CHAPTER 59
Nitrate, Non-Seasalt Sulfate and Methanesulfonate over the Pacific Ocean
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CHEMICAL OCEANOGRAPHY
VOLUME 10 ISBN 9-12-588610-3
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The atmospheric nitrogen and sulfur cycles are causes of major concern because of the substantial impact the various nitrogen and sulfur species can have on the environment. For example, gaseous nitrogen oxides are major factors controlling the oxidation state of the remote troposphere. They are also directly involved in establishing the O₃ concentration and, both directly and indirectly, that of the OH radical. For the most part, reduced sulfur compounds act as sinks for these oxidants, although they do not play a major role in this regard. The major oxidation products, HNO₃ and H₂SO₄, are substantial contributors to the acidity of precipitation and particles in remote, as well as polluted, regions. By reducing the pH of these components, they can increase both the volatility of weaker acids, inorganic as well as organic, and the extent of dissolution of various minerals which can release metals that are active as catalysts for numerous reactions. Similar processes can dramatically affect the biosphere when the acid constituents are either wet or dry deposited directly on the biota or within their environment. Sulfate readily forms aerosols which affect weather and climate through their interaction with solar and terrestrial radiation and by their role as condensation nuclei. In the latter capacity, they may play a significant part in defining surface-cloud coverage and precipitation patterns on the local, regional, and perhaps, even the global scale (Charlson et al., 1987). Although nitrate also exists in the particulate phase, it is most often found attached to other particles, such as sea-salt and mineral dust, rather than forming new ones.

The atmospheric cycles of nitrogen and sulfur are among the most complex of those currently being studied. Both elements exist in a myriad of gaseous and particulate forms which have a variety of sources both natural and anthropogenic. Research during the last two decades has shown that the long-range transport of materials from the continents to the oceans can have a major impact on the marine atmosphere. For example, the transport of material from Europe and North Africa accounts for about 60% or more of the nitrate and non-seasalt (nss) sulfate measured thousands of kilometers downwind at Barbados in the West Indies (Savoie et al., 1988a). Higher concentrations of nitrate and nss sulfate in rain-water at Bermuda have been directly linked to the transport of pollutants from North America (Galloway and Whelpdale, 1987). Similarly, high concentrations in aerosol particles over the northwestern Indian Ocean have been attributed to atmospheric transport from the Middle East (Savoie et al., 1987a).

However, both nitrate and nss sulfate also have sources, atmospheric and/or marine, which support natural concentrations over the ocean. Thus, before the impact of the long-range transport of pollutants from the continents can be quantified very accurately, the natural level of the
constituents must be known. These natural concentrations can vary from one location to another and as a function of time. Unfortunately, data on the large-scale spatial and temporal variations of the various atmospheric sulfur and nitrogen species are extremely sparse. This paucity of data severely limits the ability to assess quantitatively the importance of these atmospheric/marine sources. Consequently, our ability to determine the impact of the continental sources on the marine environment is also limited.

The major atmospheric/marine sources of nitrate and its precursors have generally been considered to be NO production by lightning and atmospheric conversion of NO from the stratosphere, in which it is produced by the photolysis of NO₂. However, the production by lightning continues to be a difficult quantity to estimate because of, (i) the lack of information on lightning activity over the ocean and (ii) the substantial uncertainty in the amount of NO produced by each stroke. Nitrite photoysis in surface sea-water is generally considered unimportant, although it may be a minor source (Zahniser and McFarland, 1981). Another potential biological source is the oxidation of marine-derived organic nitrogen compounds, e.g. amino acids and proteinaceous material, which are highly enriched in marine aerosols and rain (Mopper and Zika, 1987). Such a source is certainly possible, as Dupe (1983) has estimated that the concentration of organic nitrogen is a factor of about three greater than that of nitrate nitrogen in marine aerosols over pristine oceanic areas. How much, if any, of this organic nitrogen is actually oxidized to nitrate in the atmosphere remains to be determined.

For nss sulfate and its precursors, the major oceanic sources are believed to be the emissions of reduced sulfur gases which are produced by biological activity in marine ecosystems. The concentrations of dimethyldisulfide (DMS) which have been found in surface sea-water and marine air indicate that the oceanic emission of this compound represents a major flux of sulfur to the marine atmosphere (Andreae and Raemdonck, 1983; Andreae, 1985, 1988; Cline and Bates, 1983; Saltzman and Cooper, 1988). In the unpolluted marine atmosphere, DMS is oxidized primarily by reaction with OH radicals to form methanesulfonate (MSA) and SO₂; the latter is further oxidized to form sulfate. Although the MSA produced from the oxidation of DMS only constitutes c. 10% of the total mass of nss sulfur in marine aerosols, it appears to be a useful tracer for oceanic emissions of organosulfur compounds. The few measurements on aerosols which have been made (Saltzman et al., 1983; Hatakeyama et al., 1985) indicate that the size distribution of MSA is similar to that of nss sulfate, both being predominantly on submicrometer particles. Results from samples separated into two size classes by filter packs consisting of a coarse (8 μm pore size Nuclepore) and a fine (1 μm pore size Zefluor) particle filter also indicated that MSA and nss sulfate have similar size distributions (Andreae et al., 1988). Consequently, the two species are expected to be subject to similar removal
rates and their ratios should reflect the components of the sulfur sources. Recent estimates (Saltzman and Cooper, 1988) indicate that the oxidation of DMS provides about 87% of the marine-derived H2S sulfate with the oxidation of H2S adding an additional 11%. A few percent may be derived from reactions of COS and CS2.

One of the major goals of the Sea-Air Exchange (SEAREX) sampling program was the study of the temporal and spatial variations of the nitrate and sulfate concentration over the Pacific Ocean. A principal objective was to use these variations and their correlations with those in meteorology and in other concurrently measured chemical constituents to define more clearly the major sources and atmospheric pathways and fluxes of these constituents. In an effort to better understand the natural sulfur cycle over the oceans and to assess more precisely the sources of the sea sulfate, determinations of the spatial and temporal variations in the MSA concentrations were also a major part of the program. This chapter summarizes the results of those studies.

59.2. SAMPLING AND ANALYSIS

The aerosol samples used in this study were collected at a network of thirteen island stations extending from 53°N to 29°S in the Pacific Ocean. Site locations are presented in Fig. 58.1 (Chapter 58). Measurements considered in this report include those from 1981 to 1987 for the North Pacific sites and 1983 to 1987 for those in the South Pacific.

As described in Chapter 58, aerosol samples were collected continuously for one-week periods using high-volume air sampling systems (1.1 m³ min⁻¹) and Whatman 41 filters (20 × 25 cm). Sections of each filter were analysed to determine the concentrations of mineral dust. For determination of the water-soluble ions, a quarter section of each filter was extracted with 20 ml of water (one 10 ml wash followed by two 5 ml washes) in a filtering crucible tube, a procedure that results in 99% extraction (Savoie and Prospero, 1982). The concentration of Na⁺ in the extract was measured by atomic absorption spectrophotometry while those of SO₄²⁻, NO₃⁻, and MSA were measured by ion chromatography using the techniques described in Saltzman et al. (1983, 1986) and Savoie et al. (1987a). The precision of the measurements for nitrate, sulfate, and MSA was ±5%. The results of studies using dual Whatman 41 filters indicate that these filters have efficiencies of greater than 90% for MSA SO₄²⁻ and MSA and 95% for NO₃⁻ and sea-salt.

