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Comparisons of trace constituents from ground stations and the DC-8 aircraft during PEM-West B

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Abstract. Chemical data from ground stations in Asia and the North Pacific are compared with data from the DC-8 aircraft collected during the Pacific Exploratory Measurements in the Western Pacific Ocean (PEM-West B) mission. Ground station sampling took place on Hong Kong, Taiwan, Okinawa, and Cheju; and at three Pacific islands, Shemya, Midway, and Oahu. Aircraft samples were collected during 19 flights, most over the western North Pacific. Aluminum was used as an indicator of mineral aerosol, and even though the aircraft did sample Asian dust, strong dust storms were not encountered. The frequency distribution for non-sea-salt sulfate (nss SO_4^-) in the aircraft samples was bimodal: the higher concentration mode ($\sim 1 \mu\text{g m}^{-3}$) evidently originated from pollution or, less likely, from volcanic sources, while the lower mode, with a peak at $0.040 \mu\text{g m}^{-3}$, probably was a product of biogenic emissions. In addition, the concentrations of aerosol sulfate varied strongly in the vertical: arithmetic mean SO_4^- concentrations above 5000 m ($\bar{x} = 0.21 \pm 0.69 \mu\text{g m}^{-3}$) were substantially lower than those below ($\bar{x} = 1.07 \pm 0.87 \mu\text{g m}^{-3}$), suggesting the predominance of the surface sources. Several samples collected in the stratosphere exhibited elevated SO_4^- , however, probably as a result of emissions from Mount Pinatubo. During some boundary layer legs on the DC-8, the concentrations of CO and O_3 were comparable to those of clean marine air, but during other legs, several chemically distinct air masses were sampled, including polluted air in which O_3 was photochemically produced. In general, the continental outflow sampled from the aircraft was substantially diluted with respect to what was observed at the ground stations. Higher concentrations of aerosol species, O_3 , and CO at the Hong Kong ground station relative to the aircraft suggest that much of the continental outflow from southeastern Asia occurs in the lower troposphere, and extensive long-range transport out of this part of Asia is not expected. In comparison, materials emitted farther to the north apparently are more susceptible to long-range transport.

Introduction

Ground-based studies conducted for the Pacific Exploratory Measurements in the Western Pacific Ocean (PEM-West) mission complement the program's DC-8 aircraft missions because they provide a longer-term record of the composition of the atmosphere than can be obtained with the aircraft. Thus one set of objectives for the PEM ground station studies was to determine the geographical variability, to establish the seasonality, and for many stations the interannual variability patterns, in the concentrations of various aerosol constituents.

A second focus of the ground studies concerns the atmospheric transport of natural materials, including mineral dust, and various air pollutants, especially aerosol sulfate, from Asia

to the North Pacific. Previous studies have shown that large quantities of dust and pollutants are transported via this route to the mid-North Pacific, especially during the late winter and early spring [Duce *et al.*, 1980; Shaw, 1980; Tsunogai and Kondo, 1982; Uematsu *et al.*, 1983; Merrill *et al.*, 1989; Prospero *et al.*, 1989]. Ground station data from the first PEM-West experiments (called PEM-West A) indicate that anthropogenic sources dominate the concentrations of aerosol sulfate in Asia and are significant even over the remote Pacific [Arimoto *et al.*, 1996].

In this manuscript, we compare the ground station data with the data for a subset of samples collected from the DC-8 aircraft during PEM-West B; this was the second PEM aircraft mission, and its timing was chosen to facilitate studying the continental outflow from Asia. The first set of comparisons deals with aerosols and concerns mineral dust, sulfate, and various trace elements. The second set of comparisons deals with ozone and carbon monoxide; in the latter case, comparisons and contrasts were made using data from Hong Kong [Lam *et al.*, 1997] and Oki Island, Japan [Kajii *et al.*, this issue], and from the boundary layer legs of the aircraft flights. Additional studies of the transport of O_3 , CO, and aerosols at ground stations on Shemya, Guam, Midway, and Mauna Loa are reported by Jaffe *et al.* [this issue].

A separate study for PEM-West B at the Hong Kong ground station focused on the relationships between the optical prop-

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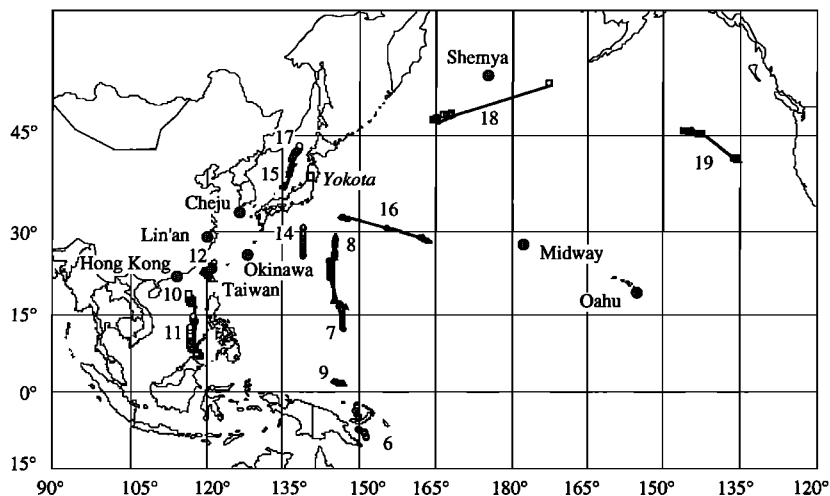


Figure 1. Locations of the PEM-West ground stations and the DC-8 flight tracks for boundary layer legs. Flight numbers are indicated.

erties and the physical and chemical characteristics of aerosols (J. M. Prospero et al., unpublished manuscript, 1997). As part of that study, a set of size-separated aerosol particle samples was collected using cascade impactors deployed at Cape D'Aguilar on the southeastern coast of Hong Kong Island. We determined the concentrations of a suite of trace elements in the cascade impactor samples to characterize their mass-particle size distributions; this information was used as a means for assessing the sources for the trace elements.

Experiment: Sampling and Analysis

Sampling and Analysis Sampling for aerosols at most of the PEM-West ground sites (Figure 1) began in the autumn of 1991 and continued until late spring to early summer of 1994. During the PEM-West B mission, which was in February and March 1994, a set of atmospheric aerosol samples was collected using the NASA DC-8 aircraft. During PEM-West B and the prior PEM-A aircraft mission in September and October 1991, aerosol collections at the ground stations were made daily, but at other times the samples were collected weekly. For the ground station studies, sampling at Kenting (Taiwan, 21.87°N, 120.87°E) began on September 7, 1991, at Kato (Hong Kong, 22.55°N, 114.30°E) on August 16, 1991, at Okinawa (Japan, 26.92°N, 128.25°E) on September 1, 1991, at Cheju (Korea, 33.52°N, 126.48°E) on September 10, 1991, at Lin'an (People's Republic of China, 30.27°N, 119.72°E) on February 24, 1994, and at the remote Pacific Islands of Oahu (Hawaii, 21.33°N, 157.70°W, September 7, 1991), Midway (28.22°N, 177.35°W, January 3, 1991), and Shemya (Aleutian Islands, 52.92°N, 174.06°E, September 16, 1991). Sampling was not continuous at all stations, and the locations of the Cheju and Hong Kong stations changed on April 22, 1992, and December 23, 1993, respectively.

Bulk aerosol particle samples were collected at the ground stations using single unwashed Whatman 41 filters (Whatman International Ltd., Maidstone, England). The high-volume pumps for the samplers operated at $\sim 45 \text{ m}^3 \text{ h}^{-1}$, and the volumes of air sampled were calculated from flow tubes with calibrated orifice plates. Errors in the volumes of air sampled are approximately 5–10%. To minimize contamination from local sources, sampling was electronically controlled with re-

spect to wind speed and direction. Minimum volumes for the trace element analyses at the University of Rhode Island (URI) were nominally 50 m^3 ; however, at the University of Miami (UM) all of the samples collected were analyzed by ion chromatography. In addition to the data generated during PEM-West, we make use of longer-term data sets for Midway, Oahu, and Shemya that have been obtained for the Sea/Air Exchange Program (SEAREX) and related projects [Uematsu et al., 1983; Savoie et al., 1989; Prospero et al., 1989].

