

University of New Hampshire

University of New Hampshire Scholars' Repository

Earth Sciences Scholarship

Earth Sciences

12-20-1997

Transport of sulfur dioxide from the Asian Pacific Rim to the North Pacific troposphere

D C. Thornton
Drexel University

A R. Bandy
Drexel University

Byrin W. Blomquist
Drexel University

R. Talbot
University of New Hampshire, robert.talbot@unh.edu

Jack E. Dibb
University of New Hampshire, jack.dibb@unh.edu

Follow this and additional works at: https://scholars.unh.edu/earthsci_facpub



Part of the [Atmospheric Sciences Commons](#)

Recommended Citation

Thornton, D. C., A. R. Bandy, B. W. Blomquist, R. W. Talbot, and J. E. Dibb (1997), Transport of sulfur dioxide from the Asian Pacific Rim to the North Pacific troposphere, *J. Geophys. Res.*, 102(D23), 28489–28499, doi:10.1029/97JD01818.

This Article is brought to you for free and open access by the Earth Sciences at University of New Hampshire Scholars' Repository. It has been accepted for inclusion in Earth Sciences Scholarship by an authorized administrator of University of New Hampshire Scholars' Repository. For more information, please contact Scholarly.Communication@unh.edu.

Transport of sulfur dioxide from the Asian Pacific Rim to the North Pacific troposphere

Donald C. Thornton, Alan R. Bandy, and Byron W. Blomquist¹

Department of Chemistry, Drexel University, Philadelphia, Pennsylvania

Robert W. Talbot and Jack E. Dibb

Institute for the Study of Earth, Oceans, and Space, University of New Hampshire, Durham

Abstract. The NASA Pacific Exploratory Mission over the Western Pacific Ocean (PEM-West B) field experiment provided an opportunity to study sulfur dioxide (SO₂) in the troposphere over the western Pacific Ocean from the tropics to 60°N during February–March 1993. The large suite of chemical and physical measurements yielded a complex matrix in which to understand the distribution of sulfur dioxide over the western Pacific region. In contrast to the late summer period of Pacific Exploratory Mission-West A (PEM-West A) (1991) over this same area, SO₂ showed little increase with altitude, and concentrations were much lower in the free troposphere than during the PEM-West B period. Volcanic impacts on the upper troposphere were again found as a result of deep convection in the tropics. Extensive emission of SO₂ from the Pacific Rim land masses were primarily observed in the lower well-mixed part of the boundary layer but also in the upper part of the boundary layer. Analyses of the SO₂ data with aerosol sulfate, beryllium-7, and lead-210 indicated that SO₂ contributed to half or more of the observed total oxidized sulfur (SO₂ plus aerosol sulfate) in free tropospheric air. The combined data set suggests that SO₂ above 8.5 km is transported from the surface but with aerosol sulfate being removed more effectively than SO₂. Cloud processing and rain appeared to be responsible for lower SO₂ levels between 3 and 8.5 km than above or below this region.

Introduction

The NASA Pacific Exploratory Mission-West (PEM-West) program was designed to study the impact of anthropogenic activity on the western Pacific Ocean from ozone, ozone precursors, nitrogen oxides, and oxidized sulfur. During the phase A field experiment in September–October 1991, sulfur dioxide (SO₂) was found extensively throughout the western Pacific [Thornton *et al.*, 1996]. In addition to long range transport of anthropogenic SO₂ from Asia, the Mount Pinatubo eruptions during June 1991 caused a major perturbation of the Pacific troposphere and stratosphere with respect to sulfur dioxide. The effects of the Pinatubo volcano were observed in the midlatitude and high-latitude regions but not in the tropical troposphere. During the late summer of 1991, typhoons were also found to be significant in distributing SO₂ in the upper troposphere of the western Pacific [Newell *et al.*, 1996].

The phase B field experiment of PEM-West was designed to study this same region during the late winter when transport from the Asian continent would be climatologically favored compared to the autumnal equinox period [Hoell *et al.*, this issue]. During the intervening period between these programs no cataclysmic eruptions of volcanos have occurred in the study region. Like the earlier period this phase also studied the southwestern tropical Pacific to compare that region with the Pacific nearer to the continent. While

typhoons were absent during PEM-West B, deep tropical convection was encountered near New Britain and New Guinea.

Experiment

The SO₂ measurements were made by gas chromatography-mass spectrometry using a highly purified ³⁴SO₂ internal standard with cryogenic sample collection and immediate analysis in flight. The details of gas chromatography-mass spectrometry system with addition of an isotopically labeled internal standard have been described recently [Bandy *et al.*, 1992, 1993]. In short, the technique involves adding an isotopically labeled sulfur gas (e.g., ³⁴SO₂) to the air sampling inlet as the air is drawn into the aircraft. During PEM-West B usually two samples were obtained simultaneously from the same inlet manifold for the determination of SO₂ and dimethyl sulfide (DMS). The sampling time was typically 4 min with a turnaround time of 5–6 min controlled by the chromatography. Each sample was enriched cryogenically with liquid argon and then injected onto its own column. The effluents of the columns were then switched to the mass spectrometer in a timed sequence to obtain a determination of each ambient sulfur analyte along with the corresponding enriched isotopomer.

The concentration of the SO₂ in the ambient air was determined relative to the internal standard after correcting for the isotopic distribution of the ambient isotopomers. The cylinder containing the isotopically labeled SO₂ was prepared by Scott-Marrin Inc. (Riverside, California) from SO₂ containing 99.99 mol % ³⁴S supplied by Icon Services (Mount Marion, New York). The working calibration cylinder had a concentration of 214 parts per billion by volume (ppbv), whose concentration was determined by comparison to three permeation tubes maintained in our laboratory.