The filter blanks (and standard deviations) for NO₃⁻ and SO₄²⁻ were 7.6 (3.9) and 28.4 (9.5) ng per filter. During one week of sampling at a 100% duty cycle, about 2500 m³ of air would pass through a quarter section of the
filter. For a defined detection limit equal to twice the standard deviation of the blank values, the detection limits for a sampled volume of 2500 m$^3$ are 0.008 µg m$^{-3}$ and 0.002 µg m$^{-3}$ for NO$_3^-$ and SO$_4^{2-}$, respectively.

Intercomparisons of the Whatman 41 filters with similar filters impregnated with NaCl and Na$_2$CO$_3$ indicate (Savoie, 1984) that, for nitrate collection in the near-surface marine boundary layer, the unimpregnated filters are as efficient as the latter filters which collect total nitrate with essentially 100% efficiency (Appel et al., 1980, 1981; Forrest et al., 1980; Okita et al., 1976). Although the results presented by Savoie and Prospero (1982) indicate that less than ~10% of the nitrate exists in the gas phase in the near surface marine boundary layer, there is still some controversy surrounding this issue. None the less, we take the conservative approach that our nitrate values are totally inorganic nitrate rather than simply the particulate fraction.

The concentration of SO$_4^{2-}$ from sources other than the dissolved salts in sea-water (nmol SO$_4^{2-}$) was computed by assuming that the sea-water-derived SO$_4^{2-}$ is equal to 0.2517 times the Na$^+$ concentration. The absolute error for measurements of nmol SO$_4^{2-}$ was equal to ± 0.05 SO$_4^{2-}$ + 0.01 Na$^+$. Cellulose filters such as Whatman 41 do not produce significant amounts of sulfate aerosol artifact from SO$_2$(Costant, 1977; Forrest et al., 1980)—the primary gaseous sulfur compound of concern in remote marine areas. However, as some stations, the concentration of surf-generated sea spray was often so great that the computed values of nmol SO$_4^{2-}$ had unacceptable large error limits. To minimize the impact of such measurement errors, calculations of the computed means, all SO$_4^{2-}$ values were deleted where the sodium concentration exceeded 20 µg m$^{-3}$, a value that is equivalent to a sea-salt concentration of 65 µg m$^{-3}$, at this cut off value, the standard error for a nominal nmol SO$_4^{2-}$ concentration of 0.5 µg m$^{-3}$ would be 100%.

59.3. Geographical Variation of Mean Concentrations

The mean concentrations of nitrate, nss sulfate and MSA exhibit substantial spatial variations which differ markedly from one another (Figs 59.1–3). The overall mean concentrations of nitrate range from about 0.11 µg m$^{-3}$ at Funafuti to 0.36 µg m$^{-3}$ at Gaba. Those of nss sulfate range from 0.23 µg m$^{-3}$ at Norfolk Island to 0.67 µg m$^{-3}$ at Panning Island. At five of the sites (Shemeya, Enewetak, Nauru, Barroonda and Funafuti), the sea-salt sodium concentrations were nearly always greater than the 20 µg m$^{-3}$ upper limit for reasonable precision in the nss sulfate concentrations. Consequently, the nss sulfate concentrations at those stations will not be discussed here. The mean concentrations of MSA range from 0.02 µg m$^{-3}$ at New Caledonia to 0.097 µg m$^{-3}$ at Shemeya.

For the purpose of discussion, the sites are separated into four groups
Fig. 59.1. Latitudinal variation in the mean concentrations of nitrate over the Pacific Ocean. The horizontal bars indicate the 95% confidence limits for the means.

Fig. 59.2. Latitudinal variation in the mean concentrations of NSS sulfate over the Pacific Ocean. The horizontal bars indicate the 95% confidence limits for the means.
which are based on the spatial variations in the concentrations of mineral dust (Chapter 5B) and are generally distinct indicators of significant continental input. The North Pacific sites (Midway and Oahu) are strongly influenced by the transport of material from Asia during the late winter and spring and at Midway during the fall as well. Oahu may be affected by transport from North America during the summer and fall. Transport to the equatorial stations (Fanning Island and Nauru) is strongly dependent on the location of the intertropical convergence zone (ITCZ) which determines the hemisphere to which the stations are meteorologically tied. Although they do occasionally receive input of dust from Asia during the spring, such events are considerably less numerous than at the more northerly latitudes. The remote tropical South Pacific (Funafuti, American Samoa and Rarotonga) is generally a region that is minimally affected by transport of dust from the continents. There is fairly strong evidence indicating that the region to the east of Australia (New Caledonia and Norfolk Island) is often affected by transport of materials from that continent, particularly during the austral summer.

59.3.1. NITRATE

The highest mean nitrate concentrations occur at the mid-latitude stations in the North Pacific (Fig. 59.1). At Midway and Oahu, the mean concentra-
tions (0.29 and 0.36 µg m⁻³, respectively) are factors of 2.5 to 3 higher than those over the remote tropical South Pacific and about double those over the equatorial region (see below). Both of these stations are known to be strongly influenced by the transport of dust from Asia during the spring. The concentrations at Oahu may also be affected by transport from North America during other periods.

The mean nitrate concentrations at the two equatorial stations, Fanning Island and Nauru, do not differ significantly from one another and are consistent with that of 26 samples collected aboard the R/V Oceanographer during cruises within 5° of the equator between 105° W and 170° E: mean 0.167 ± 0.023 µg m⁻³ (± represents the 95% confidence limits) (Savoie, 1984). Although the mean reported for these equatorial regions by Huebert and Lazrus (1980), 0.20 µg m⁻³ (x = 0.079, n = 10), is slightly higher it does not differ significantly from that given above for Nauru and Fanning Island. Interestingly, a similar mean has been reported for the equatorial Indian Ocean during the southwest monsoon (Savoie et al., 1987a). For the 23 samples collected aboard the R/V Researcher when the airflow was from the southern hemisphere, the mean nitrate concentration was 0.159 ± 0.022 µg m⁻³. These results indicate that there may be a fairly consistent mean nitrate concentration between 0.16 and 0.17 µg m⁻³ over the relatively remote regions of the equatorial oceans.