During PEM-West B, modified Sierra-type, cascade impactors (CIs) were used to collect size-separated aerosol particles for a series of aerosol-radiation studies at the Hong Kong station. The CI samples also were used to investigate the mass-particle size distributions of trace elements. The sampler used was a high-volume slotted impactor with the following 50% cutoff diameters (expressed in μm , aerodynamic equivalent diameters): stage 1 = 18, stage 2 = 9.1, stage 3 = 4.6, stage 4 = 2.3, stage 5 = 1.2, stage 6 = 0.58, and backup filter < 0.58 . For the CI sampling, slotted Whatman 41 filters were used as the impaction surfaces, and Whatman 41's were also used for the backup filters. Particles in the CIs can be lost to the walls of the impactors, especially on the upper stages, which sample large particles. Particle bounce also can cause shifts in the size distributions [e.g., Walsh et al., 1978], but this is normally not a problem in marine environments, where the relative humidity is high. Mass median diameters were calculated by interpolating between the two stages whose concentrations straddled 50% of the cumulative mass.

The procedures for the trace element analyses of the bulk aerosol samples have been described elsewhere [Arimoto et al., 1996]. Briefly, the samples are analyzed by instrumental neutron activation analysis (INAA) using the 2 MW nuclear reactor (flux $8 \times 10^{12} \text{ neutrons cm}^{-2} \text{ s}^{-1}$) operated by the Rhode Island Nuclear Science Center. Two protocols are used routinely: (1) a "short" ($\sim 1 \text{ min}$) irradiation for Al, Na, and V, and (2) a "long" (7 hour) irradiation for Sb, Se, and Zn. After allowing for the decay of radioactive products, the samples are counted using Ge(Li) detectors with multichannel analyzers interfaced to a VAX workstation. The gamma ray spectra are analyzed using a combination of commercial and proprietary software. Uncertainties in the concentrations of most elements

at the PEM-West coastal sites are estimated to be ~10%, mainly due to uncertainties in the flow measurement system and blank corrections. Uncertainties for Sb and Zn are higher, 20–30%, owing to the lower sensitivity of INAA for these elements and to the fact that larger blank corrections are needed for these elements.

A subset of PEM-West B bulk aerosol samples was analyzed to assess the concentrations of several nuclides whose half-lives are intermediate between those determined by the long and short INAA. These procedures also were used to analyze the cascade impactor samples from Hong Kong and a subset of the bulk aerosol samples taken from the aircraft. The same aliquots (25% of the Whatman 41 filters for the ground station samples) or two punches (2% of some heavily loaded hivol samples and all of the Zeffluor filters (Gelman Sciences, Ann Arbor, Michigan) from the aircraft; see below) were used for the short (1-min), intermediate, and long irradiation procedures. For the intermediate and long INAA procedures, the samples were irradiated for 7 hours using an in-core device machined from aluminum. The radioactive samples were then retrieved and allowed to decay for ~5–7 days; at that point the radiation dosage was less than 100 mrad h⁻¹. The gamma ray spectra were then acquired for ~3 hours using Ge(Li) detectors, and those counts were used to determine the concentrations of the elements with intermediate half-lives. The samples were allowed to decay further, for a total of at least 21 days, and then they were recounted ~11 hours for the long-lived nuclides.

The intermediate INAA procedure provides data for several elements not determined by the short or long INAA. Arsenic (⁷⁶As half-life, $t_{1/2} = 1.10$ days) is potentially interesting because it has strong pollution and volcanic sources [Nriagu and Pacyna, 1988; Nriagu, 1989]. Two rare earth elements, lanthanum (¹⁴⁰La half life, $t_{1/2} = 1.68$ days) and samarium (¹⁵³Sm $t_{1/2} = 1.95$ days), also are determined using this procedure, and these elements are of interest because elevated La/Sm ratios in aerosols have been linked to emissions from oil-fired power plants and refineries [Olmez and Gordon, 1985; Hashimoto et al., 1994]. High La/Sm ratios are found in oil combustion by-products owing to contamination from zeolite catalysts used in the cracking of hydrocarbons. Some of the other useful nuclides from the intermediate INAA include ²⁴Na ($t_{1/2} = 0.63$ day), ⁸²Br ($t_{1/2} = 1.47$ days), and ⁵⁹Fe ($t_{1/2} = 45.1$ days). These include the same isotope of Na quantified by the short-INAA procedure and the isotope of Fe that also is measured by the long-INAA procedure. The intermediate-INAA procedure generates data for ¹²²Sb, a different isotope than is determined by the long-INAA procedure (¹²⁴Sb). The determination of these elements by two different procedures provides a means of internally validating the results.

Analyses of nitrate and sulfate for the ground station samples are performed at UM using one-quarter sections of the aerosol sample filters and suppressed ion chromatography [Savoie et al., 1989]. The filter aliquots are extracted with 20 mL of deionized water (resistivity ≥ 18 M Ω cm⁻¹) in three steps using volumes of 10, 5, and 5 mL. Sodium is determined by atomic absorption spectrometry. Uncertainties in the concentrations of NO₃⁻ and SO₄⁼ are of the order of 5%, while the uncertainty for Na is ~2%. Non-sea-salt sulfate (nss SO₄⁼), i.e., the concentration of sulfate above what is expected from atmospheric sea salt, was calculated as the total SO₄⁼ minus the Na⁺ concentration times 0.2516, which is the seawater refer-

ence ratio for sulfate to sodium according to *Millero and Sohn* [1992].

Onboard the DC-8 aircraft, a suite of aerosol samples was collected using tandem shrouded inlets equipped with curved leading-edge nozzles. The aerosol inlets were fabricated from stainless steel, while the nozzles and shrouds were made of alodined aluminum (alodining hardens the surface of the aluminum). Sample flow rates and integrated volumes were measured using linear mass-flow meters. Isokinetic sampling was maintained by varying the sample flow rate. A pitot tube mounted near the nozzle entrance was used to monitor the air velocity through the shroud assembly. A description of the aerosol probes and associated analytical procedures are given elsewhere [Dibb et al., 1996].

Only a subset of 20 DC-8 aerosol samples was analyzed for trace elements by INAA, but the concentrations of sulfate and methanesulfonate were determined in all samples collected from the aircraft platform. Aerosol sodium concentrations were usually only measurable in the boundary layer, as the levels were indistinguishable from the filter blank values in the free troposphere. This situation was exacerbated by the small concentration of sea-salt aerosols above the marine boundary layer and the short sampling times used [Dibb et al., this issue].

Although we have not tested the passing efficiency of the aerosol sampling probes used on the DC-8, we believe that large particles are sampled with good efficiency. For example, sodium concentrations at 0.3 km were typically a few micrograms per standard cubic meter, similar to those observed at the ground stations along the Asian coast. In addition, calcium concentrations were about an order of magnitude larger than those attributable to sea salt, indicating that continental soil materials were effectively sampled. In general, sea salt accounts for only 10–15% of the total aerosol sulfate, and this percentage decreases with altitude. Parallel aerosol samples collected with our system during PEM-West B showed that the concentrations of soluble ions agreed to within 10%. This provides a good measure of our precision.

