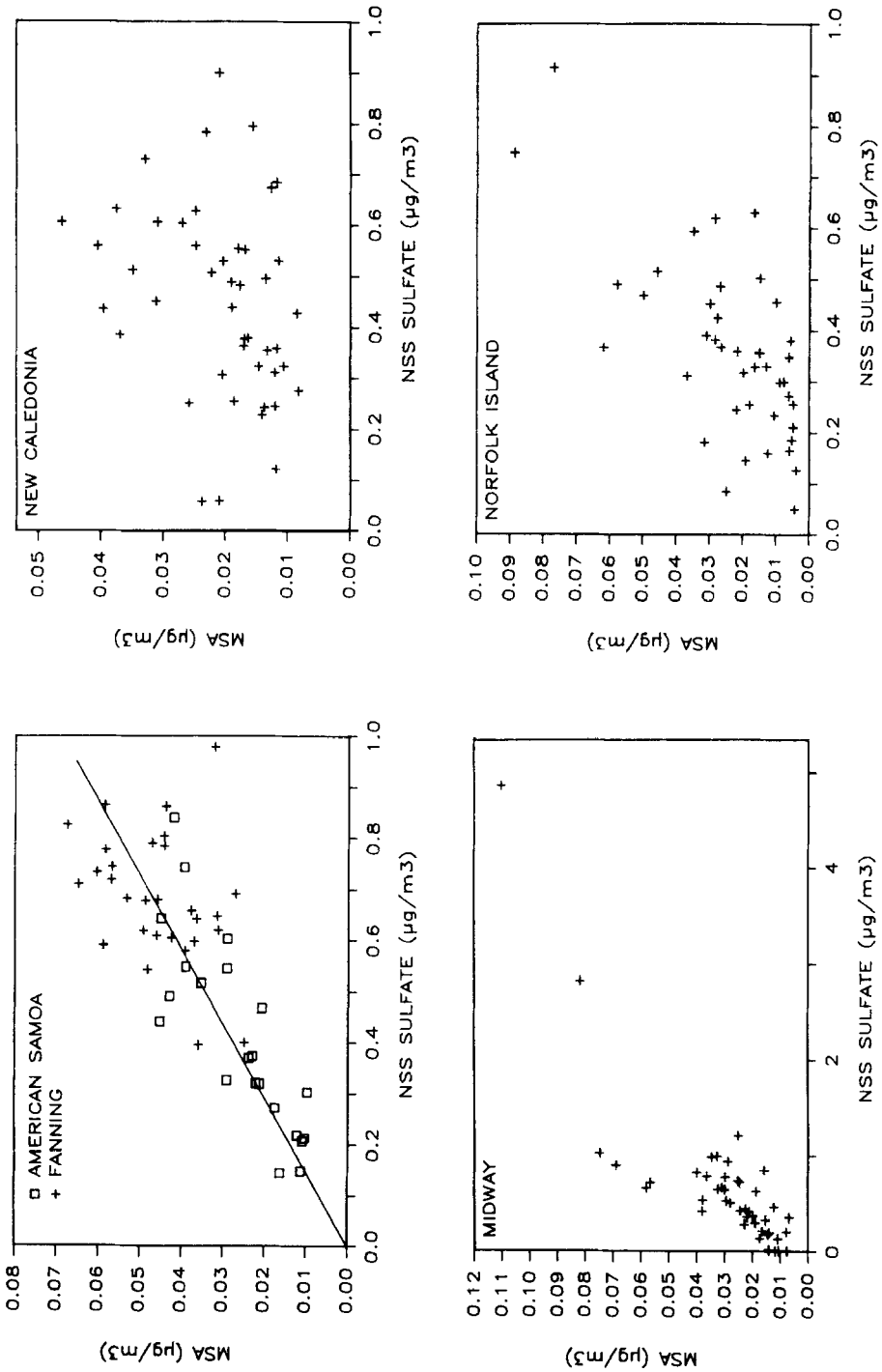


Fig. 2. MSA vs nss sulfate concentrations at Fanning and American Samoa, Midway, New Caledonia, and Norfolk.