The lowest nitrate concentrations occurred at the three most remote tropical sites in the South Pacific: Funafuti; American Samoa; and Rarotonga. At these sites, the means were essentially identical to one another, 0.11 ± 0.01 µg m⁻³. Whether or not the concentrations at these locations are representative of a relatively long-term mean for the natural marine and atmospheric sources over the tropical South Pacific remains to be proven. However, evidence indicates that the boundary layer air at American Samoa is among the least polluted that has ever been studied. In an investigation of trace elements at Samoa, Arimoto et al. (1987) reported mean concentrations of the mineral dust indicator elements, Al and Cr, that are similar to those reported recently for the South Pole (Tanneau et al., 1988). The concentrations of Cu and Zn were lower and that of Pb was much lower at Samoa than those at the South Pole, indicating that the transport of pollutants to Samoa is also minimal. These results are consistent with calculated air mass trajectories (see also Chapter 53 and Dayan and Nelson, 1988; Dayan et al., 1984) which indicate that the air, except on rare occasions, has traveled long distances over the open ocean prior to arriving at the island. In a recent evaluation using a medium resolution general circulation transport model, Levy and Moxm (1989) have indicated that fossil fuel combustion can account for only 10% or less of the nitrate concentrations which are observed over the tropical South Pacific.

At New Caledonia and Norfolk Island which are seasonally affected by
the long-range transport of mineral dust from Australia (see Chapter 58 and Savoie et al., 1988b), the mean nitrate concentrations were 0.209 ± 0.030 and 0.182 ± 0.017 μg m⁻³, respectively. These concentrations are 60–90% higher than those at the remote South Pacific sites.

59.3.2. NSS SULFATE

In contrast to nitrate, the mean NSS sulfate concentration over the North Pacific mid-latitudes is not the highest of the four regions despite the known transport from Asia (Fig. 59.2). The mean concentrations (0.55 μg m⁻³ at Midway and 0.49 at Oahu) are actually about 20–25% lower than the mean at the near equatorial station on Fanning Island. However, they are about 40–50% higher than that over the remote tropical South Pacific. The mean concentration in the marine boundary layer at Oahu is only about 20% higher than that measured above the maritime inversion at the Mauna Loa Observatory on Hawaii, 0.41 μg m⁻³ (Parrington and Zoller, 1984). The highest mean NSS sulfate concentration occurred in the equatorial region. The mean at Fanning Island, 0.67 μg m⁻³, is nearly identical to that of 0.65 μg m⁻³ (±0.27) found for 26 samples collected aboard the R/V Oceanographer between 105°W and 170°E and within about 5° of the equator (Savoie, 1984). Measurements made aboard ships during north–south transects in the Pacific have also revealed evidence of a NSS sulfate peak within about 5° of the equator (Clarke et al., 1987; Parungo et al., 1986).

Even over the remote tropical South Pacific, the NSS sulfate concentrations are quite substantial. The mean concentration at American Samoa was 0.36 μg m⁻³.

The mean concentrations at the two stations near Australia are quite disparate. At New Caledonia, the mean concentration, 0.42 μg m⁻³, is somewhat greater than that at American Samoa as might be expected from the probable impact of continental material. However, the mean at Norfolk Island (0.23 μg m⁻³) is nearly a factor of 2 lower than that at New Caledonia despite the fact that the mineral dust concentration is substantially higher. It should be emphasized here that, although the occurrence of mineral dust is a clear indication of the presence of continentally derived material, the converse is not necessarily true. Because the injection of dust into the atmosphere depends critically on wind speed and soil conditions, whereas pollutant material can be injected directly into the atmosphere, even extremely low concentrations of mineral dust do not necessarily indicate that the concentrations of other continentally derived materials are also very low. Consequently, the relative concentrations of mineral dust at two locations are not necessarily indicative of the relative pollutant
concentrations. This is particularly true if the two locations are affected by different source regions and/or different atmospheric transport pathways. Although the relative results at the two stations are somewhat surprising, they are not necessarily incompatible.

59.3.3. METHANESULFONATE

The overall mean concentrations of MSA exhibit a significant spatial variation (Fig. 59.3). The highest concentrations occur in the high-latitude region of the North Pacific, e.g. at Shemya, the average MSA concentration was 0.097 μg m⁻³. Higher than average MSA concentrations also occur in the high productivity region of the equatorial divergence, thus the mean concentration at Fanning Island was 0.044 μg m⁻³. In the oligotrophic regions of both the North and South Pacific, which are represented by the remainder of the stations, the mean concentrations vary over the relatively narrow range from about 0.02 to 0.03 μg m⁻³.

These large-scale spatial variations of MSA are in general accord with those of the DMS concentrations in the underlying oceans (Andreae, 1986; for example both species exhibit relatively high concentrations in the equatorial Pacific (Andreae and Raemdonck, 1983; Andreae et al., 1983; Barnard et al., 1982; Bates et al., 1987; Cline and Bate, 1983). Bates et al. (1987) reported mean DMS concentrations of 3.8 n mole DMS1⁻¹ for the equatorial region of the Pacific between 148°W and 180°W and between 0° and 5°N, i.e. the region encompassing Fanning Island. Further west, the mean decreased to about 1.9 n mole DMS1⁻¹ which is about equivalent to the mean of 1.72 n mole DMS1⁻¹ for the tropical North Pacific between 5°N and 20°N. From 20°N to 50°N, the average decreases further to about 1.44 n mole DMS1⁻¹. However, from 50°-65°N, the region in which Shemya is located, the mean exhibits a substantial increase to 2.4 n mole DMS1⁻¹.

Comparisons of the DMS concentrations with those of chlorophyll-a (which is taken as an indicator of the standing stock of phytoplankton) indicate that there is a significant correlation between the two constituents when large and varied data sets are considered (Andreae, 1986; Barnard et al., 1984). However, there were no clear relationships within a given region. The absence of such a clear relationship may stem from species specificity of DMS production (Barnard et al., 1984). This factor also affects the relationship between DMS concentrations and primary productivity (e.g. see Results section in Bates et al., 1987).

59.4. SEASONAL CYCLES IN THE CONCENTRATIONS

At many of the Pacific Ocean sites, the general seasonal cycles of the nitrate and nitrite concentrations mimic that of the mineral dust (see Chapter
58 and Prospero et al., 1985), suggesting that there is often a significant continental impact on the concentrations of the two anions. For example, high concentrations of nitrate and nss sulfate associated with the seasonal transport of Asian dust over the North Pacific have been noted previously (Prospero et al., 1985; Parrington and Zoller, 1984; Dzurak and Winchester, 1982). However, because the cycles of nitrate and nss sulfate are also affected by variations in the fluxes from natural atmospheric/marine sources, there are also major instances in which their cycles do not coincide with that of mineral dust. For example, the seasonal cycle of MSA, suggests that the substantial seasonal variations in the nss sulfate concentrations at high latitudes may be strongly tied to those of the DMS fluxes. With these observations in mind, the seasonal cycles of nitrate, nss sulfate and MSA will be discussed below.

