Long-term record of nss-sulfate and nitrate in aerosols on Midway Island, 1981–2000: Evidence of increased (now decreasing?) anthropogenic emissions from Asia

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[1] Increasing anthropogenic emissions from Asia, especially from regions undergoing rapid industrial development, have raised interest in the outflow of chemically and radiatively important gases and aerosols. Previous studies have shown that high concentrations of Asian pollution spread over a broad region of the North Pacific every spring. Here we report on studies of aerosol concentrations at Midway Island (28°13′N, 177°22′W) in the central North Pacific over the period 1981–2000. Using a relatively simple procedure we estimate the natural and anthropogenic fractions of sulfate and nitrate aerosol and show that the estimated anthropogenic component almost doubled from 1981 to the mid-1990s. This increase closely parallels estimates of increased emissions of SO2 from China. However, measurements in the late 1990s suggest that sulfate and nitrate concentrations have stabilized and perhaps decreased. Thus over the longer term pollution emissions from Asia and concentrations over the North Pacific may be less than earlier projections, a factor which has implications for the assessment of future climate trends.

INDEX TERMS: 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 3022 Marine Geology and Geophysics: Marine sediments—processes and transport; 3322 Meteorology and Atmospheric Dynamics: Land/atmosphere interactions; 3360 Meteorology and Atmospheric Dynamics: Remote sensing; KEYWORDS: aerosols, emissions, sulfate, nitrate, dust, trends


1. Introduction

[2] Airborne particles (aerosols) play an important role in climate by scattering and absorbing both solar and terrestrial radiation and by modifying the distribution of clouds and their radiative properties. The recent assessment of the Intergovernmental Panel on Climate Change (IPCC) [2001] finds that models that incorporate the effects of anthropogenic sulfate aerosol along with greenhouse gases are better able to reproduce the surface temperature trends in the 20th century than models that do not consider aerosols.

[3] The level of scientific understanding of aerosol effects is, however, very low and the uncertainty in estimates can be very large [IPCC, 2001; Haywood and Boucher, 2000]. At present our knowledge of global aerosol distributions and associated climate effects is largely dependent on models [IPCC, 2001; Haywood and Boucher, 2000]. There are few aerosol data from remote locations against which such models can be tested [IPCC, 2001; Haywood and Boucher, 2000] especially over the oceans [Prospero, 1996; Heintzenberg et al., 2000]. Such data are especially critical in areas impacted by transport from regions with rapidly developing economies where emission controls are often minimal and emission rates poorly documented. Much interest focuses on China, a major source of SO2 and nitrogen oxides (NOx) [Streets and Waldhoff, 2000; Streets et al., 2000; Lefohn et al., 1999; van Aardenne et al., 1999], species that react to form a large portion of the atmospheric aerosol burden. In 1990, China emitted 20% of the world’s SO2 making it the single largest source [Lefohn et al., 1999]; emissions are projected to more than double between 1995 and 2020 [Streets and Waldhoff, 2000; Streets et al., 2000; Lefohn et al., 1999; van Aardenne et al., 1999]. There is, however, considerable uncertainty in these estimates and there are often large differences among them.

[4] Past studies have shown that large quantities of pollutants are transported eastward out of Asia during the
spring [Hoell et al., 1997] yielding high concentrations of aerosols over a large area of the Pacific [Prospero et al., 1989; Savoie et al., 1989a, Arimoto et al., 1996, 1997] and sporadically over North America [Wilkening et al., 2000; Berntsen et al., 1999; Jaffe et al., 1999; Husar et al., 2001]. While such events are indicative of the potential for impacts from Asia, there is no firm evidence of the frequency and pervasiveness of such events or of long-term trends that could be linked to Asian emissions and thus might provide the basis for assessing future impacts.

[5] Here we present the results from 20 years of almost continuous aerosol chemical measurements on Midway Island in the central North Pacific, about 5000 km distant from the coasts of North America and mainland Asia (Figure 1). The objective of this study is to see if we can detect any trends in the data and if these trends could be associated with changes in emissions. To this end we compare the Midway aerosol record with estimates of anthropogenic emissions in Asia.