¹Now at Department of Oceanography, School of Ocean and Earth Science Technology, University of Hawaii, Honolulu

Copyright 1997 by the American Geophysical Union.

Paper number 97JD01818.
0148-0227/97/97JD-01818\$09.00

Because the standard cylinder contained no detectable $^{32}\text{SO}_2$, we could easily check for contamination of the sampling manifold by adding ultrapure air (Scott-Marrin Inc., Riverside, California) and $^{34}\text{SO}_2$ to the inlet so that ambient air was excluded [Bandy *et al.*, 1992, 1993]. Using our isotopically labeled standard, we found that the pump we used during this field program was generating SO_2 at a few parts per trillion by volume (pptv) depending on the operating conditions of the pump. The source of the SO_2 was determined to be the residual sulfur in the stainless steel alloy used for the metal bellows. A correction was made to the data based on the ultrapure air measurements after establishing that there were no leaks or other sources of SO_2 in the system.

The aerosol sulfate data were obtained by using large air volume samples with Teflon filter collection of the aerosols with analysis by ion chromatography [Talbot *et al.*, 1992]. The radionuclides were determined as described by Dibb *et al.* [1996].

The set of chemical and physical measurements made aboard the DC-8 is given in the overview paper describing the PEM-West B program [Hoell *et al.*, this issue]. The data archive of the PEM-

West project was used to develop the correlations and supporting information given below.

Results and Discussion

Sulfur dioxide distribution and concentrations for PEM-West B were in marked contrast to the phase A period. The maximum SO_2 levels were encountered in the lowest, well-mixed part (<600 m) of the boundary layer near Taiwan as in the earlier program, but SO_2 concentrations >0.5 ppbv were as common just above the boundary layer top, typically up to 4 km (Figures 1b and 1c). Transport in the upper part of the boundary layer at times extended more than 1000 km from land. At the other extreme, SO_2 levels were often <20 pptv and generally less than 50 pptv in the western tropical Pacific troposphere despite indications of long-range transport of recent combustion products from Asia. Dimethyl sulfide did not appear to be a major source of SO_2 primarily due to generally low source strengths and in part due to the winter season for the midlatitudes [Thornton *et al.*, this issue]. The smoking volcanos of the New Britain and New Guinea region were substantial SO_2 sources in the equatorial region [Thornton *et al.*, this issue], but long range transport from the west appeared to be a significant source for SO_2 elsewhere in the tropics.

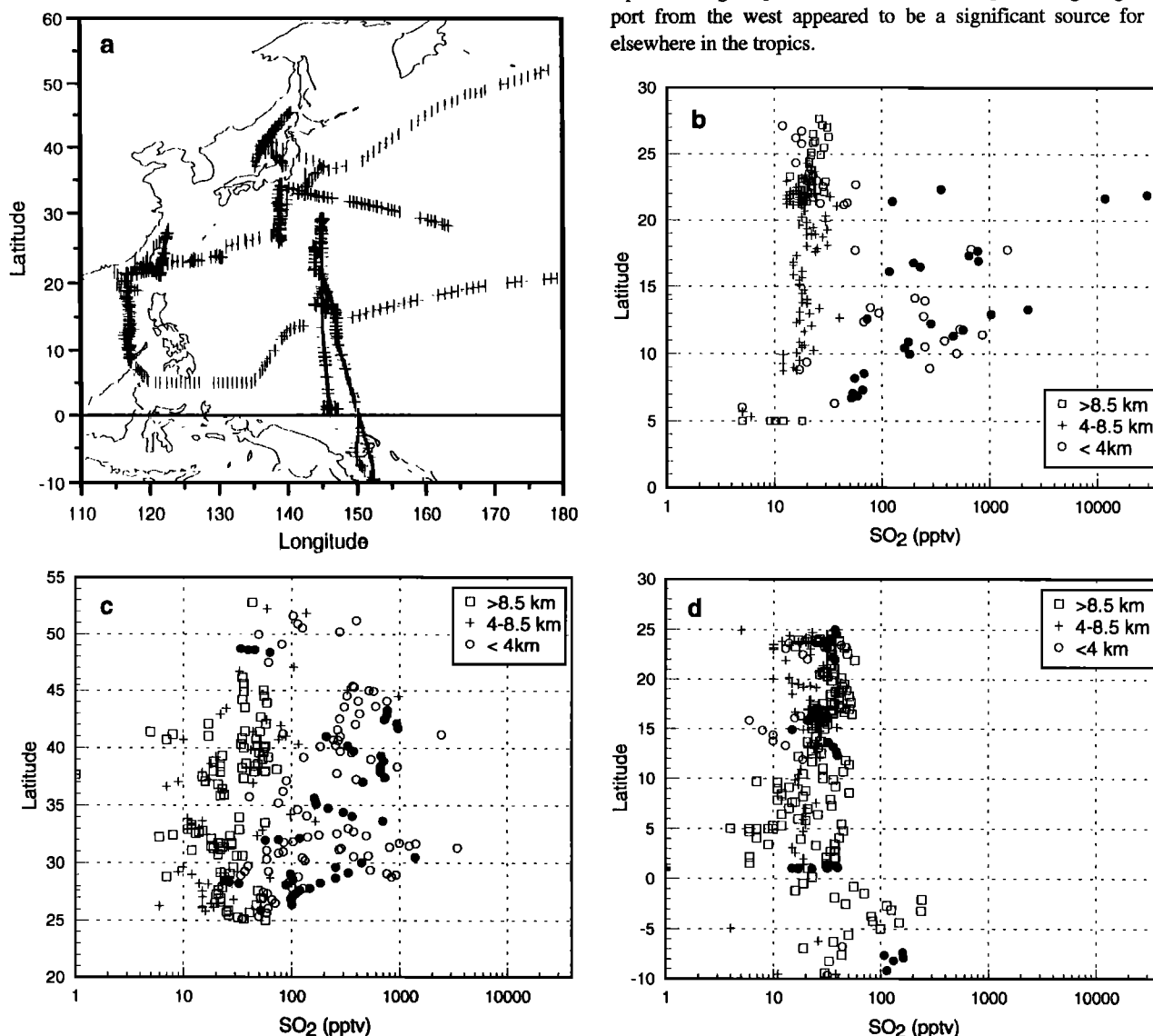


Figure 1. (a) SO_2 sample locations during PEM-West B and distribution of SO_2 with latitude and pressure altitude for (b) west of 125°E, (c) east of 125°E and north of 25°N, and (d) south of 125°E and north of 25°N. Solid circles are for pressure altitudes <600 m.