The CO and O₃ data from the aircraft were obtained by G. W. Sachse and G. L. Gregory and their co-workers, respectively, and those data were merged to the 180 s time base used for the peroxide experiments on the DC-8 [Hoell et al., this issue]. The interpretation of the CO and O₃ data focuses on the boundary layer legs of the aircraft flights, which are operationally defined as the times when the aircraft flew at an altitude of 1 km or less. The locations of the DC-8 when sampling in the boundary layer are shown in Figure 1. The discussion of the ground station CO and O₃ does not cover the entire PEM-West B sampling period because the dates on which the stations became operational did not exactly coincide with the aircraft flights. The equipment and the methods for studying these trace gases at the Oki Island ground station have been described by *Jaffe et al.* [1996] and by *Lam et al.* [1997] for the Hong Kong Station.

Results and Discussion

Aerosols

Mineral dust and trace elements. Atmospheric aluminum frequently is used as an indicator of mineral aerosol, but some recent studies indicate that atmospheric Al concentrations can be elevated by pollution emissions, at least in some parts of Asia [Arimoto et al., 1997]. The Al concentration in the Earth's upper crust is ~8% [Wedepohl, 1995; Taylor and McLennan,

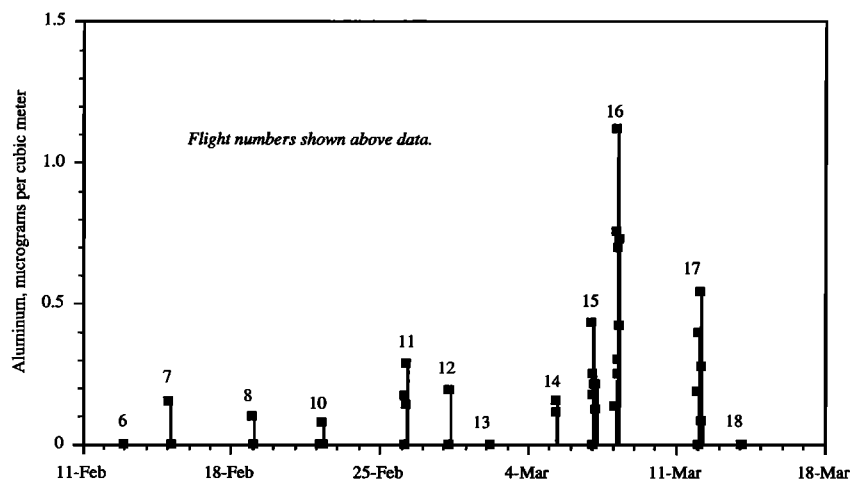


Figure 2. Time series plot of aluminum concentrations for the aerosol samples collected aboard the DC-8 aircraft.

1995], and here we use Al as a presumptive indicator of mineral aerosol while being careful to point out that anthropogenic sources for this element can be significant, at least in polluted environments. At various sites in Asia, including Beijing, the Sc/Al ratio can be higher than is typical of average crustal rock, suggesting that the cycles of other elements besides Al that normally are associated with mineral aerosol also have been perturbed.

Studies of the mineral dust particles originating from dry-land areas in central Asia are useful for investigating large-scale convection over Asia and for studying the long-range transport of continental materials to the North Pacific. Dust storms in Asia are most frequent in the late winter to early spring, but the seasonality varies with location. Data compiled by *Watts* [1969] show that at Beijing the peak in the number of dust storms occurs in March, while at Xi'an, in the loess plateau, the dust storms are most frequent in May.

A time-series plot of the atmospheric Al concentrations in the aircraft samples (Figure 2) demonstrates that the highest concentrations of this element occurred on Flights 15 (March 7, 1994), 16 (March 8, 1994), and 17 (March 12, 1994). Each was a local flight originating from and returning to Yokota, Japan. The single highest Al concentration observed ($1.2 \mu\text{g m}^{-3}$) occurred in sample 16-5, which was collected over a longitude of 160° – 162°E and a latitude of 28°N . As shown in Figure 2, the Al concentrations ($\geq 0.5 \mu\text{g m}^{-3}$) in three other samples from Flight 16 (Figures 2 and 3) also were higher than in the samples from the other flights. The equivalent dust concentrations for the three samples from Flight 16 would be greater than $5 \mu\text{g m}^{-3}$ but less than $20 \mu\text{g m}^{-3}$. Other elements, such as Sc, behaved in much the same manner as Al in the DC-8 samples: furthermore, the Sc/Al ratios for many of those samples were close to crustal values.

Okinawa and Cheju are the PEM ground stations closest to Yokota, and while the number of aircraft samples that can be compared with the data from the ground stations is small, some general trends are worth mentioning. For the ground station samples that were collected close in time to Flights 15, 16, and 17, the samples from Cheju had higher aluminum concentrations than those from Okinawa, a trend that generally held true from the beginning of 1994 until the end of the PEM-West B sampling. The Al concentrations at Cheju from

February 12 to March 15, 1994 (number of samples, $n = 25$; arithmetic mean, $\bar{x} = 1.55 \mu\text{g m}^{-3} \pm$ standard deviation, s.d. = $1.06 \mu\text{g m}^{-3}$; median = $1.11 \mu\text{g m}^{-3}$) were consistently higher than those at Okinawa ($n = 18$, $\bar{x} = 0.60 \mu\text{g m}^{-3} \pm 0.49 \mu\text{g m}^{-3}$, median = 0.35). The Al concentrations at Lin'an were higher still: from February 21, 1994, when sampling started until March 15, 1994, the Al concentrations ($n = 17$) averaged $3.36 \pm 2.99 \mu\text{g m}^{-3}$ with a median of $3.14 \mu\text{g m}^{-3}$.

The atmospheric Al concentrations for the DC-8 samples, even for Flights 15–17, generally were less than $1 \mu\text{g m}^{-3}$ (the Al concentrations in 12 of 40 samples analyzed were below detection ($<0.02 \mu\text{g m}^{-3}$), and the median concentration for all 40 samples including those below detection was $\sim 0.15 \mu\text{g m}^{-3}$). Hence the dust concentrations observed during the aircraft missions out of Yokota were much lower than those at Lin'an or Cheju and roughly a factor of 2 lower than those at Okinawa. Identical samplers were used at all of the ground stations, and the differences in Al concentrations among those sites can be discussed in the context of transport processes.

Although noncrustal sources may exert some influence on atmospheric Al, the higher concentrations at Lin'an and Cheju relative to Okinawa presumably reflect the distances of the sites from the source regions for Asia dust. Calculations by *Tsunogai et al.* [1985] indicate that the dust concentrations over

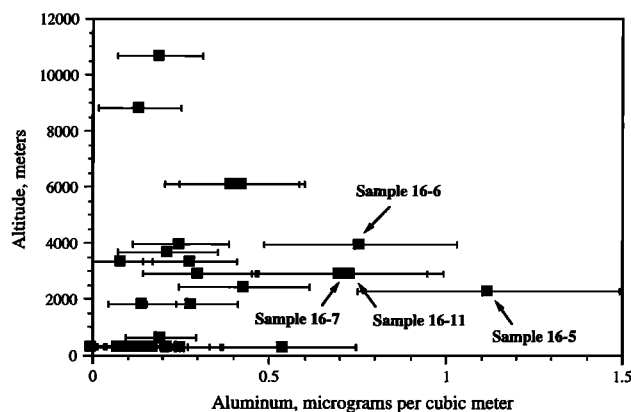


Figure 3. Vertical distribution of aluminum concentrations for the aerosol samples collected aboard the DC-8 aircraft.

the western North Pacific decrease by 50% for every 500–600 km of distance downwind. The distances between Lin'an and Cheju and between Cheju and Okinawa are of the order of 700–750 km, respectively, and the Al concentrations decreased by 65% and 68% between the two pairs of sites. Thus the decreases in dust concentrations are generally consistent with those one would predict from the Tsunogai et al. model. Furthermore, the differences between the model predictions and the observations probably are influenced by the locations of the stations in more subtle ways, i.e., Lin'an in particular, does not lie on the main transport pathway for the dust but is displaced well to the south [Watts, 1969].