59.4.1. NORTH PACIFIC

59.4.1.1. Shemya

As noted previously, the highest mean concentration of MSA was measured at Shemya. The seasonal cycle is also more dramatic at this site than at any other in the network (Fig. 59.4). During the winter months (November–March), the concentrations averaged less than 6 ng m⁻³ and rarely exceeded 10 ng m⁻³. At the height of the summer, the concentrations frequently exceeded 200 ng m⁻³ and averaged more than 150 ng m⁻³ from June to September. Similar seasonal variations have been noted at St. Lawrence Island (63°46' N, 171°45' W). Similar cycles have been reported for the gas phase precursor, DMS, in the surface waters of the Arctic in

![Diagram](image-url)

**Fig. 59.4.** Composited seasonal cycle of methanesulfonate in the atmospheric boundary layer at Shemya. The fluxes connect the monthly mean concentrations.
which the mean concentrations ranged from near zero during the winter to 1.4 nmol DMS$^{-1}$ during the summer, and of the subarctic where they increased from 6.66 nmol DMS$^{-1}$ during the winter to 4.2 nmol DMS$^{-1}$ during the summer (Bates et al., 1987).

The dramatic decrease in concentration from summer to winter may be a consequence of variations in several different processes: photochemistry; primary productivity; and meteorology. Sharply lower temperatures, water vapor mixing ratios, and light levels during the winter would all be expected to result in reduced photochemical production of OH radicals and, hence in reduced sites of oxidation of DMS and therefore in lower concentrations of MSA. However, biological activity in this region also exhibits major seasonal fluctuations. During the winter, the poor light conditions in the mixed layer and the increased spatial extent of sea-ice result in extremely low productivity, and consequently, nutrient concentrations build up at this time of year (Ryan, 1963). When the ice begins to melt and light conditions improve in the late spring, the high nutrient concentrations support intense productivity (Sambrotto et al., 1984). Because of the intense summer biological activity, the annual organic carbon production in the Bering Strait is comparable to that in many lower latitude shelf areas despite the much shorter growing season (about 120–160 days) in the high latitudes. Saltzman et al. (1986) have indicated that seasonal changes in atmospheric transport to Shemya may also play a significant role in the seasonal cycle of MSA. During the summer months included in the MSA study period, the prevailing winds at the site were westerly, suggesting that the source region during that time may have been the North Pacific or the Sea of Okhotsk rather than the Bering Sea. The sharp reduction in MSA concentrations during October 1981 occurred when the winds changed to steady southeasterly.

59.4.1.2. Midway

The major influence of transport from Asia is most apparent at Midway where the seasonal cycles of nitrate and nss sulfate are very similar to that of mineral dust (Chapter 58). A significant and substantial peak period occurred from March to May when the mean concentrations were 0.40 μg m$^{-3}$ for nitrate and 0.93 μg m$^{-3}$ for nss sulfate (Fig. 59.5). A secondary peak in nitrate (0.31 μg m$^{-3}$) was clearly evident during October and coincided with a similar weak maximum for the dust concentration. There was a hint of a similar secondary peak for nss sulfate; however, the effect was considerably less apparent than for nitrate and, in fact, was barely significant statistically at the 95% confidence level. During the five
months of the year with the lowest dust levels (July–September and December–January), the mean concentrations were 0.21 μg m$^{-3}$ for nitrate and 0.37 μg m$^{-3}$ for NSS sulfate; these values are respectively factors of 2 and 2.5 lower than those during the spring peak.

On the basis of the seasonal cycle of MSA, it can be assumed that the cycle of NSS sulfate is partially influenced by variations in the strength of the biogenic sulfur source. Although the amplitude of the seasonal variation at
Midway was considerably less than that at Shemya, the timing of the cycle was similar. The mean MSA concentration was lowest, about 10–12 ng m\(^{-1}\), during December and January. From April to September, the mean concentrations were factors of about 3 higher, usually ranging from 20 to 35 ng m\(^{-1}\). Surface water DMS concentrations of the subtropical North Pacific showed an approximately three-fold variation seasonally (Bates et al., 1987). However, a strong peak in MSA occurred during May 1981. The weekly average concentrations during that month ranged from 69 to 111 ng m\(^{-1}\); consequently, the overall average for the month of May, 62 ng m\(^{-1}\), is a factor of 2 higher than those for the other spring and summer months. Isentropic wind trajectories (J. Merrill, unpublished data) indicate that the long episode of high MSA concentrations was associated with a shift to northwesterly winds from the more normal westerlies (Saltzman et al., 1986). The relationship between the MSA concentration and the wind trajectory suggests that the variation in the MSA concentration may be more strongly related to changes in the upwind source region than to changes in the local oceanographic conditions.

9.4.1.3. Oahu

The seasonal cycles of nitrate and nss sulfate at Oahu (Fig. 59.6) differ significantly from those at Midway. Elevated concentrations certainly occur during March through May when nitrate averages 0.42 µg m\(^{-1}\) and nss sulfate averages 0.62 µg m\(^{-1}\). It is noteworthy that although the nitrate concentration during this period is about the same as that at Midway, the nss sulfate is more than 30% lower. However, the maximum monthly mean nitrate concentration at Oahu (0.60 µg m\(^{-1}\)) occurs in February with relatively high concentrations already evident in January, and the mean nss sulfate concentration in February (0.64 µg m\(^{-1}\)) is only slightly less than the maximum which occurs in May (0.68 µg m\(^{-1}\)). The lowest concentrations for both consituents occur during November and December when nitrate averages 0.27 µg m\(^{-1}\) and nss sulfate averages 0.28 µg m\(^{-1}\), factors of 1.6 and 2.2, respectively, lower than those during the major dust transport season. Similar seasonal changes in nss sulfate have been noted for clean free tropospheric air sampled at the Mauna Loa Observatory on the island of Hawaii (Parrington and Zoller, 1984). During the dust season from mid-February to June, the average nss sulfate concentration, 0.55 µg m\(^{-1}\), is about twice that of 0.31 µg m\(^{-1}\) during the remainder of the year.
59.4.2. EQUATORIAL PACIFIC

The seasonal cycles of nitrate, nss sulfate and MSA over the equatorial Pacific can be represented by those at Fanning Island (Fig. 59.7). The trends in the aluminum concentrations (see Chapter 58 and Uematsu et al., 1983; Savisie et al., 1988b) clearly indicate that these islands are sometimes affected by the transport of dust from Asia during the months of February through May. However, such events are rare and this transport has no pronounced effect on the seasonality of the nitrate and nss sulfate concentrations. The nss sulfate concentration at Fanning was essentially constant throughout the year with the monthly means varying over the range of 0.60–6.74 μg m⁻³. The MSA concentrations indicate that the source strength for biogenic sulfur is also fairly constant; the monthly mean concentrations ranged from 34 to about 60 ng m⁻³ with no distinct pattern. Surface water DMS concentrations in this region also exhibit no significant seasonal cycle (Bates et al., 1987).

The nitrate data for this region are somewhat more complicated. The
overall monthly mean concentrations at Fanning vary from 0.12 to 0.20 μg m⁻³; similar variability also occurs at Nauru. However, the seasonal variations at the two stations differ significantly; thus, an annual cycle is clearly discernible at Fanning, this is not the case at Nauru for which the data are very variable.