The analyses of the PEM-West B SO₂ data included here consist of three major parts. First, the distribution of SO₂ in the western Pacific troposphere is discussed in detail to illustrate the extent to which transport from the Asian land masses affected the western Pacific troposphere. The SO₂ data were combined with the aerosol non-sea-salt sulfate data to assess the oxidized sulfur balance in the gas phase of the western Pacific troposphere. The second part was a study of the altitude dependence and regional variations of SO₂ relative to the acetylene (C₂H₂) to carbon monoxide (CO) ratio. Use of these two tracers has proven to be very effective in estimating photochemical destruction relative to atmospheric processing resulting from transport and dilution [Smyth *et al.*, 1996; McKeen *et al.*, 1996]. Third, the oxidized sulfur values were filtered by altitude and combined with the radionuclide aerosol tracers beryllium-7 (⁷Be) and lead-210 (²¹⁰Pb). As aerosol tracers, ⁷Be and ²¹⁰Pb are complementary in assessing the sources of sulfur in the troposphere because the former has its source in the stratosphere and the latter is derived from surface emissions of radon-222 (²²²Rn).

Distribution of SO₂

The most obvious difference in the SO₂ spatial distribution for PEM-West B compared to PEM-West A was the much lower concentrations of SO₂ above 4 km (Figure 1). During PEM-West A, SO₂ increased with altitude under the influence of the Mount Pinatubo eruptions for the middle and high latitudes and from convective transport from typhoons for the region from southern Japan to the tropics [Thornton *et al.*, 1996]. The tropical western Pacific above 8 km in 1991 was also impacted by long-range transport of SO₂ from east Asia. In contrast to the earlier period, during PEM-West B, SO₂ was <60 pptv above 4 km (Figure 1) with few exceptions resulting from convective transport between 3-5.5 km near the continent and tropical deep convection to 9-12 km near New Britain. During both phases of PEM-West, low altitude (<1 km) transport of SO₂ from the western Pacific Rim land masses was significant, reaching 30 ppbv east of Taiwan during phase B.

Tropical region. The western tropical Pacific (east of 130°E and south of 23°N) during PEM-West B had lower SO₂ levels compared to the phase A program with concentrations typically <50 pptv (Figure 1d). These low concentrations are surprising considering the frequent indications of long range transport based on other anthropogenic trace gases. Air mass back trajectories and chemical analyses most often indicated continental sources with <2 days transit time [Talbot *et al.*, this issue]. Dimethyl sulfide levels were less than 30 pptv except in coastal waters near New Britain where concentrations ranged from 23 to 73 pptv (near 1100 LT). Consequently, DMS did not appear to be a significant source of the SO₂ in this region [Thornton *et al.*, this issue].

The primary sources of SO₂ in the tropical region appeared to be long-range transport from the Asian land masses and equatorial volcanoes. The numerous smoking volcanoes on New Britain and eastern New Guinea were the source of the SO₂ >100 pptv observed in the well mixed part (<600 m) of the boundary layer and above 9 km (Figure 1d) (for details, see Thornton *et al.*, [this issue]). Long-range transport from Asia appeared to be the dominant source of SO₂ for this region as evidenced by the high C₂H₂/CO. The low SO₂ concentrations are apparently the result of removal processes that do not affect other insoluble or sparingly soluble anthropogenic tracers within the relatively short (2-3 day) transit times to this region from the sources. Dimethyl sulfide did appear to be a significant source of SO₂ for flight 9 at all altitudes along 145°E to the equator and for flight 10 east of 120°E at 9.5 km [Thornton *et al.*, this issue]. For these two flight periods the track

was above clouds and the back trajectories were predominantly from the east.

The vertical distribution of SO₂ in the tropics appeared to decrease to <25 pptv between 4 and 8 km compared to altitudes <3 km and above 8 km (Figure 2). We attribute this decrease in SO₂ in the lower free troposphere in part to cloud processing associated with convection and in part from a change in the mean air flow in the lower troposphere from the west to a regime of marine air from the east around an anticyclonic center near 15°N 165°E [Merrill *et al.*, this issue]. At latitudes south of 10°N the mean 500 hPa flow was predominately easterly, while at 20°N the mean flow was still from the west. Between 15°N and 25°N the mean wind velocity at 500 hPa was about 15 m/s which would place the region around about 3 days from Southeast Asia. South of 15°N the local DMS sources of SO₂ were weak, and the volcanic sources probably were diluted by the cleaner air from the east. No trend in SO₂ with the longer-lived combustion tracers could be discerned in this region (Figure 11b; see discussion below).

Transport of SO₂ into the tropical region can be clearly seen by juxtaposing flight 14 south from Japan and flight 8 north from Guam. Transport from Japan along 139°E as far south as 26.5°N (Figure 3) provided SO₂ concentrations exceeding 100 pptv at a pressure altitude of 600 m with the wind from the north. However, near Japan a polluted layer between 1.5 and 2 km (just above the top of the boundary layer) with 3.5 ppbv SO₂ indicated that much of the SO₂ was transported out over the ocean above the boundary layer top with westerly winds. Enhancements in carbon monoxide, methane, and acetylene were also observed in this layer. Above this polluted layer, SO₂ concentrations had decreased to 40-130 pptv (Figure 3) with concentrations less than 30 pptv in the middle troposphere.