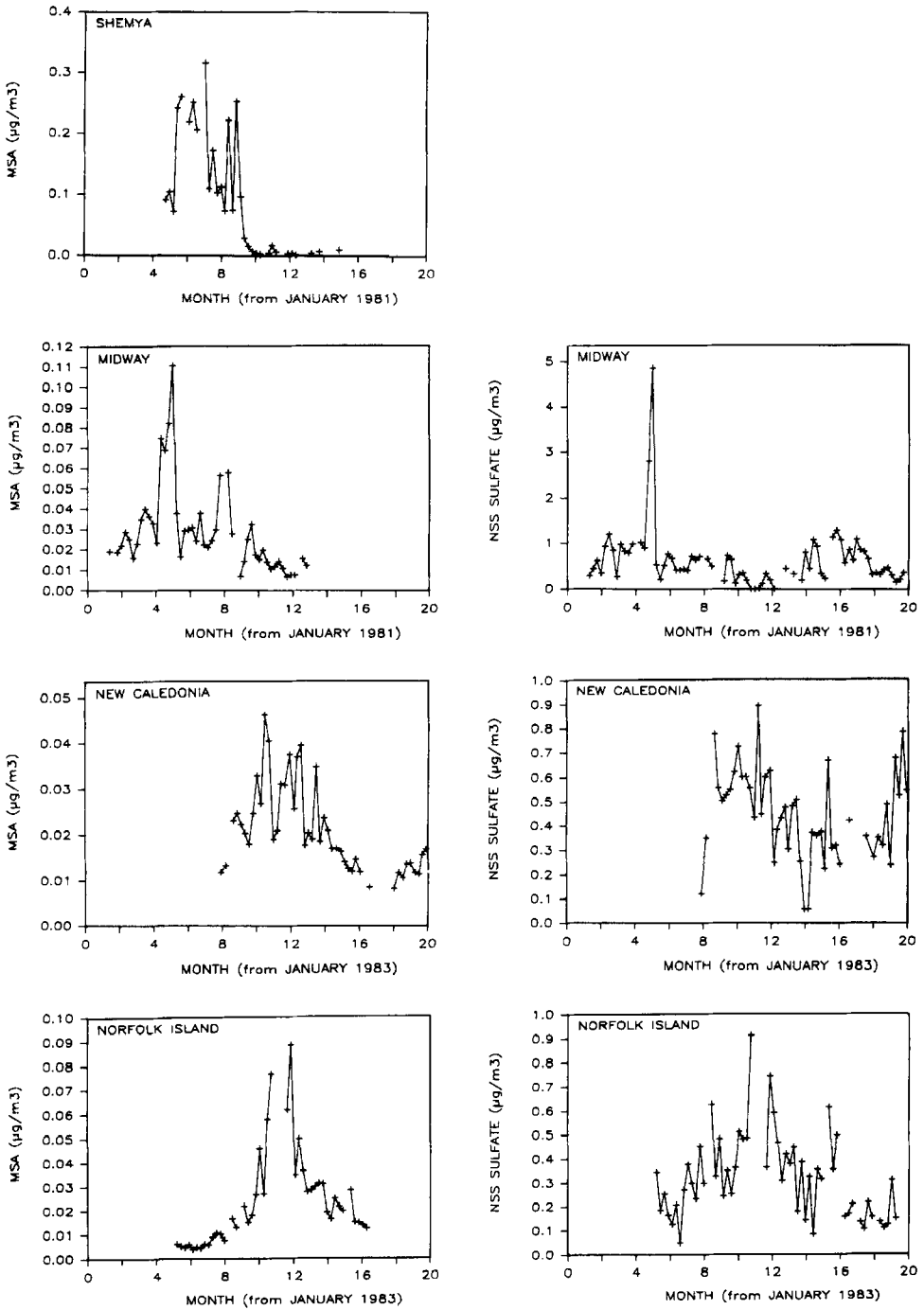


Fig. 3. MSA and nss sulfate concentrations at Shemya (1981–1982), Midway (1981–1982), New Caledonia (1983–1984), and Norfolk (1983–1984). NSS sulfate data are not reported for Shemya because of high sea salt concentrations and problematic negative values (see Experimental section for discussion).