[6] There are many physical and chemical processes that can affect the transport of gases and particles over such great distances. Indeed the year-to-year variability in meteorology and longer term climate trends over this 20-year period could seriously complicate this simple approach. The strongest climatic influence is likely to be the El Niño Southern Oscillation (ENSO). Although the effects of ENSO conditions on the transport of aerosols from Asia have not yet been studied explicitly, changes in rainfall patterns and in tropospheric winds associated with ENSO events [McPhaden, 1999] presumably affect the production, deposition and transport of various types of aerosol particles. Nonetheless the direct comparison of emissions with concentrations at a

![Figure 1. Map of the North Pacific.](image-url)

![Figure 2. Time series of aerosol NO$_3^-$, nss-SO$_4^{2-}$, and MSA concentrations at Midway Island, 1981–2000, measured on week-long filter samples. Units: Aerosol concentration, nss-SO$_4^{2-}$ and NO$_3^-$, $\mu$g m$^{-3}$; methanesulfonate (MSA), ng m$^{-3}$. Years from 1981 to 2000.](image-url)
distant receptor site such as Midway is a necessary first step to a more complete understanding of these factors.

2. History and Procedures

[7] Sampling began in 1981 [Prospéro et al., 1989; Savoie et al., 1989a; Arimoto et al., 1989] and continued through the 1990s [Arimoto et al., 1996, 1997]. Sampling is carried out on the climatological wind-ward shore on the eastern end of Sand Island. Initially we used a free-standing system at ground (2m) level on a pier. In December 1985 a 15 meter fold-over sampling tower was erected on a nearby beach where it remains in operation to this day. Samples were collected over week-long periods during onshore winds (greater than 1 m s⁻¹) from the ocean sector (330° through North to 150°). There are no major aerosol sources on Midway. Although Midway has been an active military air base since World War II, activity decreased sharply after the Vietnam War and in October 1978 Midway was redesignated as a Naval Air Facility. In April 1988 Midway Atoll was designated as an overlay National Wildlife Refuge and in October 1996 jurisdiction was transferred to the Department of the Interior. At present the resident population of Midway totals approximately 150; visitors are limited to 100 at a time.

Throughout the program we used Whatman-41 filters (20 x 25 cm) which in the marine boundary layer have a collection efficiency greater than 99% for nss SO₄²⁻, 95% for NO₃⁻ marine aerosols, and 99% for dust. Filters were subsequently analyzed for species that have both anthropogenic and natural sources. Non-sea-salt (nss) SO₄²⁻ (i.e., SO₄²⁻ from sources other than the salts in ocean-water spray droplets) is primarily derived from pollution sources and from the oxidation of dimethyl sulfide (DMS) emitted by marine phytoplankton [Kettle et al., 1999]. In remote ocean regions DMS is the dominant source of nss-SO₄²⁻ aerosol [Savoie et al., 1989a, 1994; Davis et al., 1999], and the ratio of methanesulfonate (MSA, another product of DMS oxidation) to nss SO₄²⁻ can be used to estimate the strength of this source [Savoie et al., 1989a, 1994]. Nitrate aerosol is derived from both natural and pollution sources [Holland et al., 1999]. Operational blanks are taken every fourth week. In Miami a quarter of each filter was extracted with water and analyzed for soluble species [Savoie et al., 1989a]. A quarter section of the filter was analyzed for Al by instrumental neutron activation analysis [Arimoto et al., 1996, 1997]; the Al concentration was converted to an equivalent soil aerosol value assuming an average crustal abundance, 8% Al [Taylor and McLennan, 1985]. Nss SO₄²⁻ is calculated as total SO₄²⁻ minus the Na⁺ concentration times 0.2517 (i.e., the SO₄²⁻:Na⁺ mass ratio in bulk seawater). Under most conditions, especially during the spring when continental impacts are greatest, concentrations are well in excess of detection limits. Flow rates were determined from the differential pressure across a calibrated sharp-edged orifice plate (traceable to NBS standards) located in the sampler exhaust. Excluding some periods when the system suffered from obvious leaks, the flow rates were very stable. In 1987, the beginning of a long period when the sampling configuration was basically unchanged, the annual mean flow rate (and standard deviation, SD) was 56.96 m³ hr⁻¹ (SD 1.32); in 1998, the end of this period, it was 56.84 m³ hr⁻¹ (SD 1.04). To eliminate marginal samples, we deleted all sample values where the sampler run time was less than 10% during the sampling week.