The residual effect of long-range transport of SO₂ is seen from flight 8 north from Guam along 144°N (Figure 4). Concentrations of near 100 pptv were found at 600 m between 26°N and 29°N under the influence of north winds (compare to the same latitude in Figure 3). Above the boundary layer top at 2.8 km where the winds were from the west, SO₂ concentrations ranged from 50-100 pptv similar to that seen on flight 14 (Figure 3) but nearly twice as high near 10 km. This can be contrasted to the southern portion of this flight (near 17°N) where the back trajectories indicated a marine source of the air and SO₂ levels were typical of central and equato-

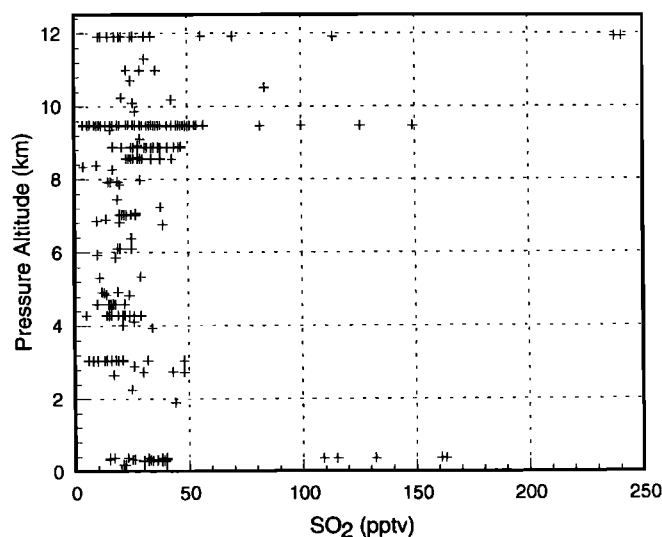


Figure 2. Vertical distribution of sulfur dioxide for the tropical ocean region east of 130°E and south of 23°N.

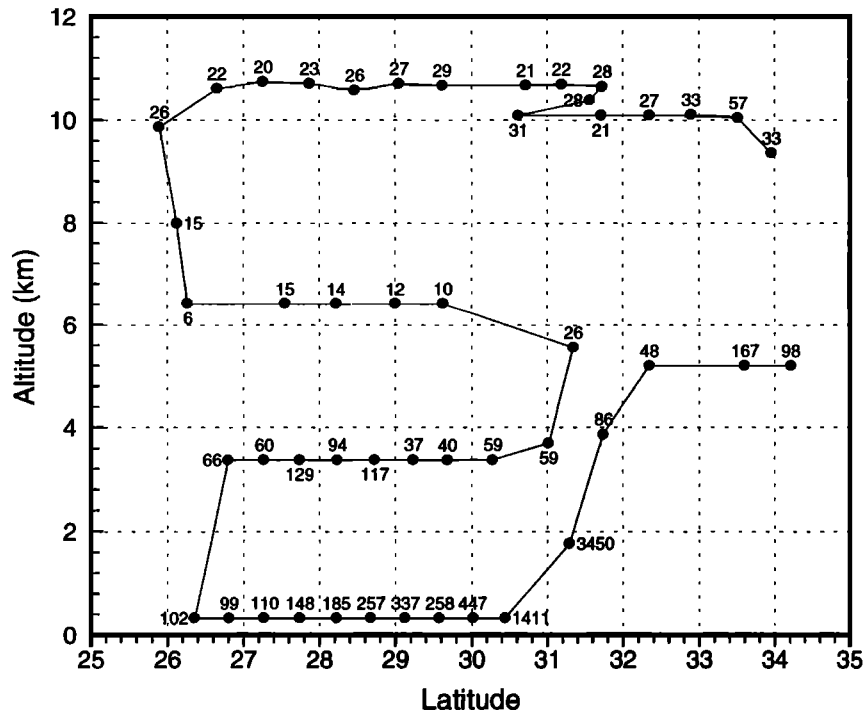


Figure 3. Flight track for flight 14 south from Japan along 139°E with the sulfur dioxide concentrations indicated.

rial Pacific [Maroulis *et al.*, 1980; Thornton and Bandy, 1993; Thornton *et al.*, 1996]. While flights 8 and 14 were separated 2 weeks in time and 6° of longitude, it indicated that transport of SO₂ from the continental sources into the tropical western Pacific was frequently occurring.

Continental Rim. Along the western Pacific Rim the transport of SO₂ over the ocean from the land masses dominated the SO₂ distribution below 4 km (Figure 5). The highest concentrations (>10 ppbv) were found near Taiwan at 600 m in the well-mixed layer. Sulfur dioxide concentrations exceeding 0.5 ppbv were found just above the upper part of the boundary layer (1.5–2.5 km) over the

South China Sea (Figure 6), the Sea of Japan (Figure 7), and the Pacific east of Japan (Figure 8). Often these higher concentrations were related to frontal activity which provided uplift from the surface. In some cases the transport of SO₂ at 1–3 km extended over 1500 km from the western rim countries (e.g., see Figure 8 near 160°E).