Another interesting feature of the data concerns the distribution of Al concentrations in the vertical. While the maximum Al concentrations in the suite of aircraft samples analyzed were too low to be representative of strong dust storms, the four samples with the highest concentrations were collected at altitudes between 2.3 and 4.0 km (Figure 3). Even though the number of samples analyzed was small and their representativeness may be questioned, these observations are consistent with previous reports that the transport of Asian dust can occur well above the boundary layer. For example, Iwasaka et al. [1983] found that Chinese desert dust can pass over Japan at altitudes of several kilometers while having little effect on conditions at the surface. Additional information on the height of dust transport has been obtained from the analysis of large-scale atmospheric motions associated with selected dust storms [Liu et al., 1981, 1982, 1985; Zhang, 1984; Chen and Chen, 1987]. One characteristic common to some dust storms is that the bulk of the transport occurs in the middle troposphere, i.e., at altitudes up to 10 km. In other dust storms, such as a severe storm in 1983, surface winds (<3 km altitude) drive the transport process. These different characteristics of the dust storms are important because the high-altitude events are more likely to disperse the mineral dust over long distances.

While most of the aluminum in the samples from the DC-8 flights out of Yokota was presumably from mineral dust, fly ash particles collected during the PEM-West B mission also contained significant quantities of Al and other elements, such as Si, that commonly are associated with mineral matter (R. F. Pueschel et al., unpublished manuscript, 1997). The cascade impactor data from the PEM ground studies at Hong Kong provide additional evidence that anthropogenic sources can increase aerosol Al concentrations. The mass median diameters (MMDs) for Al at Hong Kong were larger than one would expect based on studies of dust size distributions closer to the source regions. In some of the cascade impactor samples from

Table 1. Mass Median Diameters for Aluminum in Cascade Impactor Samples From Cape d'Aguilar, Hong Kong

Date in 1994	Mass-Median Diameter, μm AED
February 14	8.72
February 17	8.14
February 25	4.73
March 1	4.22
March 5	2.07
March 9	6.60

AED, aerodynamic equivalent diameter.

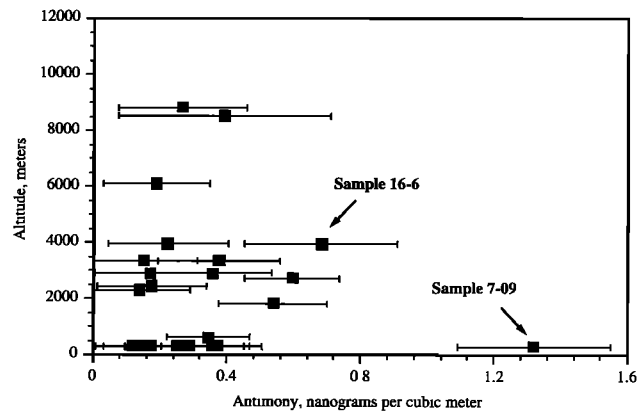


Figure 4. Vertical distribution of antimony concentrations for the aerosol samples collected aboard the DC-8 aircraft.

Hong Kong, the MMDs for Al were large, approaching $10 \mu\text{m}$ aerodynamic equivalent diameter (Table 1). This was despite the fact that Asian dust storms rarely if ever occur that far south [Watts, 1969] and no dust storms were reported as part of the routine meteorological observations at Hong Kong during PEM-West B.

For comparison, studies by Zhang et al. [1994] showed that the MMDs for dust storms in Shapoutou and Xi'an, which are in the Chinese loess plateau, were 5–10 μm , or of the same order as those in Hong Kong. As Hong Kong is much farther from the dust source regions than Shapoutou or Xi'an, the average Al concentrations there are roughly a factor of 10 lower. Therefore it is more likely that the large Al-containing particles at Hong Kong were fly ash or locally generated mineral matter as opposed to dust transported long distances. This is further evidence that the Al in the atmosphere over Asia originates from both natural and anthropogenic sources whose relative strengths vary with location.

Anthropogenic emissions affected a variety of other elements, and in contrast to mineral dust some of the highest concentrations of the pollution-derived elements, such as Sb, occurred in aircraft samples taken near the Earth's surface (Figure 4). However, the data set was too small to be generally representative of vertical distributions, and in some cases high concentrations of Sb and other pollution-derived elements occurred at altitudes of several kilometers. Furthermore, the aircraft samples with high concentrations of mineral dust did not necessarily contain high concentrations of the pollution-derived elements. This heterogeneity in aerosol composition observed from the aircraft is consistent with the longer-term studies made at the PEM-West ground stations, which show some similarities, but also important differences, in the seasonal cycles of various aerosol species.

In many of the aircraft samples, the arsenic concentrations were below detection (0.05 ng m^{-3}), but the arithmetic mean As concentration for 11 samples was relatively low, 0.20 ng m^{-3} . Few data from Asia are available for comparison, but the As concentrations in autumn at five large Chinese cities (Beijing, Chengdu, Baotou, Lanzhou, and Urumuqi) were more than a factor of 50 higher than those from the DC-8, with monthly average concentrations ranging from 13 to 85 ng m^{-3} [Hashimoto et al., 1994]. Another comparison shows that the As concentrations during an oceanic cruise between Tokyo and the Philippines [Tanaka et al., 1992] were almost a factor of 5

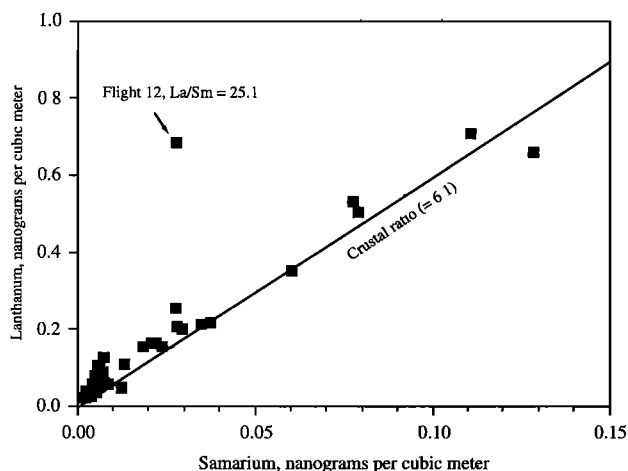


Figure 5. Lanthanum and samarium concentrations in the aerosol samples collected using the DC-8 aircraft.

higher than those in the DC-8 samples. Other pollution-derived elements, such as Mn, Zn, V, and Sb, also exhibited much lower concentrations in the aircraft samples relative to those in the Chinese cities or those at the PEM-West ground stations. Each of these elements tends to be concentrated in submicrometer particles, and the collection characteristics of the aerosol sampler on the DC-8 should not be an issue. Thus, in terms of trace elements, the air sampled from the DC-8 was not nearly so polluted as in the more heavily industrialized regions of Asia.

In many of the aircraft samples, the concentration ratios of lanthanum to samarium approached the crustal value of ~ 6 to 7 [Wedepohl, 1995; Taylor and McLennan, 1995], but other samples clearly had elevated La/Sm ratios. One sample in particular, collected at 0739 UTC on a boundary layer leg near Taiwan (Flight 12), clearly stood out from the others (Figure 5). In that sample, neither La nor Sm exhibited an especially high concentration, but the ratio of La to Sm was much higher than for any other sample, i.e., 25 ± 0.82 (the uncertainty is propagated from the errors for the INAA La and Sm data).

Emissions from oil combustion [Olmez and Gordon, 1985] are the most likely explanation for the high La/Sm ratio observed on Flight 12, but vanadium, which is another tracer for oil combustion, did not exhibit a particularly high concentration in that sample. More interesting was our observation that a remarkably large suite of substances, including carbon monoxide, ozone, sulfur dioxide, various trace organics, and aerosol numbers, also exhibited extraordinarily high mixing ratios or concentrations at precisely the same time as the high La/Sm ratio was observed on the DC-8. As discussed below, the air samples collected during that part of Flight 12 contained the highest pollutant concentrations observed during the PEM-West B campaign.