3. Results

3.1. Aerosol Temporal Variability and Trends

Nss-SO₄²⁻ and NO₃⁻ aerosol (Figure 2) show considerable short-term variability but with a strong spring max-
imum. Peak monthly means (Figure 3 and Table 1) occur in April and May largely due to transport from Asia [Prospero et al., 1989; Savoie et al., 1989a; Arimoto et al., 1989; Gao et al., 2001] as confirmed by the concurrent increase in mineral dust [Prospero et al., 1989] and 210Pb (half-life 22 years), a radioactive decay product of 222Rn emitted from soils and often used as a tracer of continental air masses [Turekian et al., 1989]. In spring back trajectories from Midway [Merrill, 1989] frequently lead to Asia. Air parcels emerge from the Asian coast generally between the altitudes of 5–10 km and travel rapidly to the east. Over the central Pacific trajectories turn southward, descend into the boundary layer over the ocean and eventually reach Midway after 4–6 days [Merrill, 1989]. Thus measurements made at Midway reflect the presence and properties of deep aerosol layers over a large area of the Pacific.

[10] MSA also peaks in spring synchronous with oceanic DMS emissions [Kettle et al., 1999] (Figure 3). A scatterplot of the individual sample data for MSA versus nss-SO\textsubscript{4}\textsuperscript{2-} yields a broad distribution which nonetheless shows a well-defined upper boundary (Figure 4, top). A line drawn along this boundary yields a mass ratio of 0.06–0.07 for MSA versus nss-SO\textsubscript{4}\textsuperscript{2-}, a value that is consistent with ratios obtained in remote pollution-free tropical-subtropical regions [Wilkening et al., 2000; Savoie et al., 1994]. A scatterplot of monthly mean MSA versus nss-SO\textsubscript{4}\textsuperscript{2-} (Figure 4, bottom) also yields a broad scatter. But here too there is an upper bound with the data points for July, August, and September falling in the slope range 0.06–0.07. The scatterplots support the conclusion that in July, August, and September, nss-SO\textsubscript{4}\textsuperscript{2-} is primarily derived from DMS oxidation.

[11] We use the MSA concentration and the “natural” tropical-subtropical mass ratio of MSA/nss-SO\textsubscript{4}\textsuperscript{2-} 0.07, to estimate the concentration of “natural” (DMS-derived) SO\textsubscript{4}\textsuperscript{2-} and we subtract this from total nss-SO\textsubscript{4}\textsuperscript{2-} to obtain “anthropogenic” SO\textsubscript{4}\textsuperscript{2-}. Figure 5 shows the monthly mean (1981–2000) values of total nss-SO\textsubscript{4}\textsuperscript{2-} and the estimated “natural” and “anthropogenic” fractions (henceforth, “nat-SO\textsubscript{4}\textsuperscript{2-}” and “anth-SO\textsubscript{4}\textsuperscript{2-}” respectively). Anth-SO\textsubscript{4}\textsuperscript{2-} increases strongly in March (0.52 μg m\textsuperscript{-3}) along with mineral dust [Prospero et al., 1989; Gao et al., 2001] and peaks in April (0.59 μg m\textsuperscript{-3}); in these months anth-SO\textsubscript{4}\textsuperscript{2-} composes 65% and 58% of total nss-SO\textsubscript{4}\textsuperscript{2-}. In May anth-SO\textsubscript{4}\textsuperscript{2-} falls off sharply along with dust while nat-SO\textsubscript{4}\textsuperscript{2-} peaks sharply to 75% of total nss-SO\textsubscript{4}\textsuperscript{2-}. In spring, 50% of nss-SO\textsubscript{4}\textsuperscript{2-} in the boundary layer at Midway is estimated to be “anthropogenic,” on an annual basis, about 40%.

[12] Monthly mean NO\textsubscript{3}\textsuperscript{-} shows minimum values around 0.20 μg m\textsuperscript{-3} in winter and summer. We take this to be an estimate of “background” NO\textsubscript{3}\textsuperscript{-} which could conceivably...
contain both natural and anthropogenic contributions [Savoie et al., 1989b]. We subtract this from total monthly mean \(NO_3^-\) to estimate anth-\(NO_3^-\). Anth-\(NO_3^-\) reaches a maximum in spring, accounting for about half the total \(NO_3^-\) (Figure 5), on an annual basis, about a third. It should be noted that the anth-\(NO_3^-\) and anth-\(SO_4^{2-}\) peaks do not coincide; the \(NO_3^-\) peak is shifted one month later.