Near the continent there was also a decrease in the SO₂ concentrations between 4 and 8 km (Figure 5a), although it was less clear than for the tropical region due to the greater variation of SO₂ and the lack of a significant source of SO₂ above 8.5 km. The trend is more apparent when the individual constant altitude flight legs are

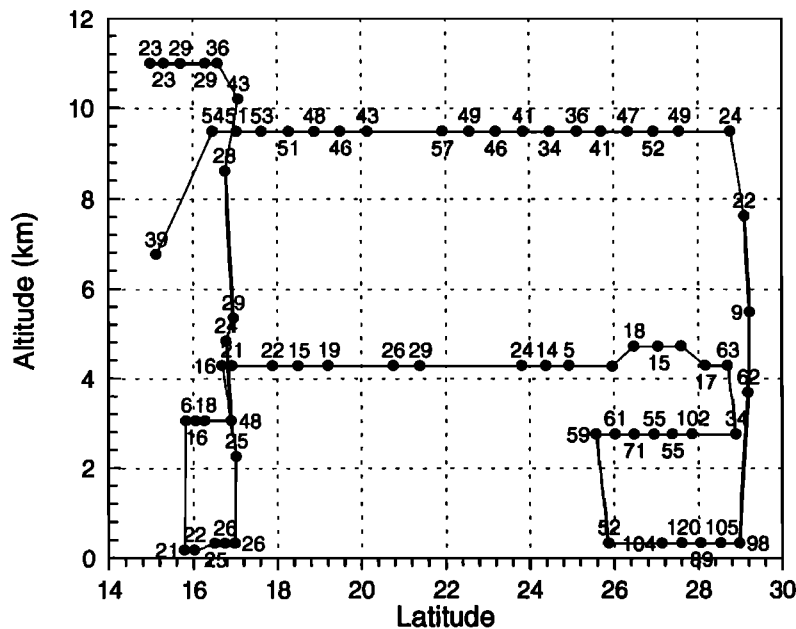


Figure 4. Flight track for flight 8 north from Guam along 145°E with the sulfur dioxide concentrations indicated.

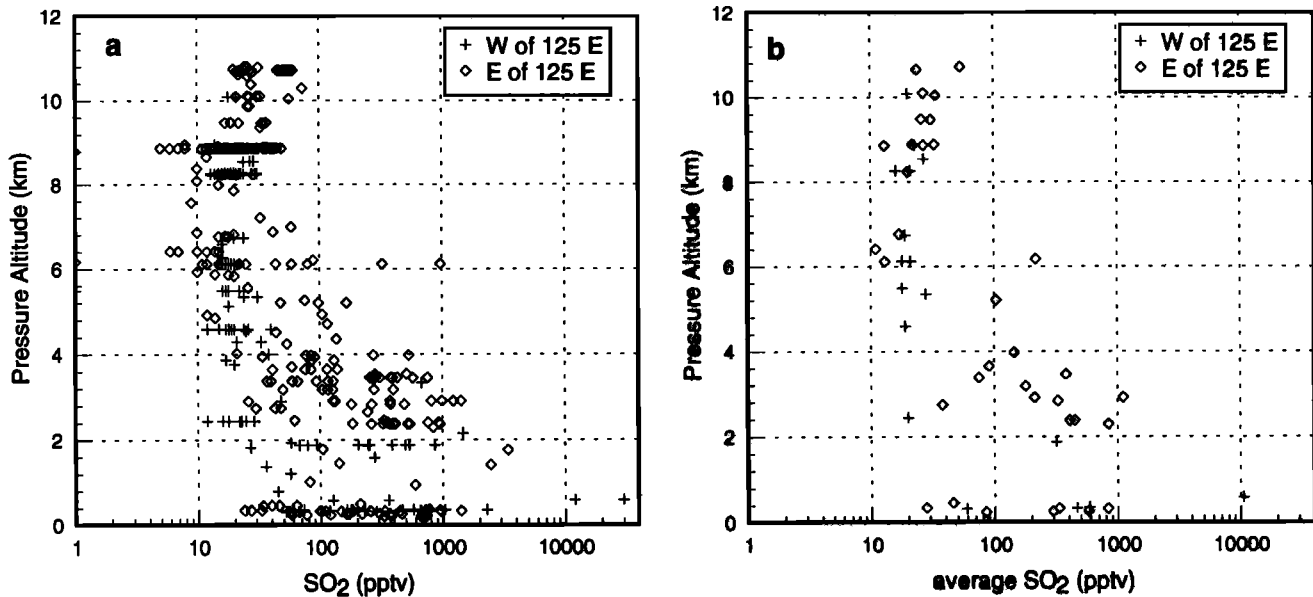


Figure 5. Vertical distribution of sulfur dioxide for the near continent regions: (a) individual measurements and (b) averages for each level flight leg.

averaged (Figure 5b). Averaging the SO₂ shows that specific flight legs intercepted fresh pollution transport episodes and contributed most of the variation in the data between 4 and 8 km. Again, we think that the reduction of SO₂ in the 4–8 km range is the result of processing in clouds during transport through the lower troposphere.

Above 8 km along the western Pacific Rim there was little stratospheric influence for SO₂ during PEM-West B. Flight 17 over the Sea of Japan (above 10 km in Figure 7) was clearly in deep stratospheric air based on the ozone (220–300 ppbv) and ⁷Be data (5618 fCi/m³), but the SO₂ maximum was only 73 pptv with an average of 55 pptv. Sulfur dioxide concentrations were 17–24% of the combined SO₂ and aerosol sulfate concentrations (SO_x) of

223–322 pptv in this stratospheric encounter. In the stratospheric air during PEM-West A, SO₂ was 40–45% of the 0.5 ppbv SO_x east of the Kamchatka Peninsula, and over the Gulf of Alaska, SO_x was 1 ppbv with about 60% SO₂.