During 1981 at Fanning, a large peak in the nitrate concentrations occurred from August to November with the highest monthly mean, 0.35 μg m⁻³, occurring in September (Prospero et al., 1985). During this
period, the ITcz was situated to the north of Fanning, and the high nitrate concentrations were tentatively attributed to the transport of material from South and Central America. The authors noted that the filters during this time were various shades of grey, a coloration that is consistent with the presence of combustion products such as soot or elemental carbon. Although a few high concentrations occurred during the same season in subsequent years, the sustained peak over several months has never been repeated.

Asian dust occasionally reaches Fanning during the late winter and early spring, when the ITcz is usually at its most southerly position. During these dust incursions, the nitrate concentrations also exhibit a significant increase; examples of this are the numerous high concentrations during the spring periods of 1983 to 1985. However, a significant spring peak is certainly not a consistent feature from year to year, and most of the concentrations tend to be distributed around the overall mean. The year-to-year variations may reflect interannual variations in the mean position of the ITcz during the spring. Because the ITcz is located near Fanning, a small shift to the north or south can change the hemisphere from which Fanning receives most of its transported material (Chapter 53).

59.4.3. REMOTE TROPICAL SOUTH PACIFIC

American Samoa can be taken as representative for the remote tropical South Pacific stations. Although the overall seasonal cycles of nitrate and nss sulfate were very similar (Fig. 59.8), there were also significant differences. As at Fanning Island, there was no distinct seasonal cycle in the nss concentrations. The lowest mean concentration of nss sulfate (0.28 μg m⁻³) occurred during April and May. During September and October, the concentrations were about 1.6 times higher, 0.45 μg m⁻³. The lowest nitrate concentrations like those of nss sulfate occurred during March, April, and May, when the average was 0.308 μg m⁻³. During September, October, and November, the average was about 1.7 times higher, 0.418 μg m⁻³. Although December, and possibly January as well, may be included in the higher concentrations period, a definitive statement cannot be made because of the greater variability in the measured concentrations during those months. The major differences in the nitrate and nss sulfate cycles occurred from June to August. During this period, the nitrate concentrations were significantly higher than during April; in contrast, the nss sulfate concentrations remained low until a rather abrupt increase occurred in September.

Despite these mid-year differences, the seasonal cycles of the concentrations of both constituents may reflect changes in the air mass trajectories to American Samoa. A review of twice per day isentropic back trajectories
from June 1983 to July 1984 (see Chapter 53) revealed a definite seasonal cycle in the transport to Samoa.

During the austral winter (primarily the months of June, July, and August, but also extending into September), most of the air masses arrived from the mid-latitudes to the south, having subsided from the mid-troposphere. Typically, the isentropic trajectories began at an altitude of 6–8 km over, or to the south of, Australia about two weeks prior to their
arrival at Samoa. The parcels were then transported eastward toward the semi-permanent high in the South Pacific. As the parcels moved counterclockwise about the high, they also descended in altitude, reaching the marine boundary layer and moving back toward the west at a location east to southeast of Samoa. From there, the west-to-northwest transit to American Samoa was often fairly short, on the order of a few days to a week. The months when this occurred corresponded neither to the maximum nor to the minimum in the annual nitrate cycle, but rather to an intermediate period when the nitrate concentrations were similar to the overall means.

In contrast, during the other nine months of the year, the air masses typically followed long trajectories from the east, essentially all within the tropical marine boundary layer. However, the paths of these trajectories did exhibit a seasonal trend. From mid-September to February, the major portion of the nearly direct east to west transport occurred in the latitude band between 10°S and 15°S. However, the more easterly portion of the trajectory varied significantly from day to day; at 11°W, the location of the trajectory ranged from about 20°S to the equator.

During March and April, the eastern ends of the trajectories were frequently much farther to the north, sometimes extending well into the northern hemisphere. Such northwesterly trajectories have been noted previously (Dayan et al., 1984; Dayan and Nelson, 1988; Chapter 53, this volume). Although CO₂ and methylchloroform increase at American Samoa during such events (Halmer, 1984), aerosol particle concentrations do not appear to be affected. It is probable that much of the northern hemisphere aerosol load is washed out as the parcels traverse the intertropical and/or South Pacific convergence zones. In fact, it is during these months that the concentrations of nitrate are at a minimum, 2Be and 210Pb also exhibit generally low concentrations during this period (Savoie et al., 1988); this is also true for both ozone (Oltmans, 1981; Oltmans and Koomly, 1986) and condensation nuclei (CN) concentrations (Bodhaine and DeLuisi, 1985). The seasonally lower concentrations could conceivably be due to the relatively short trajectory times between the washout events in the South Pacific Convergence Zone and the arrival of the air parcels at the sampling sites. The short periods may not allow enough time for the concentrations of the constituents in the boundary layer to build up to equilibrium levels.

59.4.4. EAST OF AUSTRALIA

Nitrate, nss sulfate and MSA all exhibited significant seasonal cycles at New Caledonia (Fig. 59.9) and Norfolk Island (Fig. 59.10). Although the cycles
at the two islands differed somewhat, the highest concentrations generally occurred during the austral summer when the transport of dust from Australia was the greatest (Savoie et al., 1988b; Chapter 58, this volume). At both sites, the overall monthly mean nitrate concentrations were usually greater than 0.2 μg m⁻³ from September to January, with maximum mean concentrations in the order of 0.3 μg m⁻³. During June at Norfolk Island and during both May and June at New Caledonia, the mean concentrations
decreased to levels of 0.10–0.12 µg m⁻³, which are comparable to the mean concentrations over the remote tropical South Pacific.

The seasonal cycle in NSS sulfate was much stronger at Norfolk Island than at New Caledonia. At New Caledonia, the mean concentration from May to July was 0.28 µg m⁻³ and it increased by less than a factor of 2 during the austral summer (0.49 µg m⁻³ from September to January). At Norfolk Island, the mean from June through August was 0.121 µg m⁻³,
during November and December, the means increased to more than 0.4 μg m⁻³.

The greater seasonal variation in nss sulfate at Norfolk is probably due, at least in part, to the more substantial variation in the flux of dimethyl- 

sulfide (DMS) from the ocean as indicated by the correspondence with the seasonal cycles of MSA. At New Caledonia, the monthly mean MSA 

concentrations ranged from about 8.5 ng m⁻³ during May and June to about 30 ng m⁻³ during November, December and January, about a four 

fold change from the austral winter to the austral summer. At Norfolk 

Island, the winter–summer difference was a factor of about 10, ranging 

from 5–6ng m⁻³ during June and July to 50–75 ng m⁻³ during November and December. These seasonal variations in MSA at Norfolk Island are 

similar to those at Cape Grim, Tasmania (Ayers et al., 1988) where the 

concentrations ranged from about 3 ng m⁻³ during the winter to about 50 ng m⁻³ during the summer. The reasons for the substantial differences 

between the MSA cycles at Norfolk Island and New Caledonia (which are 

separated by only 7° of latitude) are still not clear. However, they are likely 
to be more strongly related to differences in trajectories to the sites (and hence, to differences in the upwind source regions) than to major differ-

ences in the local productivities.