Sulfate. The aerosol sulfate concentrations sampled from the aircraft during PEM-West B evidently composed two log-normal populations (Figure 6). It is tempting to speculate that these two modes are related to the two putative sources for aerosol SO_4^- , i.e., marine biogenic emissions through the oxidation of dimethyl sulfide versus combustion or volcanic sources through the oxidation of sulfur dioxide, and there is some evidence that this is the case. Given the quantity of SO_2 produced from the combustion of fossil fuels [Akimoto et al.,

1994], and a study indicating that the nonbiogenic sources at the PEM-West sites in eastern Asia are dominant [Arimoto et al., 1996], one would expect that the subset of samples with the higher concentrations was strongly influenced by anthropogenic sources. This hypothesis was tested using data for methanesulfonate (MSA) as an indicator of biogenic sulfur as discussed by Saltzman et al. [1985], Bates et al. [1987], Savoie and Prospero [1989], and Savoie et al. [1994].

The basis for this approach is a series of observations showing that the mass ratio of biogenic SO_4^- to MSA ranges from about 18 to 20 for latitudes from 30°S to 30°N [Savoie et al. 1994]. Much of that work was done at American Samoa, where anthropogenic influences are minimal, but the same ratio has been found to hold over the remote North Atlantic. At latitudes greater than $\sim 30^\circ$, the nss SO_4^- /MSA ratio often is lower, most likely due to differences in the branching ratios of the oxidation pathways caused by the lower temperatures, or differences in insolation, or perhaps other conditions at the higher latitudes [Berresheim, 1987; Pszenny et al., 1989; Koga et al., 1991; Bates et al., 1992].

Differences between the SO_4^- /MSA ratios for the two subsets of the aerosol samples from the DC-8 are consistent with the hypothesis that the population with the lower SO_4^- concentrations was associated with biogenic sources, while the higher concentration mode was nonbiogenic in origin. For many of the samples, the MSA concentrations were below detection limits, but the SO_4^- /MSA ratios that could be calculated ranged from 9.3 to 500. All but four of the 21 SO_4^- /MSA ratios were a factor of 2 or more above the canonical biogenic ratio (i.e., >40), and this is consistent with the hypothesis that anthropogenic or other nonbiogenic sources dominate. This nonbiogenic SO_4^- most likely originates from anthropogenic emissions, but contributions from volcanoes also are possible, and they cannot be discounted from the data available. The four samples with the SO_4^- /MSA ratios closest to the biogenic value were all in the lower SO_4^- mode.

Despite the apparent impact of anthropogenic emissions, the highest SO_4^- concentrations determined for the aircraft samples were less than or equal to the average concentrations observed at the more polluted ground stations. The highest SO_4^- concentrations ($3\text{--}4 \mu\text{g m}^{-3}$) in the aircraft samples oc-

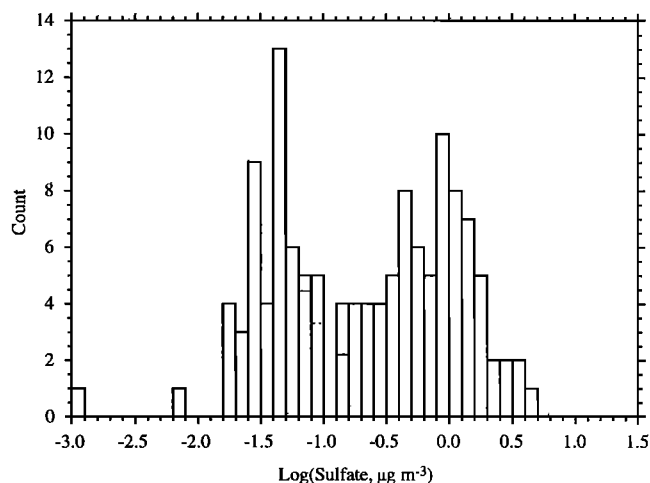


Figure 6. Frequency distribution for aerosol sulfate concentrations in the aerosol samples collected using the DC-8 aircraft.

curred on Flights 10, 11, 12, and 14, which included the transit flight from Guam to Hong Kong, two local missions out of Hong Kong, and the transit flight from Hong Kong to Yokota. From Figure 6, one can see that the frequency distribution for the lower SO_4^- mode for the aircraft samples exhibits a peak at ~ 0.04 to $0.05 \mu\text{g m}^{-3}$, while the peak in the higher concentration mode is about 0.8 – $1 \mu\text{g m}^{-3}$. The corresponding arithmetic means for the two modes, using a cutoff of $0.15 \mu\text{g m}^{-3}$ based on the saddle point in Figure 6, are 0.05 ± 0.03 and $1.0 \pm 0.82 \mu\text{g m}^{-3}$, respectively. Much higher in comparison, the arithmetic mean nss SO_4^- concentrations at the PEM ground stations for February–March ranged from $3.2 \mu\text{g m}^{-3}$ at Okinawa to $15.8 \mu\text{g m}^{-3}$ at Lin'an (Table 2).

Climatological mean SO_4^- concentrations over the open ocean in February and March range from $0.37 \mu\text{g m}^{-3}$ at Midway to 0.72 at Oahu (Table 2). Thus the typical nss SO_4^- concentrations at the open-ocean ground sites were higher than those in the aircraft samples that comprised the mode with the lower SO_4^- concentrations. Several factors help explain this observation. First, as mentioned above, the aircraft data were not corrected for sea-salt SO_4^- , but this effect should be small, of the order of 10–15%. Second, nonbiogenic sources for aerosol sulfate have been demonstrated at the PEM open-ocean sites, accounting for an annual average of 30% and 45% of the nss SO_4^- at Midway and Oahu, respectively [Savoie *et al.*, 1989; Arimoto *et al.*, 1996]. During February and March, the climatological MSA concentrations at Midway and Oahu are of the order of 10–20 ng m^{-3} ; these would be equivalent to biogenic sulfate concentrations of 0.2 – $0.4 \mu\text{g m}^{-3}$, which are still fourfold to eightfold higher than the arithmetic mean of the presumed biogenic fraction sampled by the aircraft.

A third factor that likely contributes to the differences in the ground station versus aircraft data is that the aerosol sulfate concentrations observed with the aircraft tended to decrease with height. The maximum SO_4^- concentrations above 5000 m were $\sim 1 \mu\text{g m}^{-3}$ ($\bar{x} = 0.21 \pm 0.69$, $n = 71$), which is the same order as the average concentration below 5000 m ($\bar{x} = 1.07 \pm 0.87$, $n = 57$; see Figure 7). Not shown in that figure nor included in the calculations are the five samples for which SO_4^- was below detection ($<0.02 \mu\text{g m}^{-3}$): all of those samples were collected above 5000 m. The tendency for SO_4^- concentration to decrease with height is a clear reflection of the predominance of the surface sources for this substance. Interestingly, four samples collected in the stratosphere exhibited elevated SO_4^- concentrations, probably as a result of volcanic emissions from Mount Pinatubo. However, on balance, the net

Table 2. Non-Sea-Salt Sulfate Concentrations in the Atmosphere Over Eastern Asia and the North Pacific

Site	February	March
Lin'an*	14.0	15.8 ± 4.1
Hong Kong†	8.9 ± 2.8	8.7 ± 2.8
Cheju†	7.2 ± 3.7	4.2 ± 3.4
Okinawa†	4.8 ± 1.3	3.2 ± 1.4
Midway‡	0.37 ± 0.17	0.70 ± 0.41
Oahu‡	0.72 ± 0.72	0.62 ± 0.52
Shemya§	0.42 ± 0.94	0.57 ± 1.60

Values are in units of $\mu\text{g m}^{-3}$.