To elucidate trends we focus on spring, summer and winter data. We use summer and winter data in two ways. First, on the assumption that pollution is minimal and natural long-term variability small, we use summer and winter data as a quality check, looking for changes that might be a sign of operational or analytical difficulties. Second, we look for trends in the differences between spring values and those for summer and winter. Table 2 presents a summary of the grouped spring (March, April, May), summer (June, July, August), and winter (December, January, February) aerosol concentrations for the period 1981 to 2000; these are displayed in (Figure 6).

The aerosol record at Midway is affected by climate and weather as well as by emissions from source regions in Asia. As previously stated two of the strongest ENSO events of the century occurred during our program, in 1982–1983 and 1997–1998, the latter being followed by a strong La Niña in 1998–1999 [McPhaden, 1999]. At the simplest level, ENSO-associated changes could affect our sampling statistics because the system is activated according to wind direction and speed. The sampler is located on the climatological windward shore; thus a change in wind climatology affects sampling times (and sample size), which results in smaller samples (and, hence, possibly “noisier” data) or no samples at all. ENSO could also affect transport out of Asia. Studies show a strong relationship between the El Niño/La Niña cycle and the East Asian Winter Monsoon (EAWM) [Wang, 2000; Li and Mu, 2000]. An et al. [1990] showed that over geological timescales, the highest dust fluxes to the Chinese loess plateau occurred during the cold and dry conditions associated with a strong EAWM. Thus we might expect ENSO events to affect the transport of pollutants as well as dust to the Pacific. Nonetheless, the tracking of aerosol concentrations at Midway with emissions in Asia suggests that meteorological variability was averaged out over the longer term. Also ENSO affects ocean hydrographic properties and biological processes [Chavez et al., 1999; Turk et al., 2001] over large areas of the Pacific, changes that could conceivably affect the production and emission of DMS to the atmosphere.

Nonetheless, while there are large deviations in spring concentrations in some years (e.g., 1983), there are no indications of trends in summer or winter data. Nitrate means remain essentially flat from 1986 to 1999. Summer nss-\(SO_4^{2-}\) is more variable due to low summertime nss-\(SO_4^{2-}\) values and to statistical variability introduced in computing nss-\(SO_4^{2-}\). Winter nss-\(SO_4^{2-}\) also shows increased variability because of high sea-salt concentrations often present in that season. Even so, taken as a whole, summer and winter data suggest that station operations and sampling protocols did not introduce any long-term biases in the data sets.
### Table 2. Seasonal Aerosol Concentration Statistics: Spring, Summer, Winter

<table>
<thead>
<tr>
<th>Year</th>
<th>Spring: March, April, May</th>
<th>Summer: June, July, August</th>
<th>Winter: December, January, February</th>
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<tbody>
<tr>
<td></td>
<td>nss sulfate, µg m⁻³</td>
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<td>nss sulfate, µg m⁻³</td>
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<tr>
<td></td>
<td>Mean</td>
<td>Standard Deviation</td>
<td>Count</td>
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<tr>
<td>1981</td>
<td>0.90</td>
<td>0.91</td>
<td>13</td>
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<tr>
<td>1982</td>
<td>0.82</td>
<td>0.52</td>
<td>13</td>
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<td>1984</td>
<td>0.77</td>
<td>0.50</td>
<td>12</td>
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<tr>
<td>1985</td>
<td>0.91</td>
<td>0.60</td>
<td>10</td>
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<td>1986</td>
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<tr>
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<td>0.41</td>
<td>11</td>
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<tr>
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<td>0.41</td>
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<tr>
<td>2000</td>
<td>0.34</td>
<td>0.46</td>
<td>12</td>
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</tbody>
</table>

**Abbreviations:**
- nss sulfate: Non-seaspray sulfate
- Nitrate: Nitrate
- Dust: Dust
- MSA: Methanesulfonic acid

**Notes:**
- Counts may vary due to measurement frequency and availability.
- Standard deviations reflect variability within each season.
- Values are reported in units of µg m⁻³.
In contrast, mean springtime $\text{NO}_3^-$ and $\text{nss-SO}_4^{2-}$ show considerable year-to-year variability (Figure 6) which makes it difficult to clearly discern trends. Nevertheless, the comparison of the springtime versus summertime data suggests an increasing divergence of values over the late 1980s and early middle 1990s.