59.5. SOURCES OF NON-SEASALT SULFATE AND NITRATE

It was pointed out above that both natural oceanic and atmospheric sources 
appear to contribute significant levels of nitrate and nss sulfate to the 
tropospheric marine boundary layer. Before the impact of the long-range 
transport of pollutants from the continents can be quantified accurately, 
the natural levels of these constituents must be estimated.

59.5.1. NSS SULFATE

The major natural source of nss sulfate over the oceans is believed to be the 
oxidation of reduced sulfur compounds that are emitted from the ocean (see 
Section 59.1). The dominant reduced sulfur gas, DMS, is oxidized to MSA 

and SO₂ which is subsequently oxidized to sulfate. Because MSA and 
sulfate are soluble end-products in the atmosphere and have similar physical properties, the mechanisms and rates of their removal would also be expected to be similar. If the composition of the emitted reduced sulfur 
gases and the branching ratio for DMS oxidation are reasonably consistent 
from one location to another, then it should be possible to use the MSA 
concentration to estimate that of nss sulfate which is derived from marine biogenic sources.
The authors have suggested that all the nss sulfate at American Samoa and Fanning Island is derived from natural sources. Comparisons of estimated DMS emission fluxes and nss sulfate deposition rates indicate that this assumption is not unreasonable. If it is assumed that DMS oxidation accounts for 87% of the natural nss sulfate (Saltzman and Cooper, 1988) and 100% of the MSA, the molar flux of DMS from the ocean should equal about 93-94% of the molar deposition flux of nss sulfate. For estimating the nss sulfate deposition flux, a dry-deposition velocity of 0.05 cm s⁻¹ has been assumed (Savoie, 1984). The wet-deposition flux is calculated from the mean aerosol concentration using the regional rainfall and a wash-out ratio of 0.36 (μg m⁻³ rain)/(μg m⁻³ air) (Savoie et al., 1987b). Using the mean nss sulfate concentration at American Samoa, 0.36 μg m⁻³, and the average rainfall for the tropical South Pacific, 100 cm yr⁻¹ (Elliott and Reed, 1984), yields a nss sulfate flux of 730 μg m⁻³ m⁻² d⁻¹ for this region. Multiplying by 0.93, yields a required DMS molar flux of 3.6 μmol m⁻² d⁻¹. The few surface water DMS concentration measurements in this region (5-20°S) averaged 1.09 nmol S m⁻³ (Bates et al., 1987). Using this concentration and the piston velocity of 2.7 m d⁻¹ (the average used by Bates et al. (1987) for the tropical North Pacific) yields a DMS flux of 2.9 μmol m⁻² d⁻¹. Considering the substantial uncertainties in each of the calculations, the 20% difference between the estimated flux of DMS and the flux necessary to support the nss sulfate deposition is clearly not significant.

For the region of Fanning Island, the uncertainty is even larger, primarily because of the stronger latitudinal gradients in both the rainfall and the surface water DMS concentrations. For the nss sulfate flux estimates, the rainfall average for 0-5°N, of 144 cm yr⁻¹ has been used (Elliott and Reed, 1984) together with the mean nss sulfate concentration at Fanning of 0.67 μg m⁻³. The estimated nss sulfate deposition flux, 980 μg SO₄⁻² m⁻³ m⁻² d⁻¹, requires a DMS emission flux of 9.5 μmol m⁻² d⁻¹. For the region from 5-18°S, the mean surface seawater DMS concentration, 3.8 nmol l⁻¹, and mean piston velocity, 1.78 m d⁻¹ (Bates et al., 1987), yield an estimated DMS emission flux of 6.8 μmol m⁻² d⁻¹, about 28% less than the estimated required flux. Again, the differences in the estimates are probably not significant, given the uncertainties in the parameters being used. Moreover, the MSA to nss sulfate ratios at Fanning Island and American Samoa average 0.065 with 90% of the values between 0.044 and 0.103 (Fig. 59.11). Similar ratios have been measured in the marine boundary layer over the northeast Pacific near the coast of Washington (Andreae et al., 1988). After subtracting the portion of the nss sulfate that was apparently derived from continental sources, comparable ratios were also found to exist at Barbados, West Indies (Savoie et al., 1988b) and at Barrow, Alaska (Li and Winchester, 1988). Ratios of this magnitude are consistent with recent laboratory measurements of the
oxidation products of DMS (Grosjean, 1984; Bates et al., 1987) and with studies of the reaction kinetics (Hynes et al., 1986).

It should be noted, however, that these ratios may not apply at all locations. For example, evidence has been presented that, particularly in the polar regions, the ratio may vary substantially and differ significantly from that found in the tropics. The results from laboratory studies of DMS oxidation by OH radicals (Hynes et al., 1986) indicate that the addition of OH increases in importance, relative to H abstraction, as the temperature decreases. Hence, the MSA/nss sulfate ratio from biogenic sources may be considerably higher in the polar and near polar regions than in the warmer tropics. The few field studies which have been completed thus far have provided inconclusive results. Although the overall average MSA/nss sulfate ratio at Cape Grim was similar to that at Fanning and American Samoa, the ratio exhibited a strong seasonal cycle with values of about 0.2 during the summer and 0.02 during the winter (Ayers et al., 1986). Interestingly, an analogous trend occurs in our data for Norfolk Island where the ratio was 0.2 during the summer and 0.03 during the winter. Since there is likely to be some input of nss sulfate from Australia, the ratios at both Cape Grim and Norfolk must be considered as lower limits of the MSA/nss sulfate ratio from the biogenic source. It should be pointed out, however, that the seasonal trends in the ratios are exactly the opposite of those that would have been expected from the temperature dependence of the branching ratio (see above). Aerosols collected over the Drake Passage

Fig. 59.11. Plot of the methanesulphonate (MSA) concentrations versus those of nss sulfate at two remote sites in the southern tropical and equatorial Pacific: American Samoa and Fanning Island. The mean MSA/nss sulfate ratio, 0.005, is illustrated by the regression line ($y = 0.005x$, $r = 0.76$).
and the Gerlache Strait had MSA/nss sulfate ratios of 0.6-1.0, a factor of 10 higher than those in the tropics (Berresheim, 1987). However, the sea-salt sulfate is the latter study was the dominant fraction of the total sulfate, the nss sulfate usually accounting for less than 20% of the total. Since the estimated sea-salt fraction must be subtracted from the total to estimate the non-seasalt fraction, the random errors associated with the nss sulfate concentrations are quite substantial. MSA/nss sulfate ratios in Antarctic ice cores are also extremely variable (Ivey et al., 1986).