*Data collected from February 21, 1994, to March 31, 1994.

†Data collected from February 1, 1992, to March 31, 1994.

‡Data collected from February 1, 1981, to March 31, 1994.

§Data collected from February 1, 1982, to March 31, 1994.

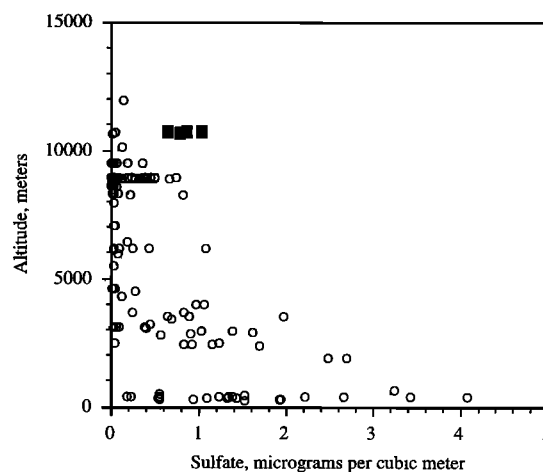


Figure 7. Vertical distribution of sulfate concentrations for the aerosol samples collected aboard the DC-8 aircraft. The four shaded symbols near the top of the figure denote samples collected in the stratosphere.

effect of the samples from the upper troposphere, with their relatively low SO_4^- concentrations, would be to shift the aircraft SO_4^- data toward lower values relative to the ground stations.

Carbon Monoxide and Ozone

Although a variety of physical and chemical characteristics of the atmosphere were studied during PEM-West B at the ground stations, we only consider CO and O_3 in our subsequent comparisons of the ground station and aircraft data. This is because the types of substances and physical parameters investigated varied somewhat from site to site, largely as a result of the equipment available and the interests of the personnel and their sponsors. Furthermore, the data for CO and O_3 are particularly important in the context of the PEM mission objective of investigating the atmospheric chemistry of ozone and its precursors. Finally, we limit our discussion to the boundary layer legs for the aircraft flights because the data for the higher altitude legs are dealt with in other articles of this special issue.

The CO and O_3 concentrations in the entire suite of DC-8 boundary layer samples were highly correlated (number of samples, $n = 215$; correlation coefficient, $r = 0.75$; probability for chance occurrence, $p < 0.01$, Figure 8), and several features of the individual flights are revealing. For example, on Flight 12 (February 27, 1994), which originated out of Hong Kong, a boundary layer leg began at ~ 0724 UTC and continued until 0752 UTC. During that leg, the aircraft was off the southwestern side of Taiwan, maintained an altitude of ~ 600 m, and had a heading of $\sim 130^\circ$. The wind during that sampling leg was from the north-northwest with a velocity of roughly 5 – 10 m s^{-1} . The O_3 mixing ratio at the start of the leg was 40.2 ppbv; it reached a peak of 116 ppbv at 0737, and then decreased steadily to 42.6 ppbv at 0745. The mixing ratios for CO paralleled those of O_3 , rising from 241 ppbv at the start of the leg to 525 ppbv at 0737 and then returning to 223 ppbv at 0745. The CO and O_3 mixing ratios during the boundary layer leg of Flight 12 were highly correlated ($n = 13$, $r = 0.98$), with a slope (CO to O_3) of 4.0 ± 0.23 and an intercept for CO of 69 ± 14 .

The peak CO and O_3 mixing ratios observed during this leg were the highest of the more than 200 observations in the

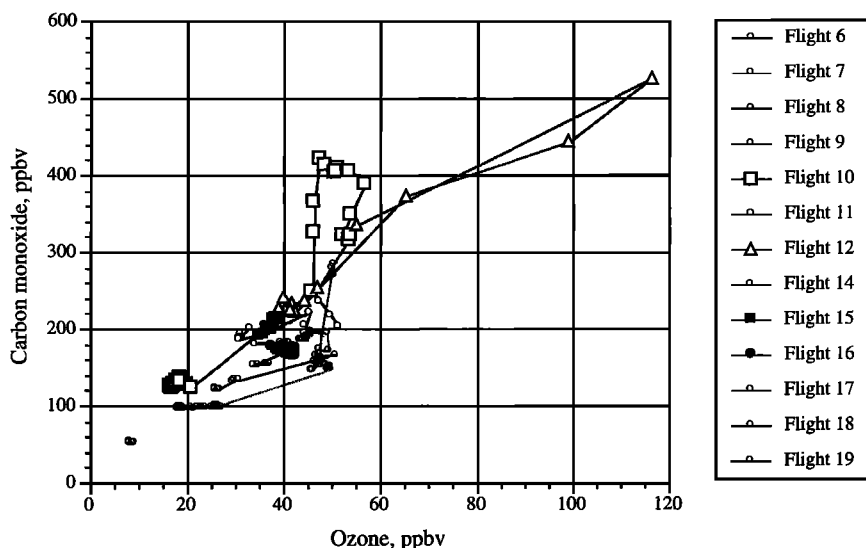


Figure 8. Carbon monoxide and ozone mixing ratios for the DC-8 boundary layer legs. The data were merged to the peroxide time base [Hoell *et al.*, this issue].

boundary layer database for PEM-West B. More interesting is the fact that the peaks in CO and O₃ were matched by peaks in the mixing ratios or concentrations of an extraordinarily large number of substances, including sulfur dioxide; methane; carbon dioxide; total odd nitrogen (NO_y, as measured both by J. Bradshaw *et al.* (unpublished data, 1995) and by Kondo *et al.* [this issue]); hexane; methylcyclopentane; 2-methylpentane; 3-methylpentane; cyclohexane; benzene; n-heptane; 2, 4-dimethylpentane; toluene; 2, 2, 4-trimethylpentane; ethylbenzene; p-, m-, and o-xylene; nonane; propylbenzene; nitrate; ammonium; formic acid; and aerosol particles. This is also the time when the aerosol sample with the high La/Sm ratio was collected. The coherence in the signal for this suite of substances demonstrates that during that boundary layer leg of Flight 12, the aircraft briefly encountered an air mass containing high concentrations of pollutants from a wide variety of sources.

Another important feature of the data for this portion of Flight 12 is that the high concentrations of NO, NO_y, and O₃

are consistent with the photochemical production of O₃. Previously, Jaffe *et al.* [1996] concluded that the diurnal photochemical production of O₃ in the region around Oki Island was on average 3.5 ppbv. Their estimate was based on data collected during the PEM-West A experiments in September and October of 1991. The boundary layer data for Flight 12 collected near Taiwan suggest a much higher O₃ production rate because the concentration of O₃ increased by almost 70 ppbv (from 47 to 116 ppbv) in the plume, which was only 1 or 2 days downwind of Taiwan and several days downwind of the mainland. Model calculations by D. Davis (Georgia Institute of Technology, personal communication, 1995) shown in Figure 9 indicate that when the DC-8 intercepted the boundary layer plume containing high NO mixing ratios, the instantaneous rate of ozone production was of the order of 150 ppbv/d.