To investigate for trends in anth-$\text{SO}_4^{2-}$ we separated out DMS-derived $\text{SO}_4^{2-}$ from total $\text{SO}_4^{2-}$ using two different procedures. First, for the six years in which we measured MSA (1981, 1983, 1990, 1991, 1993, 1994), we converted the measured MSA values to equivalent nss-$\text{SO}_4^{2-}$ using the “natural” tropical-subtropical MSA/nss-$\text{SO}_4^{2-}$ mass ratio, 0.07. Second, using the same ratio we converted the mean springtime MSA for the entire data set, 33.3 ng m$^{-3}$, to the equivalent $\text{SO}_4^{2-}$, 0.48 µg m$^{-3}$, and subtracted this from the individual springtime nss-$\text{SO}_4^{2-}$ means. Although there are considerable year-to-year changes in MSA concentrations (and, presumably, DMS-derived $\text{SO}_4^{2-}$), this should not obscure any large long-term trend in anth-$\text{SO}_4^{2-}$. We also estimated the long-term trend in anth-$\text{NO}_3^-$ using the assumed “background” $\text{NO}_3^-$ concentration, 0.2 µg m$^{-3}$, and subtracting this from the spring means. These data (Figure 7) show an increasing trend from the early 1980s, with anth-$\text{SO}_4^{2-}$ and anth-$\text{NO}_3^-$ almost doubling by the mid-1990s. As expected anth-$\text{SO}_4^{2-}$ values calculated on the assumption of a constant DMS-$\text{SO}_4^{2-}$ source are considerably more variable than those based on actual MSA measurements but both yield similar trends.

Our conclusion that anthropogenic aerosols increased at Midway from the early 1980s to the middle 1990s is based on the visual inspection of concentrations. It is difficult to assess the statistical significance of trends in atmospheric composition because of the stringent requirements on data sets [Weatherhead et al., 1998] especially for aerosols because of their great temporal variability. To statistically test the trends at Midway, we calculated the arithmetic mean concentrations for springtime anth-$\text{SO}_4^{2-}$ for three years in which MSA data were available for estimating the biogenic $\text{SO}_4^{2-}$ fraction directly. The mean anth-$\text{SO}_4^{2-}$ concentrations increased from 0.24 µg m$^{-3}$ (standard error, SE = 0.12) in 1981 to 0.48 µg m$^{-3}$ (SE = 0.13) in 1990 to 0.65 µg m$^{-3}$ in 1993. However the difference in the means as tested by an analysis of variance was at most marginally significant, with a probability for chance occurrence of 0.076. A comparable calculation for total $\text{NO}_3^-$ shows that concentrations increased from 0.38 µg m$^{-3}$ in 1981 (SE = 0.055) to 0.45 µg m$^{-3}$ (SE = 0.060) in 1990 to 0.58 µg m$^{-3}$ (SE = 0.075) in 1993, with the difference in $\text{NO}_3^-$ means being closer to conventional levels of statistical significance, p = 0.050. Thus, even though these analyses are only marginally significant statistically, they support our conclusion that there has been an increase in $\text{NO}_3^-$ and $\text{SO}_4^{2-}$ aerosol at Midway.