The low stratospheric SO₂ concentrations in the western Pacific were in marked contrast to the eastern Pacific Rim 6 weeks earlier during test flights at Ames Research Center. Along the northwest California coast near 39°N, SO₂ was 2–3 ppbv in deep stratospheric air at 12.8 km. We think that this difference is the result of where the stratospheric air was intercepted relative to the polar jet and the location of the active volcanoes along the northwestern ring of fire around the Pacific. The high SO₂ levels found in the stratospheric

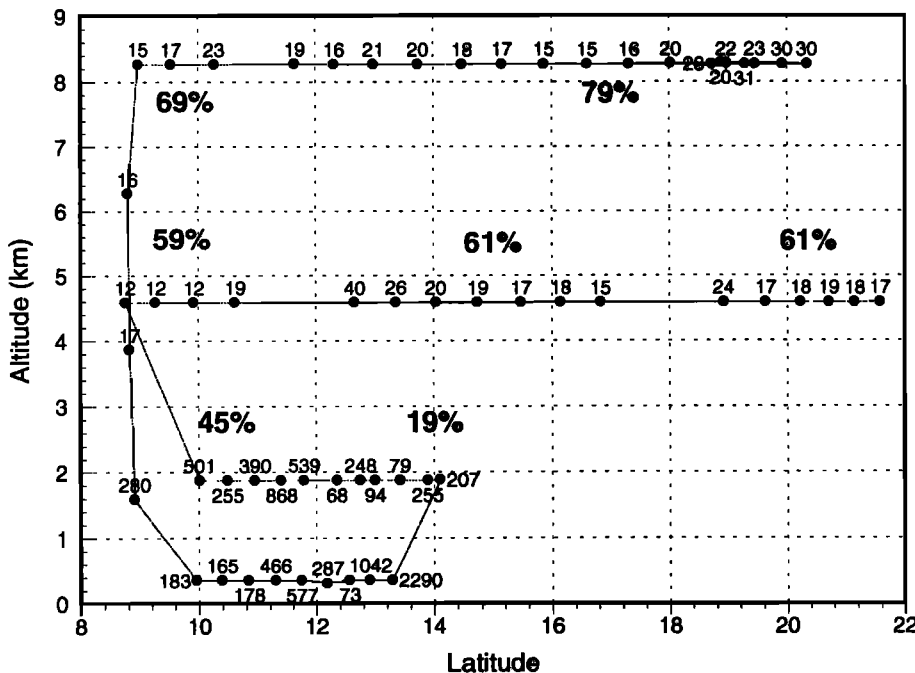


Figure 6. Flight profile for flight 11 south from Hong Kong along 117°E with the sulfur dioxide concentrations indicated for each sample. The fraction of the total oxidized sulfur that is SO₂ is given in percent.

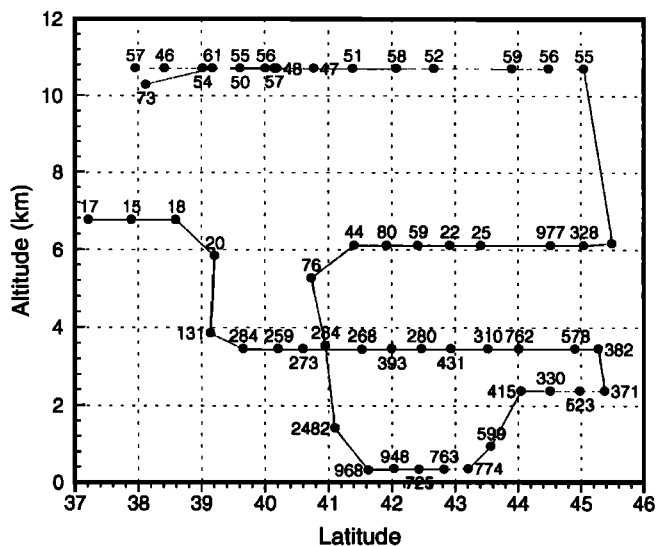


Figure 7. Flight profile for flight 17 over the Sea of Japan with the sulfur dioxide concentrations indicated.

air in the northeastern Pacific are probably the result of the Mount Bezymiyan eruptions in October-November 1993 which reached 15 km [Venzke et al., 1993]. The tendency for the tropopause to descend to <10 km along the California coast during the winter [Danielson et al., 1987] provided the opportunity to sample deep stratospheric air that had been impacted by the Bezymiyan eruptions. The SO₂ injected by the volcano may have been localized and circulating in the lower stratosphere and not intercepted during the western Pacific sampling period.

SO₂ compared to sulfate. The conversion of SO₂ into aerosol sulfate has been recognized as having an indirect effect on climate by modifying the scattering properties of clouds through changes in droplet size, mass, index of refraction, and number density. To assess the balance between the two primary oxidized sulfur species (SO₂ and aerosol sulfate) outside of cloud droplets, we compared the SO₂ concentration to the sum of SO₂ and aerosol non-sea-salt sulfate, and this sum is referred to here as SO_x. This sum was obtained by averaging the SO₂ data coincident with the period of each sulfate measurement. The ratio of SO₂/SO_x was evaluated with respect to three regions: tropical, flights 6-10 east of 125°E and

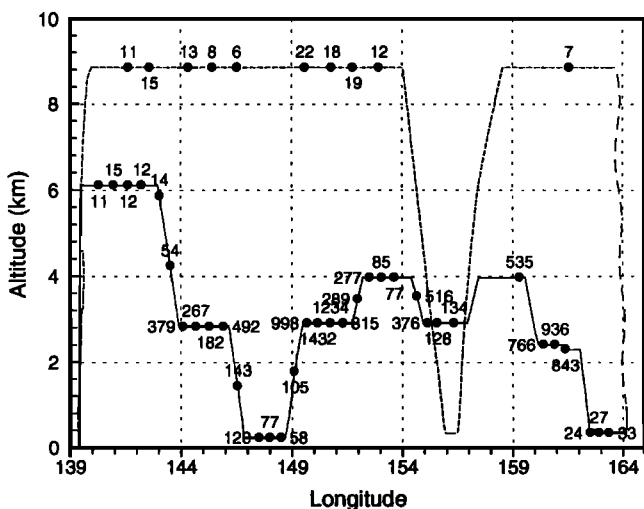


Figure 8. Flight profile for flight 16 east from Japan near 30°N with the sulfur dioxide concentrations indicated.

south of 25°N; subtropical, flights 10-13 west of 120°E; midlatitude, flights 13-18 north of 25°N and between 125°E and 165°E.