values, reflecting the fact that Fanning lies in the highly productive equatorial upwelling zone. No seasonal trends in MSA are apparent in the data from these two low latitude stations.

There is a significant positive correlation between MSA and nss sulfate at Fanning and American Samoa (Figure 2). The mean MSA/nss sulfate ratio was 0.065, with 90% of the data between 0.044 and 0.103. The  $y$ -intercept of the regression line is not significantly different from zero. The spread of MSA/nss sulfate ratios is assumed to represent natural variability in the composition of oceanic organosulfur emissions and in the atmospheric conversion of these emissions to MSA and nss sulfate.

### 3.2. Shemya

The concentration of aerosol MSA at Shemya ( $52^{\circ}\text{N}$ ,  $174^{\circ}\text{E}$ ) was measured in 42 samples collected from 5/20/81–4/7/82 (Figure 3). This high latitude ( $52^{\circ}\text{N}$ ,  $174^{\circ}\text{W}$ ) station shows the most dramatic seasonal contrast of all stations studied to date. From May through September, the mean MSA concentration was  $0.170 \pm 0.079$  ( $n = 17$ ), the highest atmospheric MSA concentrations yet observed. During a three week period in October, MSA levels dropped to below  $0.01 \mu\text{g}/\text{m}^3$ . MSA levels remained low throughout the winter, with a mean value of  $0.014 \pm 0.023$  ( $n = 15$ ) for the period from late October through March 1982. Winter levels of MSA at Shemya are among the lowest levels reported from any marine station.

The elevated MSA concentrations during warm months suggest that there is a major high latitude source of oceanic organosulfur emissions in the Pacific. The prevailing winds at Shemya during the summer months were predominantly between southerly and westerly suggesting that the source region may lie in the North Pacific, outside of the Bering Sea. Emissions from this source must be several times greater than those normally found in coastal or shelf waters. Intense summertime levels of biological activity are common at high latitudes, resulting from the utilization of nutrients accumulated during winter months. High concentrations of DMS have been found in the southeastern Bering Sea, related to the abundance of the phytoplankton *Phaeocystis* (Barnard *et al.*, 1983).

The transition period between the high summer and low winter MSA levels was marked by a change in wind direction from the predominantly westerly summertime flow to steady southeasterly winds, and a small ( $2\text{--}3^{\circ}\text{C}$ ) drop in surface air temperatures. More rapid cooling ( $7\text{--}8^{\circ}\text{C}$ ), and a return to westerly air flow occurred in November. It seems most likely that the initial drop in MSA levels was due to a change in the source area from highly productive high latitude shelf waters to lower productivity oligotrophic waters in the central Pacific. Bates and Cline (1986) reported very low DMS concentrations,  $26 \pm 8 \text{ ngS/L}$ , in the North Pacific surface ocean ( $35\text{--}55^{\circ}\text{N}$ ,  $158^{\circ}\text{W}\text{--}170^{\circ}\text{E}$ ). It is interesting that the MSA levels at Shemya remained low after westerly air flow resumed. This may indicate a rapid decrease in productivity of the source area due to lower temperatures, decreased light levels and deepening of the mixed layer. It may also be due to decreased photochemical activity during winter. Falling temperatures, water vapor and light levels, leading to reduced photochemical production of OH, and reduced reaction rates of



temperature dependent steps in the oxidation of DMS may all result in low atmospheric MSA concentrations.