Clearly, the primary causes of the "real-world" variations in the MSA/nss sulfate ratio must be understood before we can be certain that MSA-based estimates of the biogenic nss sulfate are indeed valid. The results which have been obtained over the tropical regions of the world ocean are, at least, fairly consistent. On the basis of this consistency, the authors feel that an MSA/nss sulfate ratio of 0.06-0.07 can be used with measured concentrations of MSA to obtain reasonable estimates of the concentrations of nss sulfate in these regions. In fact, since it is not known what parameters substantially affect the branching ratio in the real atmosphere, it is not certain that significant variations do not occur in other tropical regions. The appropriate ratio to use for the higher latitude sites is even more obscure; however, the summertime ratios of about 0.2 at Cape Grim and Norfolk Island may serve as useful lower limits. They can only be considered to be lower limits because some of the nss sulfate may have been derived from sources other than marine biogenic sulfur emissions.

59.5.2. NITRATE

Current knowledge of NO3 in the remote marine atmosphere does not allow an unequivocal assessment of the natural sources of the nitrate to be made. Because of this, knowledge of the atmospheric cycle of nitrogen oxides lags well behind that of sulfur. Without a better understanding of the sources which contribute to the nitrate concentrations over remote regions of the ocean, the difficulty and uncertainty involved in attempts to assess the impact of long-range transport from anthropogenic sources will remain.

The extremely low mineral dust and trace metal concentrations at American Samoa, and the consistency of their mean concentrations over a broad area of the tropical South Pacific makes it difficult to implicate a continental source. On the basis of recent model calculations, Levy and Moxim (1989) have concluded that fuel combustion accounts for less than 10% of the mean nitrate concentration in this region. Furthermore, the nss sulfate at Samoa appears to be derived almost exclusively from marine biogenic sources.

Although the stratosphere is probably a significant source of the NO3,
precursors (Levy et al., 1980), the absence of even a weak correlation between nitrate and \(^{238}\)U appears to rule out the possibility that it is the major source. \(^{238}\)U is produced by the spallation of nitrogen atoms in the stratosphere and upper troposphere.) If the stratosphere were the major source of the precursor NO\(_x\), then nitrate would be expected to be, at least, significantly correlated with other constituents that are derived dominantly from this same source. However, the linear coefficient of determination \((r^2)\) between nitrate and \(^{238}\)U was only 0.08 at American Samoa, which is not significantly different from zero (Savoie et al., 1988c).

The oxidation of biologically produced organic nitrogen compounds should probably also be considered as a potential source of nitrate. Although there is currently no hard evidence for such a source, it would be consistent with the higher mean nitrate concentrations found in the highly productive equatorial region. Nitrite photolysis in surface seawater is generally considered to be unimportant, although it may be a minor source (Zahrone and McFarland, 1981). Another potential biological source is the oxidation of marine-derived organic nitrogen compounds, e.g., amino acids and proteinaceous material, which are highly enriched in marine aerosols and rain (Nopper and Zika, 1987). Duec (1983) had previously estimated that the concentration of organic nitrogen is a factor of about 3 greater than that of nitrate-nitrogen in marine aerosols over pristine oceanic areas.

Despite the extremely low trace-metal concentrations in the aerosol at American Samoa, a continental source must not be less than considered. Here, the nitrate concentrations are significantly correlated with those of \(^{228}\)Ra, which is derived almost exclusively from the radioactive decay of \(^{222}\)Rn emitted from soils. A continental source for the nitrate is not incompatible with the extremely low concentrations of pollutants at Samoa since the continental source is not necessarily anthropogenic. An alternative is the production of NO\(_x\) by lightning which occurs most frequently over the tropical regions of the continents (Corell, 1981; Turman and Edgar, 1982). Both trajectory analyses and what is known climatologically about the mid-tropospheric winds suggest that the most likely source region is South America. In fact, the results presented by Turman and Edgar (1982) indicate that the frequency of lightning over northern South America is in tune with the seasonality of nitrate concentrations at Samoa. Such a source has been previously proposed to account for the major fall peak in nitrate at Fanning Island during 1981 (Prozorov et al., 1985). The active convection that is usually associated with lightning could be instrumental in rapidly transporting the \(^{222}\)Rn and \(^{238}\)U to higher altitudes where they as well as the NO\(_x\) could be effectively transposed over long distances. Furthermore, the stronger and gustier winds associated with these storms may actually result in a more efficient ventilation of the Rn from the soils. The model by Cruzen and Gidel (1983) suggests that lightning and stratospheric sources
can readily account for the mean nitrate concentrations over the equatorial and southern tropical regions of the Pacific Ocean. However, the production rate of NO, by lightning is still a subject of considerable discussion and research, and current estimates vary by more than an order of magnitude. If the mean atmospheric nitrate concentrations of about 0.11 $\mu$g m$^{-2}$ are indeed representative of natural levels over the tropical South Pacific, then what can be said about the mean concentrations (0.16 $\mu$g m$^{-2}$) over the equatorial region which are about 50% higher? Are they representative of natural levels in that region and higher because of stronger sources or more direct and/or consistent transport from the major source regions? Without a clear understanding of the major nitrate sources, these questions cannot be adequately addressed.

59.5.3. IMPACT OF CONTINENTAL SOURCES

As was noted in Section 59.4.1, the concentrations of nitrate and NSS sulfate at Midway and Oahu are significantly affected by the transport of material from Asia, and Oahu may be affected by transport from the United States as well. Using the above discussion as a basis, estimates can be made of the effect of these sources on the mid-latitude region of the North Pacific. The annual average MSA concentration at Midway is 0.029 $\mu$g m$^{-3}$ (Saltzman et al., 1980). If an MSA/SO$_4^{2-}$ ratio of 0.07 is assumed for the marine biogenic source, then this source supplies an average of about 0.41 $\mu$g m$^{-2}$ of NSS sulfate. If a ratio of 0.2 is more appropriate, then the biogenic source supplies only 0.15 $\mu$g m$^{-2}$ of the NSS sulfate. Since the total annual NSS sulfate at Midway is 0.55 $\mu$g m$^{-3}$, the natural marine source can provide between 25 and 75% of it. A similar biogenic source would yield 30–80% of the 0.49 $\mu$g m$^{-3}$ of NSS sulfate at Oahu. The Asian source must then supply an average NSS sulfate concentration of between 0.08 and 0.4 $\mu$g m$^{-2}$ at these stations.

At New Caledonia, the mean MSA concentration (0.021 $\mu$g m$^{-3}$) yields an estimate of 0.1–0.3 $\mu$g m$^{-3}$ for marine biogenic sulfate. These values account for about 25–70% of the total mean NSS sulfate. On the basis of the mean MSA concentration of 0.24 $\mu$g m$^{-3}$, the estimated biogenic NSS sulfate (0.12–0.34 $\mu$g m$^{-3}$) at Norfolk Island accounts for 50% to more than 100% of the total measured NSS sulfate.