The constancy in proportions of CO to O₃ during the boundary layer leg of Flight 12 is strongly suggestive of conservative mixing. In this case, the concentrations of both CO and O₃ changed by almost a factor of 3, while the ratio of CO to O₃

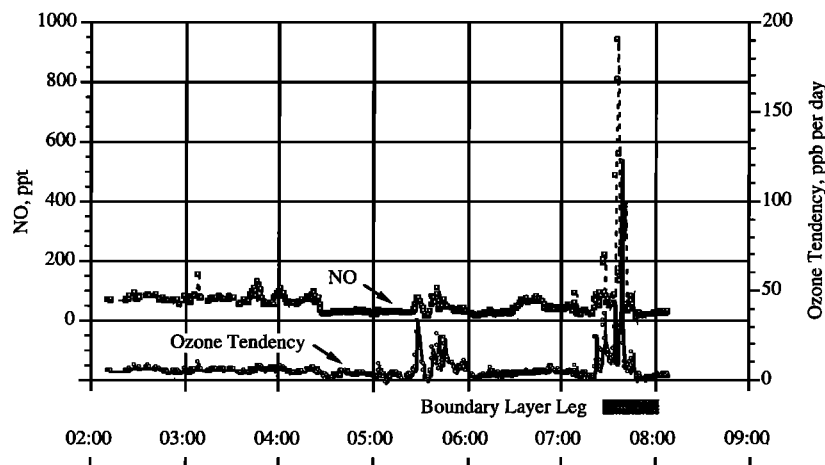


Figure 9. Observed NO mixing ratios (J. Bradshaw *et al.*, unpublished data, 1995) and modeled ozone tendency (D. Davis, Georgia Institute of Technology, personal communication, 1996) during Flight 12. The time of the boundary layer sample discussed in the text is indicated.

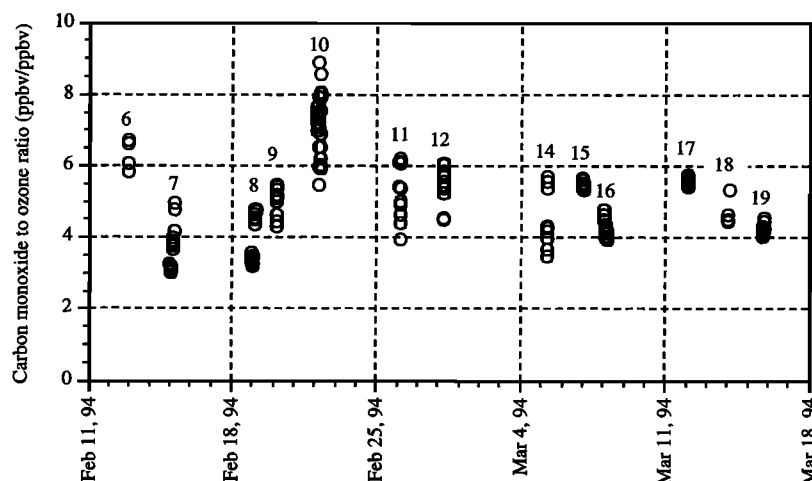


Figure 10. Ratios of carbon monoxide to ozone for the samples collected during the DC-8 boundary layer legs.

remained relatively constant ($\bar{x} = 5.42 \pm 0.48$). Further inspection of the data showed that the difference between the largest and smallest CO/O₃ ratio was only 36%, ranging from 4.6 to 6.1 (ppbv/ppbv). If one extrapolates the CO and O₃ concentrations based on a regression model, the lower mixing end-member would have CO and O₃ concentrations similar to those in clean marine air at the ground stations (see below). It is noteworthy, however, that the two lowest CO/O₃ ratios occurred when the CO concentrations were the highest, suggesting either multicomponent mixing or additional chemical processing as discussed below.

The CO/O₃ ratios for the entire suite of boundary layer aircraft samples ranged from 3 to 9 (ppbv/ppbv), and the highest CO/O₃ ratios occurred during Flight 10 (Figure 10). In a scatterplot of CO versus O₃ (Figure 8), many of the points representing Flight 10 can be seen to fall above the major trend line. During that flight, when the plane was in transit from Guam to Hong Kong, samples were collected during two boundary layer legs, one from 0505 to 0547 and the other from 0717 to 0752 (all times in UTC on February 21, 1994). The first boundary layer leg during Flight 10 was over the southwestern side of the Sulu Sea with the plane heading $\sim 320^\circ$ at an altitude ≤ 350 m. During that leg, the concentrations of both CO and O₃ were low and relatively invariant, 130 ± 3.9 and 18.2 ± 1.19 ppbv, respectively, over a distance of more than 300 km. Concentrations of this order are typical of those in clean marine air observed at the PEM-West ground stations [Lam et al., 1997; Kajii et al., this issue]. Furthermore, the chemical data are consistent with the air mass trajectories (not shown), indicating that during the preceding 5 days, the air mass that was sampled from the DC-8 had briefly passed over the Philippines but spent most of its time over the Philippine Sea.

The second boundary layer leg during Flight 10 was over the South China Sea, with the aircraft generally heading northwest at an altitude similar to that during the earlier boundary layer leg on that flight. For the second boundary layer leg as a whole, CO and O₃ were essentially uncorrelated ($r = 0.15$); nevertheless, on closer inspection, the data show substantial structure (Figure 8). For the first 8 min of the leg, the CO concentrations increased by almost 70% from 250 to 420 ppbv, while the O₃ concentrations increased only a few percent from 45.9 to 47.6 ppbv. In the next 13 min the CO concentration steadily decreased from 422 to 406 ppbv, while O₃ showed the opposite

trend, increasing from 47.6 to 53.9 ppbv. Finally, over the last 10 min of the leg, both CO and O₃ decreased slightly, from 390 to 323 ppbv and 56.9 to 54 ppbv, respectively. These changing trends were quite different from what was observed during either the first boundary layer leg of Flight 10, when the concentrations of CO and O₃ changed little over 40 min, or during the boundary layer leg of Flight 12, when a plume of pollutants was briefly encountered near Taiwan. Rather, the data for the second boundary layer leg of Flight 10 are most compatible with the existence of several chemically distinct air masses.

The ground station data provide further insight into the nature of the compositional differences among the air masses. For example, the ground station data from Cape d'Aguilar [Lam et al., 1997] show that during the spring, the concentrations of CO and O₃ in the near-surface troposphere of the Hong Kong region are mainly influenced by two types of air masses. Marine air in the vicinity of Hong Kong exhibits low concentrations of both CO and O₃, of the order of 130 and 15 ppbv, respectively [Lam et al., 1997]. Compared with this clean marine air, those air masses containing fresh continental emissions have much higher concentrations of CO (>500 ppbv) due to combustion by-products and low O₃ (<15 ppbv) owing to the titration of ozone with nitrogen oxides, reactions with hydrocarbons, and surface deposition. As shown above for Flight 12, photochemical reactions in the polluted air also can lead to the production of ozone. Therefore, when the aircraft encountered continental outflow, the CO mixing ratio invariably rose, but O₃ could either decrease if the emissions were fresh or, more likely, increase as a result of photochemically produced O₃.

At times the CO/O₃ ratio at Hong Kong increases sharply due to the influx of polluted air, which usually arrives from the northwest or north [Lam et al., 1997]. A time-series plot of the CO/O₃ ratio at Cape d'Aguilar (Figure 11) shows that CO/O₃ ratios typically are 5–30, but these background conditions are punctuated by pollution episodes lasting a few hours to a few days, during which the CO/O₃ ratios can rise abruptly to several hundred. If we arbitrarily consider the 33 hourly averages during the PEM-West B period for which CO/O₃ > 50 as strong pollution events ($\bar{x} = 119 \pm 124$), we find the arithmetic mean and standard deviation for CO at Cape d'Aguilar to be 625 ± 146 ppbv and the arithmetic mean O₃ to be 7.82 ± 3.34 ppbv. These values, which represent the upper $\sim 6\%$ most