### 3.3. *Midway*

The data from Midway were obtained from 44 samples collected from 1/19/81–1/21/82 and analyzed for nss sulfate; of these, 47 were analyzed for MSA. Mean aerosol concentrations were  $0.029 \pm 0.021 \mu\text{g}/\text{m}^3$  MSA and  $0.66 \pm 0.79 \mu\text{g}/\text{m}^3$  nss sulfate. Figure 3 clearly shows the seasonal trends in MSA at Midway: the mean MSA concentration from late April to September is more than twice that of the remainder of the year. While the amplitude of the seasonal variations is greatly reduced at Midway compared to that of Shemya, the timing of the cycle is similar; the transition from the high summer levels to the low winter levels occurs in early October.

Two episodes of elevated MSA occurred during the sampling period; one during May and the other during late July/early August. Analysis of air mass trajectories for Midway (J. Merrill and R. Bleck, unpublished data) shows that both episodes coincided with shifts to northwesterly air flow. This data suggests that the MSA peaks are related to a change in source area, rather than to local oceanographic phenomena, and supports the hypothesis that the northwestern Pacific is a major source of organosulfur emissions.

Aluminum concentrations (Uematsu *et al.*, 1983) indicate that Midway was significantly impacted by continental aerosols, presumably dust from Asia, particularly during the period from late February to early June. Two of the samples from the MSA peak in May had extremely elevated Al, V, and nss sulfate. Is the elevated sulfate in these samples associated with the dust, or is it related to the source of the MSA peak?

As noted in previous studies (Saltzman *et al.*, 1983, 1985) the MSA/nss sulfate ratio is fairly constant at remote marine stations, with a mean value of about 0.06. If the Midway samples were affected by a significant input of dust derived sulfate, it should be reflected in this ratio. The Midway samples show a large range of MSA/nss sulfate ratios (Figure 2), with many significantly lower ratios than those found at Fanning and American Samoa; the low ratios suggest that these samples contain relatively large amounts of continentally derived sulfate. This is clearly evidenced in the nss sulfate peak during late May/early June; these high Al samples exhibit very low MSA/nss sulfate ratios.

### 3.4. *New Caledonia*

The data from New Caledonia consist of 60 samples collected between 8/23/83 and 8/13/84 and analyzed for nss sulfate. 52 of these were analyzed for MSA (Figure 3). The mean concentrations of MSA and nss sulfate at New Caledonia were  $0.021 \pm 0.009 \mu\text{g}/\text{m}^3$  and  $0.50 \pm 0.39$ , respectively. One sample with anomalously high nss sulfate and Al was deleted from the data set. A seasonal trend in both MSA and nss sulfate is clearly evident in the data; both increase during the austral summer. The transition to higher summer values occurred during mid-September, and the return to lower values occurred

in early March. Dust transport, presumably from Australia, occurred from September to December, as evidenced by increased Al levels at this time.

The MSA/nss sulfate ratios at New Caledonia (Figure 2) show a large amount of scatter. Roughly half of the data has significantly lower ratios than those at Fanning and American Samoa. No correlation is observed between the MSA/nss sulfate ratio and Al (Uematsu *et al.*, 1985), and there is no evidence to suggest that the low MSA/nss sulfate ratios are related to the dust. The low ratios at New Caledonia may simply reflect natural variability in the composition of oceanic sulfur emissions, or in atmospheric conversion processes. Another possibility is that there is some input of sulfate from smelter emissions; however, smelting takes place primarily in the Noumen area on the opposite side of the island from Yate, where the sampler is located. Analysis of trace metals involved in the smelting may shed some light on this problem.