Similar calculations for nitrate are also very uncertain since it is not clear exactly how mean concentration needs to be subtracted from the overall mean to obtain the estimate for the impact from continental sources. There is at least some evidence that the nitrate concentrations at Fanning Island are not strongly influenced by transport of material from Asia even though the miner dust concentrations certainly are, albeit to a very small degree.
At Midway, the mean nitrate concentration during the spring peak is 0.40 μg m⁻³. If it is assumed that the natural level would be similar to that over the tropical South Pacific (0.11 μg m⁻³), then the transport from Asia accounts for about 0.29 μg m⁻³ during this period. The average dust concentration at Fanning during the spring is about an order of magnitude less than that at Midway. Consequently, it is suggested that the nitrate at Fanning Island that is attributable to dust transport from Asia was probably less than 0.03 μg m⁻³ during the four-month period of major dust transport and would have contributed less than 0.01 μg m⁻³ to the overall average. It should also be pointed out that, for the five years that samples were collected at Fanning, the average of all concentrations during February to May (0.167 μg m⁻³) is essentially identical to the average for all of the data. Attribution of the nitrate primarily to natural sources certainly makes the chemistry at Fanning more consistent since the nss sulfate has been attributed exclusively to marine biogenic sources.

For the current estimate, it is simply assumed that the natural level is somewhere between that of the tropical South Pacific (0.11 μg m⁻³) and that of the equatorial region (0.16 μg m⁻³). These levels would account for 38–55% of the mean nitrate at Midway and 31–45% of that at Oahu. The mean nitrate concentrations attributable to the continental sources are then 0.13–0.18 μg m⁻³ at Midway and 0.20–0.25 μg m⁻³ at Oahu.

The mean nitrate concentrations at New Caledonia and Norfolk Island were 0.21 and 0.18 μg m⁻³, respectively. On the basis of the arguments used for the North Pacific, the natural nitrate levels account for 50–75% of the mean nitrate concentration at New Caledonia and 60–90% of that at Norfolk Island. These results are very uncertain but do suggest that continental sources probably account for less than half of the nitrate measured at these sites.

59.6. GLOBAL IMPACT OF THE NATURAL ATMOSPHERIC/MARINE SOURCES

Despite the major uncertainties, the results given above indicate that natural atmospheric and/or marine sources may supply major fractions of both the nitrate and the nss sulfate atmospheric concentrations over the Pacific Ocean. If the mean concentration of the natural nitrate is assumed to be between 0.11 and 0.16 μg m⁻³, then the total flux to the Pacific Ocean (area = 67.71 x 10⁸ km²; mean rainfall = 104 cm y⁻¹) is 6.3 to 9.2 TgNO₃⁻ y⁻¹. These fluxes represent 40–60% of the total nitrate deposition of 15 TgNO₃⁻ y⁻¹ (calculated as described by Savoie, 1984, but using the updated nitrate concentrations and rainfall information). Using results presented by Bates et al. (1987), the present authors estimate that the
total DMS flux from the Pacific Ocean is about 250 Gmol S y⁻¹. The reduced sulfur compounds are then estimated to account for a ns sulfur flux of about 26 TgS₂y⁻¹, or about 65% of the estimated total ns sulfur deposition of 40 TgS₂y⁻¹ (updated estimate based on the results of Savoie, 1984).

There are major regions of the world ocean which are strongly affected by the transport of pollutants from the continents; prominent among these areas are the Mediterranean Sea, the Red Sea, the North Atlantic Ocean and the northern Indian Ocean. Consequently, the percentage of the nitrate which is attributable to natural atmospheric and/or marine sources over the world ocean is somewhat less than those over the Pacific. In contrast, for ns sulfate, the percentage for the world ocean is similar to that for the Pacific. For the world ocean, the atmospheric/marine nitrate yields a deposition flux of 11–16 TgNO₃⁻y⁻¹, 25–40% of the total oceanic deposition flux of about 40 TgNO₃⁻y⁻¹ (Savoie, 1984). The input from the oxidation of reduced sulfur compounds emitted from the ocean accounts for about 52 TgS₂y⁻¹ (Baies et al., 1987), or about 70% of the total ns sulfate deposition of 73 TgS₂y⁻¹ (Savoie, 1984).

Recently, Charlson et al. (1987) have hypothesized that marine biota might play a significant role in regulating the earth's climate. The reduced sulfur compounds produced by the biota are emitted from the ocean and, subsequently, oxidized to sulfur in the atmosphere. Since the sulfur which is produced from gas-to-particle conversion is generally believed to be the dominant component of submicrometer particles and cloud condensation nuclei (CCN), the sulfate ultimately derived from the biota could significantly affect the surface cloud coverage and precipitation patterns on scales ranging from local to global. The results presented above indicate that the biota may well control the CCN concentrations over some large areas of the oceans and play a major role in controlling them over the world ocean in general. Since nitrate over the ocean is generally associated with sea-salt particles, it does not add to the CCN concentrations directly. However, depending on the actual source of the natural atmospheric/marine nitrate, the precursor NO₃ may play a major role in controlling the oxidation state of the atmosphere over major regions of the ocean, and hence, may indirectly control the rate of oxidation of the reduced sulfur precursors.

59.7. Summary

The nitrate and ns sulfate data from the SEAREX Program have provided some interesting insights into the large-scale picture of the nitrogen and sulfur cycles over the Pacific Ocean. The seasonal cycles of the two constituents closely parallel that of the
Asian dust over the North Pacific. The present authors' estimates indicate that the Asian source provides about 15–25% of the nss sulfate and perhaps 45–70% of the nitrate in northern mid-latitudes.

For the Pacific as a whole, it is estimated that natural atmospheric and/or oceanic sources account for about 40–46% of the nitrate and about 65% of the nss sulfate. For the world ocean, the percentages are about 25–40% for nitrate and 70% for nss sulfate.

Marine organisms are apparently responsible for the major fraction of the nss sulfate over the entire Pacific and may provide essentially all of the nss sulfate over the regions of the equator and the southern tropics. Because nss sulfate aerosols comprise a major fraction of the condensation nuclei, these particles strongly affect cloud processes. Consequently, the results indicate that biological sources in the ocean may play a major role in controlling weather and climate over the Pacific Ocean and, by analogy, over other relatively remote marine areas of the ocean such as the Indian and the South Atlantic Oceans.

Natural sources may also account for essentially all of the nitrate over the equatorial and southern tropical regions. However, the actual sources of this nitrate are extremely uncertain. Depending on what those sources are, the natural nitrogen cycle may also play a major role in controlling atmospheric chemistry over the Pacific and other remote regions of the ocean, particularly its oxidation state.

Despite the amount of data that has been accumulated and analysed and the amount of information that has been gained in the process, present knowledge of the natural cycles of nitrogen and sulfur in the marine troposphere remains decidedly inadequate. Until the major questions regarding those natural cycles are answered, the inability to assess the role played in the marine cycle by continental sources will continue.

ACKNOWLEDGEMENTS

We gratefully acknowledge the numerous people who have helped to set up, run and maintain the Pacific aerosol network and the various people who have provided analytical and technical assistance over the past years. We specifically thank R.T. Nees (U. Miami) for her continued analytical support and T. Snowdon (U. Miami) for his technical assistance and management of the network. This work was supported by National Science Foundation grants OCE-8112106, ATM-8311335, ATM-8405921, OCE-8405609 and ATM-8709802.