The vertical distribution of SO_x (Figure 9a) not surprisingly was similar to that of SO₂ (Figures 2 and 5) with somewhat higher values above 8 km from the sulfate contribution. As the SO_x concentration decreased or increased from about 100 pptv, the SO₂/SO_x increased (Figure 9b). The SO₂/SO_x ratio as a function of SO_x concentration and region was significantly different for the midlatitude group compared to the tropical group, while the subtropical group appeared to follow the midlatitude group for high SO_x concentrations and the tropical group for low SO_x. The variation of the SO₂/SO_x with altitude further illustrates the difference in region. For the tropical and subtropical regions, SO₂/SO_x increased with altitude (Figure 10a) where the subtropical data with SO₂/SO_x <0.4 are the high SO_x values that were observed at low altitude near Taiwan and west of Palawan, The Philippines. For the variation of SO_x with altitude the tropical and subtropical groups appear to form a consistent group that had an intercept on the SO_x axis greater than that of the midlatitude group (Figure 9b).

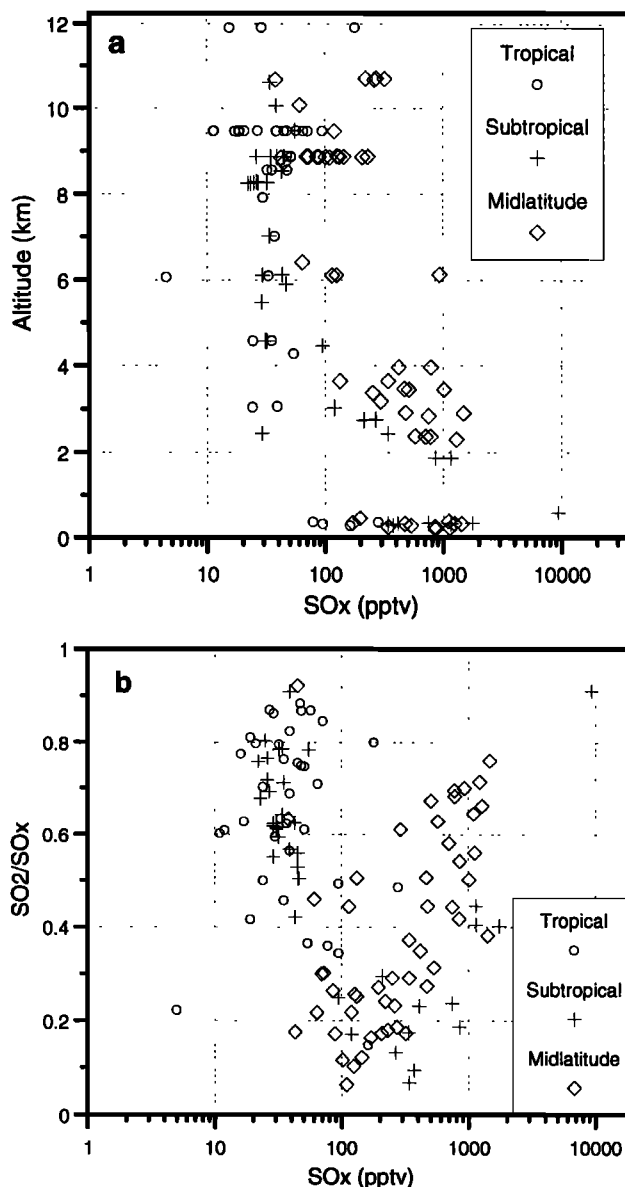


Figure 9. (a) Vertical distribution of total oxidized sulfur SO_x and (b) the fraction of SO_x as SO₂ as a function of SO_x concentration.

The midlatitude region had the opposite trend with altitude compared to the tropical and subtropical regions. For the midlatitude region the vertical transport of SO_x to 2-4 km occurred with about the same proportion of SO_2/SO_x as for the 600 m level (Figure 10b). This similarity reflects the faster transport from east Asian sources in the midlatitudes compared to the region south of 25°N [Merrill *et al.*, this issue]. Above 8 km the midlatitude SO_2/SO_x dropped to $\leq 30\%$ for most of the data unlike the subtropical group which had the highest SO_x concentrations and lowest SO_2/SO_x values below 4 km.

For the midlatitude data this can be explained by considering that during PEM-West B, high speed west winds were often encountered, and recently polluted air masses were quickly transported over the ocean before large fractions of the SO_2 was lost to the ocean surface or converted to sulfate. From the low SO_2/SO_x above 8 km there appeared to be a source of sulfate at high altitude that was unrelated to the east Asian surface source for the midlatitudes. One possible source is return of sulfate aerosol from the stratosphere which appeared to be depleted in SO_2 relative to sulfate for the Asian region during PEM-West B (see above discussion). A second alternative is that SO_2 could have been transported from western Asia above 8 km and was transformed into sulfate during the transport time. The majority of the back trajectories above 8 km for the Japan-based flights lead to western Asia with 3-5 day transit times. A third possibility is that the SO_2 above 8 km may have been

volcanic and had been at altitude for a much longer time so that SO_2 was converted to sulfate.

The low SO_2/SO_x values below 4 km for the subtropical region indicate that more conversion of SO_2 to sulfate had occurred by the time the air mass was intercepted. In this region, OH levels would have been higher than in the midlatitudes during winter, and consequently, greater SO_2 conversion rates would have existed. Also, the air masses reaching the region south of 25°N had some long-range components from southeastern Asia as well as India [Merrill *et al.*, this issue] with more time available for processing before being sampled.