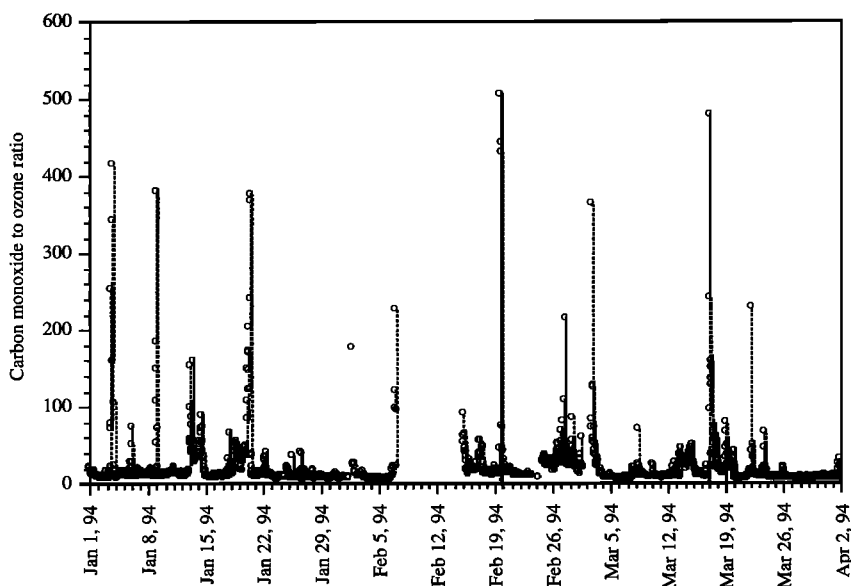


Figure 11. Ratios of carbon monoxide to ozone at the Cape d'Aguiar ground station. Data from *Lam et al.* [1997].

polluted samples, are in sharp contrast to the clean marine conditions at Cape d'Aguiar discussed above.

Clean air identified by using the differential absorption lidar (DIAL) on the DC-8 (E. V. Browell et al., unpublished manuscript, 1997) had CO/O_3 ratios of ~ 3 , which are even lower than those measured under clean conditions at Cape d'Aguiar. Taken together, all the PEM-West B results based on the CO and O_3 data from the DC-8 suggest that strong pollution episodes are superimposed on a low level of air pollution that pervades the Hong Kong region. Changing the arbitrary criteria for pollution events would affect the mean values of the various categories somewhat, but the general trend of high CO, low O_3 , and high CO/O_3 ratios in polluted continental outflow would remain.

The Oki Island ground station frequently samples clean marine air [*Jaffe et al.*, this issue], and the CO and O_3 mixing ratios observed at Oki are much lower than those at Hong Kong. Comparisons of the hourly averages of CO, O_3 , and the ratio of CO to O_3 at Oki and Hong Kong Island showed that the differences in these three variables were all highly significant, with $p < 0.001$ in each case (Table 3). The average concentrations of CO at Oki Island were lower than those at Hong Kong, but the opposite held true for O_3 : it naturally follows that the CO to O_3 ratio was lower at Oki. These comparisons covered the period from February 26 to March 16, which included most of the PEM-West B sampling period, and not

surprisingly, they show that there were pronounced differences in the levels of CO and O_3 at the ground sites during the aircraft mission. It is noteworthy that the transport of pollutants to Oki Island is not from the north-northwest, as is the case for Hong Kong [*Lam et al.*, 1997], but from the west-southwest and south [*Jaffe et al.*, 1996]. Thus the major source regions for the pollutant are likely to be different: Hong Kong is primarily affected by emissions from China, while Oki Island is downwind of pollution sources in Japan, Korea, and parts of the former Soviet Union.

Stratospherically influenced air masses, which have high concentrations of ozone (~ 200 ppbv) and low carbon monoxide (~ 70 ppbv and thus CO to O_3 ratios of ~ 0.3 (E. Y. Browell et al., unpublished manuscript, 1997), are another type of mixing end-member that can affect the relative concentrations of these two gases in the troposphere. At the ground stations a stronger influence of stratospheric air at Oki Island probably contributed at least in part to the lower CO/O_3 ratios there compared with Hong Kong. On the aircraft, an increasing level of stratospherically influenced air would cause O_3 to increase and CO to decrease in a way consistent with what was observed during the second part of the second boundary layer leg on Flight 10. The third trend observed during that portion of Flight 10, i.e., decreases in both CO and O_3 , suggests a strengthening marine influence. In any case, the observed trends clearly attest to systematic differences in the chemical

Table 3. Comparison of the Mixing Ratios Carbon Monoxide and Ozone and the Carbon Monoxide to Ozone Ratios at Hong Kong and Oki Island

	Hong Kong		Oki Island		t-Value	Degrees of Freedom	Probability*
	<i>n</i>	$\bar{x} \pm s$	<i>n</i>	$\bar{x} \pm s$			
O_3	410	31.2 ± 14.4	441	39.8 ± 4.62	11.9	849	<0.0001
CO	343	441 ± 148	431	218 ± 44.9	29.6	772	<0.0001
CO/O_3	336	22.4 ± 27.9	431	5.51 ± 1.08	12.5	765	<0.0001

Here *n*, number of samples; \bar{x} , arithmetic mean; and *s*, standard deviation. Data given in ppbv.

*Probability for chance occurrence based on a two-sided t-test.

composition of the air masses sampled during the second boundary layer leg of Flight 10.

The UV-DIAL data presented by E. V. Browell et al. (unpublished manuscript, 1997) show that the influence of stratospheric intrusions in the western Pacific region tends to increase at higher latitudes. However, layers of air with high mixing ratios of ozone and high potential vorticity, i.e., indicators of stratospherically influenced air, were observed as far south as 10–15°N during PEM-West B (E. V. Browell et al., unpublished manuscript, 1997); thus this phenomenon is likely to have far-reaching effects on the chemistry of ozone and other trace constituents in the atmosphere over the Asia/Pacific region.

Conclusions

While the survey nature of the trace element sampling from the aircraft makes it difficult to draw many generalizations, several points are clear. First, for the DC-8 samples analyzed, the dust concentrations never exceeded $15 \mu\text{g m}^{-3}$, which is a moderate level of dust at most. For comparison, atmospheric dust concentrations at ground level during strong storms can exceed $1000 \mu\text{g m}^{-3}$ over the loess plateau [Zhang et al., 1993] or even further downwind over Korea [Chung, 1992]. Even at remote islands in the open Pacific such as Oahu, the dust concentrations at the Earth's surface can exceed the highest concentrations observed on the aircraft. Thus none of the samples from the aircraft are likely to be representative of a severe outbreak of Asian dust.

Similarly, on the DC-8 the highest concentrations of pollution-derived elements, such as Sb and aerosol sulfate, were substantially lower than the peak concentrations observed at the ground stations. This means that the plumes of continental outflow sampled from the aircraft were substantially diluted with respect to the trace element and sulfate concentrations observed at the ground stations.

Comparisons between the CO and O₃ data from the DC-8 and ground stations provided further evidence that the aircraft never encountered an extended period when high concentrations of continental emissions were sampled. A second feature of the aircraft data revealed by this comparison was that air masses with concentrations of CO and O₃ comparable to those typical of clean marine conditions were sampled during some of the DC-8's boundary layer legs. Further, data for these two gases alone can provide considerable insight into the types of air masses being sampled.

The combination of ground station and aircraft data also provides some insight into the nature of the transport processes. Higher concentrations of aerosol species, O₃, and CO at the Hong Kong ground site relative to the aircraft suggest that much of the outflow from southeastern Asia during the experiment occurred in the lower troposphere. As aerosol and ozone lifetimes in the marine boundary layer are relatively short owing to the removal of aerosols and the destruction or surface deposition of ozone, we would not expect to see extensive long-range transport out of this part of Asia. Our conclusion is supported by advanced very high resolution radiometer (AVHRR) satellite images showing little aerosol transport from southeastern Asia at any time of year [Lacis and Mishchenko, 1995]. This situation contrasts with previous studies of dust and pollution transport out of Asia in the midlatitudes, where low precipitation rates and strong winds are favorable for long-range transport in the middle troposphere [Merrill et

al., 1985; Merrill, 1989]. These conclusions regarding continental outflow have important implications for the fluxes of industrial emissions throughout the Asia/Pacific region. In particular, the pollutants emitted in southeastern Asia are most likely to cause local- to regional-scale effects, whereas materials emitted farther to the north are more susceptible to long-range transport.

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