### 3.5. Norfolk

Norfolk Island samples were collected from 5/27/83–8/17/84; of these 46 were analyzed for both MSA and nss sulfate (Figure 2, 3). Mean values of MSA and nss sulfate were  $0.024 \pm 0.009$  and  $0.33 \pm 0.15 \mu\text{g}/\text{m}^3$ . Both MSA and nss sulfate show significant seasonal trends, with the highest concentrations occurring during the late spring and early summer. From June through early September, 1983, both MSA and nss sulfate levels were low, averaging about  $0.01 \mu\text{g}/\text{m}^3$  MSA and  $0.25 \mu\text{g}/\text{m}^3$  nss sulfate. During September, both MSA and nss sulfate began to increase, reaching maximum concentrations during late November/early December of  $0.089$  and  $0.75 \mu\text{g}/\text{m}^3$ , respectively. Concentrations began to decline in January, falling to below  $0.015 \mu\text{g}/\text{m}^3$  MSA and  $0.2 \mu\text{g}/\text{m}^3$  nss sulfate by late May, 1984. The MSA/nss sulfate ratio shows a distinct seasonal variability that mirrors the trends in MSA; low (0.02) during the cooler months and high (0.07–0.12) during the warmer months. Aluminum data (Uematsu *et al.*, 1985) indicate that input of dust occurred at Norfolk during the austral summer. There appears to be a consistent relationship between the input of dust and the MSA/nss sulfate ratio, with higher MSA/nss sulfate ratios during the dust season. This is somewhat unusual; high dust levels are usually accompanied by input of terrestrially derived sulfate, resulting in low MSA/nss sulfate ratios. Both the MSA/nss sulfate ratios and the lack of correlation between nss sulfate and Al in the high dust samples suggest that dust at Norfolk is not associated with input of nss sulfate. The strong covariance between MSA and nss sulfate at Norfolk during the summer suggests that the increased summer nss sulfate levels are due to increased oceanic sulfur emissions. The seasonal change in the MSA/nss sulfate ratio implies that the composition of these emissions varies seasonally, with organosulfur emissions increasing in importance over other possible sources, such as  $\text{H}_2\text{S}$ , during warmer months.

## 4. Discussion

The MSA data from the Pacific islands exhibit systematic regional and seasonal variabil-

Table I. Summary of MSA and nss sulfate results from Pacific islands. Concentrations are reported in  $\mu\text{g}/\text{m}^3$  as follows; mean (number of samples, standard deviation). To illustrate seasonal trends, the data from each station was divided into two 'seasons': April–September and October–March. NSS sulfate data are not reported for Shemya; see Experimental section for discussion.

| Location                    | MSA               |                   |                   | NSS sulfate     |                 |                 |
|-----------------------------|-------------------|-------------------|-------------------|-----------------|-----------------|-----------------|
|                             | All               | Summer            | Winter            | All             | Summer          | Winter          |
| Shemya (52°N, 174°E)        | 0.097 (32, 0.098) | 0.170 (17, 0.079) | 0.014 (15, 0.023) |                 |                 |                 |
| Midway (28°N, 177°W)        | 0.029 (47, 0.021) | 0.040 (24, 0.024) | 0.017 (23, 0.007) | 0.66 (44, 0.79) | 0.95 (22, 0.99) | 0.38 (22, 0.32) |
| Fanning (4°N, 159°W)        | 0.044 (29, 0.012) | 0.040 (14, 0.010) | 0.049 (15, 0.012) | 0.63 (55, 0.18) | 0.59 (32, 0.13) | 0.71 (23, 0.14) |
| Am. Samoa (14°S, 170°W)     | 0.026 (22, 0.012) | 0.023 (6, 0.011)  | 0.028 (16, 0.012) | 0.39 (42, 0.16) | 0.44 (14, 0.19) | 0.37 (28, 0.15) |
| New Caledonia (22°S, 166°E) | 0.021 (44, 0.009) | 0.026 (26, 0.009) | 0.014 (18, 0.004) | 0.50 (46, 0.39) | 0.47 (26, 0.18) | 0.54 (20, 0.55) |
| Norfolk (29°S, 168°E)       | 0.024 (43, 0.019) | 0.035 (23, 0.019) | 0.010 (20, 0.006) | 0.33 (41, 0.15) | 0.38 (22, 0.15) | 0.27 (19, 0.13) |