### 3.2. Comparison with Asian Emissions

There are many estimates of Asian emissions to be found in the literature but only two track annual emissions over a multi year period during our program [Lefohn et al., 1999; Streets et al., 2000]. Both show strong increases over the 1980s, which continued into the mid-1990s [Streets et al., 2000]. In East Asia (China, Japan, the Koreas), China is by far the largest source, emitting in 1997 24,971 Gg yr$^{-1}$ of $\text{SO}_2$, 91.6% of the total in the region [Streets et al., 2000]. In Figure 8 we show the Midway record of estimated anth-$\text{SO}_4^{2-}$ along with the emissions reported by Lefohn et al. [1999] and Streets et al. [2000]. There are substantial differences between these two estimates both in terms of absolute amounts and the rates of increase. Nonetheless, the trend in anth-$\text{SO}_4^{2-}$ at Midway matches the estimated emissions in a general way, most closely those of Streets et al. [2000]. More specifically, we compare the average anth-$\text{SO}_4^{2-}$ calculated on the basis of the measured MSA concentrations using two-year means to minimize year-to-year variations. The mean spring anth-$\text{SO}_4^{2-}$ for 1981 and 1983 was 0.35 µg m$^{-3}$; for 1990–91, 0.50 µg m$^{-3}$; and for 1993–94, 0.65 µg m$^{-3}$. Thus the concentration of anth-$\text{SO}_4^{2-}$ in 1990–91 was 1.43 times that in 1981 and 1983 while that for 1993–94 was 1.85 times greater. The emission data in Streets et al. [2000] yield increases of 1.49 and 1.61 for these same time periods. A similar comparison using the Lefohn et al. [1999] data for 1989–1990 relative to 1981 and 1983 yields an increase of 1.60.

Estimates of $\text{NO}_x$ emissions in Asia also suggest a strongly increasing trend. From 1990 to 1997, $\text{NO}_x$ emissions in China increased 60% while those in East Asia as a whole...
increased by 49% [Streets and Waldhoff, 2000]; in contrast, SO$_2$ emissions increased 12% in China and 8% in East Asia [Streets et al., 2000]. A longer-term estimate [Zheng et al., 2002] shows emissions of reactive nitrogen doubling between 1980 and the mid 1990s, a rate roughly twice that of SO$_2$ emissions. At Midway we see no systematic change in the relative concentrations of anth-SO$_4^{2-}$ to anth-NO$_3^-$.

However the ratios are quite variable from year to year, ranging from 1.4 to 3.1 (mean, 2.1) based on years where MSA was measured and from 1.5 to 2.8 (mean, 2.0) using the mean MSA for the entire period. Thus it is not clear that we would be able to readily detect the estimated relative changes in emissions, given the many variables beyond emission rates that effect the concentration of these two species. Another consideration is that while both NO$_3^-$ and SO$_4^{2-}$ are largely produced from the combustion of fossil fuels, the source distributions are likely to differ substantially. For example, in Asia 76% of the sulfur emissions are from the combustion of coal [Streets et al., 2000], while nitrogen oxides are mainly from the transportation sector [Elliott et al., 1997]. This could also explain the fact that the seasonal peak in anth-SO$_4^{2-}$ occurs one month before that in NO$_3^-$ (Figure 5).

4. Discussion and Conclusions

[21] Our measurements on Midway Island show that estimated anthropogenic sulfate and nitrate aerosol concentrations almost doubled from 1981 to the mid 1990s paralleling increased emissions from China. Our estimates must be qualified by certain assumptions that we make in our assessment. First of all we assume that all spring-time SO$_4^{2-}$ in excess of the DMS-derived (MSA-based) SO$_4^{2-}$ is due to anthropogenic sources in Asia. With the exception of volcanoes [Graf et al., 1997], there are no natural sources on the continents that could account for the large amounts of “anth-SO$_4^{2-}$” that we see on Midway. Volcanic emissions would be sporadic and we would not expect to see coherent long-term trends as we do in our data. In contrast there are substantial natural NO$_x$ sources on the continents, for example, lightning, soil emissions, biomass burning [Holland et al., 1999]. In total, these are relatively small compared to anthropogenic sources and furthermore some of them (e.g., biomass burning) would not be strong in the spring. Finally, the long-term coherence of the Midway NO$_3^-$ trends and the match to anthropogenic emissions argues against a substantial and changing natural contribution.

[22] Midway aerosols certainly contain materials from non-Asian sources but their contribution is probably minor. The North Pacific is impacted by pollutants from Europe and the former Soviet Union [Newell and Evans, 2000]. Over the period of our study, however, the emissions of SO$_2$ from these regions have been relatively flat [Lefohn et al., 1999]. Moreover the impact of these sources over the North Pacific is greatest (but still small) during the winter, decreases during the spring, and is minimal during the summer [Newell and Evans, 2000].
The good match between our estimates of anthropogenic SO$_4^{2-}$ and NO$_3^-$/CO aerosol at Midway and the temporal trends of emissions in China suggests that either our assumptions are reasonable or that there was a remarkable coincidence of offsetting factors that result in a fortuitous match.