ity. The data are summarized in Figure 4 and Table I. Although there is a relatively limited basis for comparison, the distribution of MSA over the Pacific Ocean appears to be in qualitative agreement with the measurements of DMS in surface waters. This comparison is restricted to the North Pacific, as no DMS measurements have yet been made in the western South Pacific. Both DMS and MSA measurements indicate a major high latitude source of organosulfur emissions in the North Pacific (Barnard *et al.*, 1983), low emissions in the central North Pacific gyre (Bates and Cline, 1986), and higher emissions in the Pacific equatorial divergence zone (Barnard *et al.*, 1982; Cline and Bates, 1983). Detailed comparisons between MSA and DMS will require simultaneous measurements of both compounds; efforts are presently underway to collect such data.

Significant seasonal trends in MSA were observed in the Pacific data, with higher MSA concentrations during warmer months. The amplitude of these variations is a function of latitude, with the greatest seasonal changes occurring at higher latitudes (see Figure 4). Several factors may contribute to this seasonality. The most important factor is probably seasonal changes in oceanic organosulfur emissions, reflecting changes in biological productivity and speciation with changing temperature, light, and nutrient levels. Another possible factor is seasonal changes in atmospheric reaction rates and pathways. The formation of MSA is a result of free radical oxidation reactions. Under most marine conditions the oxidation of organosulfur compounds is initiated by OH radicals. Under high-latitude, winter conditions slower oxidation rates are expected because of reduced temperatures, light levels, and production of photochemical oxidants. The reaction pathway may also be affected; non-photochemical reaction pathways, perhaps involving  $\text{NO}_3$  radicals, would play a more important role under these conditions. Both of the effects described above are in phase with the observed seasonality of MSA; higher concentrations in warmer months.

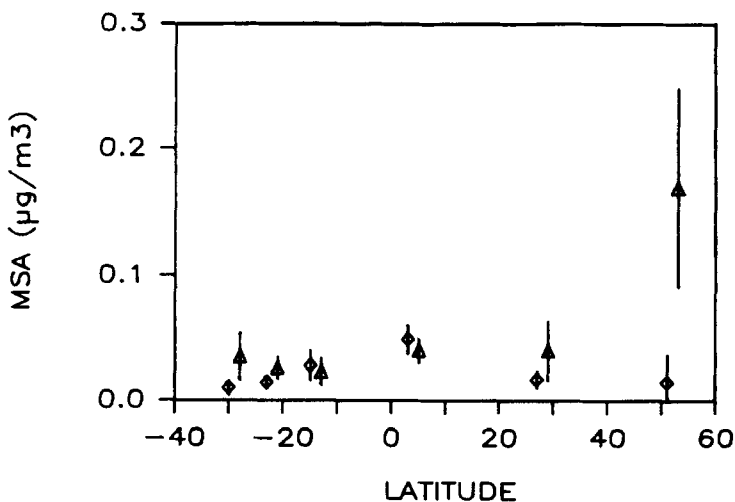


Fig. 4. Plot of MSA concentration as a function of latitude for data from Shemya, Midway, Fanning, American Samoa, New Caledonia, and Norfolk using data shown in Table I. The data are divided into summer ( $\Delta$ ) and winter ( $\diamond$ ) (see Table I).

Several workers have discussed the influence of wind speed and sea state on the emissions of DMS from the sea surface (Nguyen *et al.*, 1984; Andreae *et al.*, 1985). While these factors are undoubtedly important, the seasonal variations in MSA (summertime maxima and winter minima) are out of phase with those of the wind stress; hence, variations in wind stress are probably not a primary factor controlling seasonal changes in DMS emissions.

A final consideration regarding seasonal variations is air mass trajectory changes resulting in changes in source area. Synoptic scale collection of both chemical and meteorological parameters are needed in order to differentiate between temporal changes in ocean chemistry and spatial variations in atmospheric transport.

In the remote marine atmosphere there is positive correlation between MSA and nss sulfate (Saltzman *et al.*, 1983, 1985) as a result of the fact that organosulfur compounds are a major component of oceanic sulfur emissions. At Fanning and American Samoa, which are not impacted by continental sulfur sources, variability in the MSA/nss sulfate ratio is taken to reflect natural variability in the proportions of the various organic and inorganic (presumably  $\text{H}_2\text{S}$ ; Hermann and Jaeschke, 1984; Saltzman *et al.*, unpublished data) sulfur compounds comprising the oceanic source. To some extent it may also reflect variability in the atmospheric oxidation process, affecting the yields of MSA and sulfate. At the other Pacific stations the oceanic MSA/nss sulfate ratios are further altered by the input of continentally derived sulfur, resulting in lower ratios and increasing scatter in the data.

There are several aspects of the chemistry of MSA which need to be better understood before its role in the sulfur cycle in marine air can be evaluated on a quantitative basis. Of particular importance are the mechanisms of oxidation of alkylsulfide compounds in air and the factors which control the product distribution. Experimental studies of these reactions in systems containing DMS, OH, and  $\text{NO}_x$  found MSA and  $\text{SO}_2$  to be major products (Niki *et al.*, 1983; Hatakeyama *et al.*, 1985; Grosjean, 1984). The high yields of MSA (>50%) found in some systems are difficult to reconcile with the low MSA/nss sulfate ratios observed in marine air, considering the high concentrations of DMS in marine waters and air. There is some evidence to suggest that the mechanism of the reaction studied in experimental systems may have been influenced by the  $\text{NO}_x$  used to generate OH radicals. If this is the case, then the experimental product distributions do not necessarily apply to marine air, where  $\text{NO}_x$  levels are low.

Another factor which may affect MSA concentrations is the oxidation of MSA to sulfate in cloud droplets or aerosols. MSA is very stable towards oxidation by  $\text{H}_2\text{O}_2$  or  $\text{O}_3$ , but reacts rapidly with free radicals such as OH in gas phase or aqueous solution. The importance of gas phase oxidation is limited by the rapid uptake of MSA into the aqueous phase by hydration, nucleation, coagulation, and scavenging by cloud droplets. The observed particle size distribution of MSA in marine air argues against an appreciable gas phase concentration of MSA, as this would lead to scavenging by the larger, and more alkaline, sea-salt aerosols. This conclusion is supported by recent solubility measurements by Clegg and Brimblecombe (1985), whose data indicate that the vapor pressure of MSA over aerosols and cloud droplets should be negligible.

The oxidation of MSA to nss sulfate by aqueous free radical reactions in cloud water and aerosols is potentially important. Modeling results (Chameides and Davis, 1982; Saltzman *et al.*, 1983) suggest that the lifetime of MSA in cloud droplets may be as short as a few minutes. In marine aerosols, model results suggest that MSA should be stable (Saltzman *et al.*, 1984). However, model calculations of the uptake of free radicals from gas phase by cloud droplets and aerosols are subject to considerable uncertainty at present, and the lifetime of MSA in atmospheric solutions is not well constrained.

The MSA data collected over the Pacific ocean in this study demonstrates that systematic spatial and temporal variations in MSA and nss sulfate exist on a regional and seasonal scale. These variations are related to the composition, magnitude, and atmospheric chemistry of oceanic sulfur emissions, and to the input of continentally derived sulfur. It is clear that many fundamental questions about the atmospheric chemistry of organo-sulfur compounds need to be addressed before the use of MSA as a tracer of oceanic and atmospheric processes can be fully exploited.

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