We point out that our data also suggest that anth-SO$_4^{2-}$ and anth-NO$_3^-$ at Midway have decreased since the mid 1990s. We caution that we have less confidence in the later data although we have no specific reason to exclude it. During that time the US Navy Air Facility was in the process of being decommissioned and island operations turned over to the US Fish and Wildlife Service. Our sampling program was often compromised during that time. The number of useable samples decreased (Table 2) and the accumulated run times on samples was somewhat reduced. Also, as previously stated, the strong El Niños in 1982–1983 and 1997–1998 complicates interpretations because of expected changes in transport paths and precipitation.

Nonetheless, a downward trend in anth-SO$_4^{2-}$ concentrations in the late 1990s would be consistent with recent estimates [Streets et al., 2000] which show that in the middle 1990s fossil fuel emissions from China had flattened and had begun to decline. The estimates of reactive nitrogen emissions [Zheng et al., 2002] also show a marked downturn in the late 1990s. The estimate for 2000 [“Streets, China 2000”] is an estimate provided by D. G. Streets (personal communication, 2001) using the same data sources and procedures as those in Streets et al. [2000].

Figure 8. Anthropogenic sulfate aerosol concentrations on Midway and SO$_2$ emissions from China. Springtime concentrations of estimated anthropogenic SO$_4^{2-}$ at Midway (see Figure 7) are shown along with estimates of SO$_2$ emissions from China: “Lefohn et al., China” [Lefohn et al., 1999]; “Streets et al., China” [Streets et al., 2000]. To facilitate comparison with the data by Lefohn et al., the data shown as “Streets et al., extrapolated” were linearly back-extrapolated from Streets et al. [2000] using data for the years 1985–1990, which are themselves linear. The emission rate for 2000 (“Streets, China 2000”) is an estimate provided by D. G. Streets (personal communication, 2001) using the same data sources and procedures as those in Streets et al. [2000].
We point out a curious feature in the data (Figure 7) where over much of the record we see a very pronounced “saw-tooth” pattern in the concentrations of spring-time ant-SO$_4$$. This pattern in not seen in the six years when ant-SO$_4$ was estimated from measured MSA. This suggests that the saw-tooth pattern is largely an artifact generated by assuming constant DMS emissions. We see a similar saw-tooth pattern in spring-time NO$_3$ which matches that of nss-SO$_4$$. This suggests that the “background” NO$_3$, which we assumed to be constant in our estimates (0.2 µg m$^{-3}$), is also variable and in phase with the oceanic source of DMS-SO$_4$$. The variability could be due to meteorological or hydrological factors that modulate the “background” concentrations of these species or of their production processes.

Our measurements focused on a limited number of aerosol species. The springtime air masses also carry high concentrations of other pollutants [Hoell et al., 1997]. Of particular interest are organic species including black carbon (BC), aerosols which can have a strong effect on radiative forcing [Jacobson, 2001]. There is evidence that aerosols emitted from Asia contain relatively large amounts of BC due to the widespread use of fossil fuels and biofuels under conditions where emissions are largely uncontrolled [Lelieveld et al., 2001]. Thus the air masses emerging from China in the spring carry with them a complex mix of aerosol and gas species which could have a strong impact on chemical processes and the oxidizing capacity of the atmosphere [Lelieveld et al., 2001]. Moreover, the high concentration of dust could further complicate the chemical processes in such air masses because of the large surface area afforded by the dust [Phadnis and Carmichael, 2000]. The evolution of these chemical processes with time, and the changing profile of emissions in China, could have implications for the long-range transport of pollutants across the North Pacific to North America.

Taken as a whole, the Midway data show that Asian emissions have had a great impact on aerosols over a large area of the North Pacific and possibly North America. This impact has changed markedly and rapidly over the past two decades. The assessment of the future climate effects of Asian aerosols over the Pacific will be challenging because of the complex composition of the windborne particles and their rapidly changing concentrations. This has implications regarding estimates of global warming because aerosols as a whole are believed to have, on balance, a cooling effect that partially offsets the warming due to greenhouse gases [IPCC, 2001].

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