The SO_x concentrations < 80 pptv for the tropical and subtropical regions above 4 km had sources farther west than the east Asian region and more influence from equatorial and southern hemisphere marine regions with low SO_2 concentrations [Merrill *et al.*, this issue]. It appeared that the SO_x at high altitude for the subtropical region was unrelated to the higher concentrations near the surface offshore of the land masses. The lower SO_2/SO_x values above 4 km could be explained by sulfate aerosols being more efficiently removed by cloud processing than was SO_2 because the aerosols would be more easily incorporated into cloud droplets than gases (see radionuclide discussion below).

Comparison with Anthropogenic Combustion Tracers

While widespread indications of anthropogenic influence (especially acetylene and carbon monoxide) on the western Pacific troposphere were clear, SO_2 levels were particularly low in the free troposphere relative to the longer-lived trace gas species. Comparison of SO_2 to the $\text{C}_2\text{H}_2/\text{CO}$ ratio showed that removal of SO_2 was primarily influenced by processes other than dilution and homogeneous chemistry. Given the high levels of SO_2 observed below 3 km, dry deposition, cloud processing, rainout, and washout must have been very effective in removing SO_2 and sulfate while transporting sparingly soluble species to the free troposphere.

The SO_2 data were paired with the acetylene and CO data which were averaged over the sample period for the SO_2 measurement before computing the $\text{C}_2\text{H}_2/\text{CO}$ ratio. These $\text{SO}_2 - \text{C}_2\text{H}_2/\text{CO}$ pairs were then segregated into altitude and region as described above. For altitudes < 3 km, only a portion of the subtropical data decreased as the $\text{C}_2\text{H}_2/\text{CO}$ ratio decreased (Figure 11a). The tropical data had reached a background level of 20-40 pptv even for $\text{C}_2\text{H}_2/\text{CO}$ ratios > 1 , which indicated a combustion source within 2 days. The large range of SO_2 values (30-30000 pptv) with $\text{C}_2\text{H}_2/\text{CO}$ values between 2 and 4 indicated that rapid removal of SO_2 in the boundary layer occurred. Given that the highest SO_2 concentrations occurred in the well-mixed layer (< 600 m), dry deposition to the ocean surface was probably a significant loss mechanism for SO_2 .

In the middle troposphere (3-8.5 km), only the midlatitude data showed any indication of slower loss for SO_2 (Figure 11b). Again, all of the tropical data and nearly all of the subtropical data were near background levels (< 40 pptv) over a wide range of $\text{C}_2\text{H}_2/\text{CO}$ ratios. Of the midlatitude data > 100 pptv only two points (from flight 17; Figure 7 at 6 km) were above 5.5 km. With a range of 100-1000 pptv of SO_2 for a narrow range of 2 to 3 for $\text{C}_2\text{H}_2/\text{CO}$ indicated that rapid removal of SO_2 was also occurring in the lower free troposphere (3-5.5 km) in the region where the SO_2 surface source strength was large. Some of the decrease in SO_2 in this region may have been from dilution which would not be as apparent from the $\text{C}_2\text{H}_2/\text{CO}$. Because of the widespread elevated levels of C_2H_2 and CO, which are only slowly removed from the troposphere, it becomes difficult to dilute a given air parcel in this anthropogenically impacted region. For SO_2 , dilution may still play

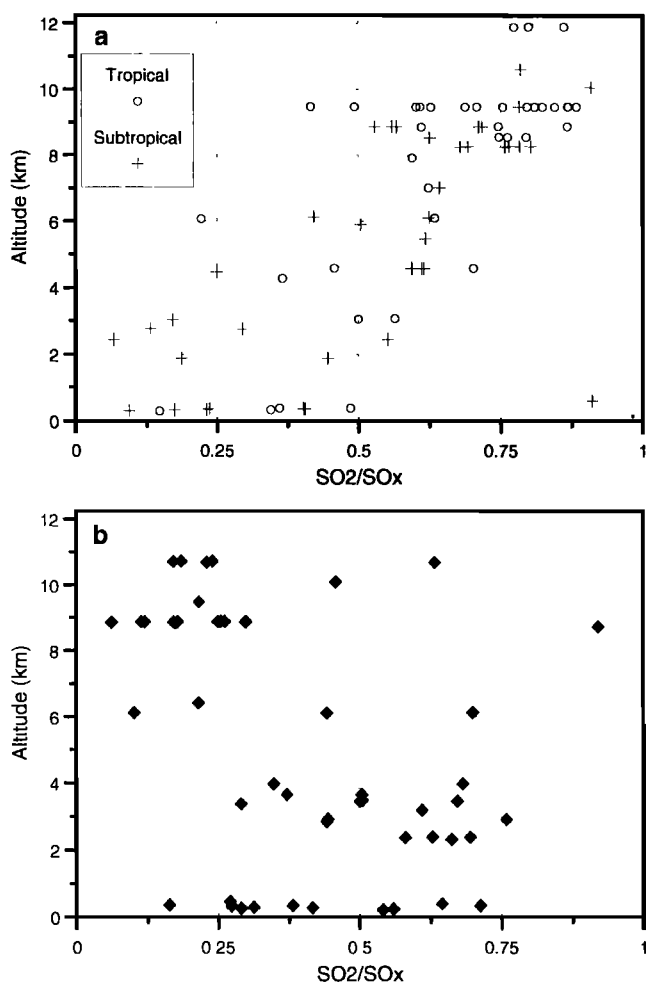


Figure 10. Fraction of oxidized sulfur that is SO_2 as a function of altitude: (a) tropical and subtropical regions south of 25°N and (b) midlatitude regions north of 25°N .

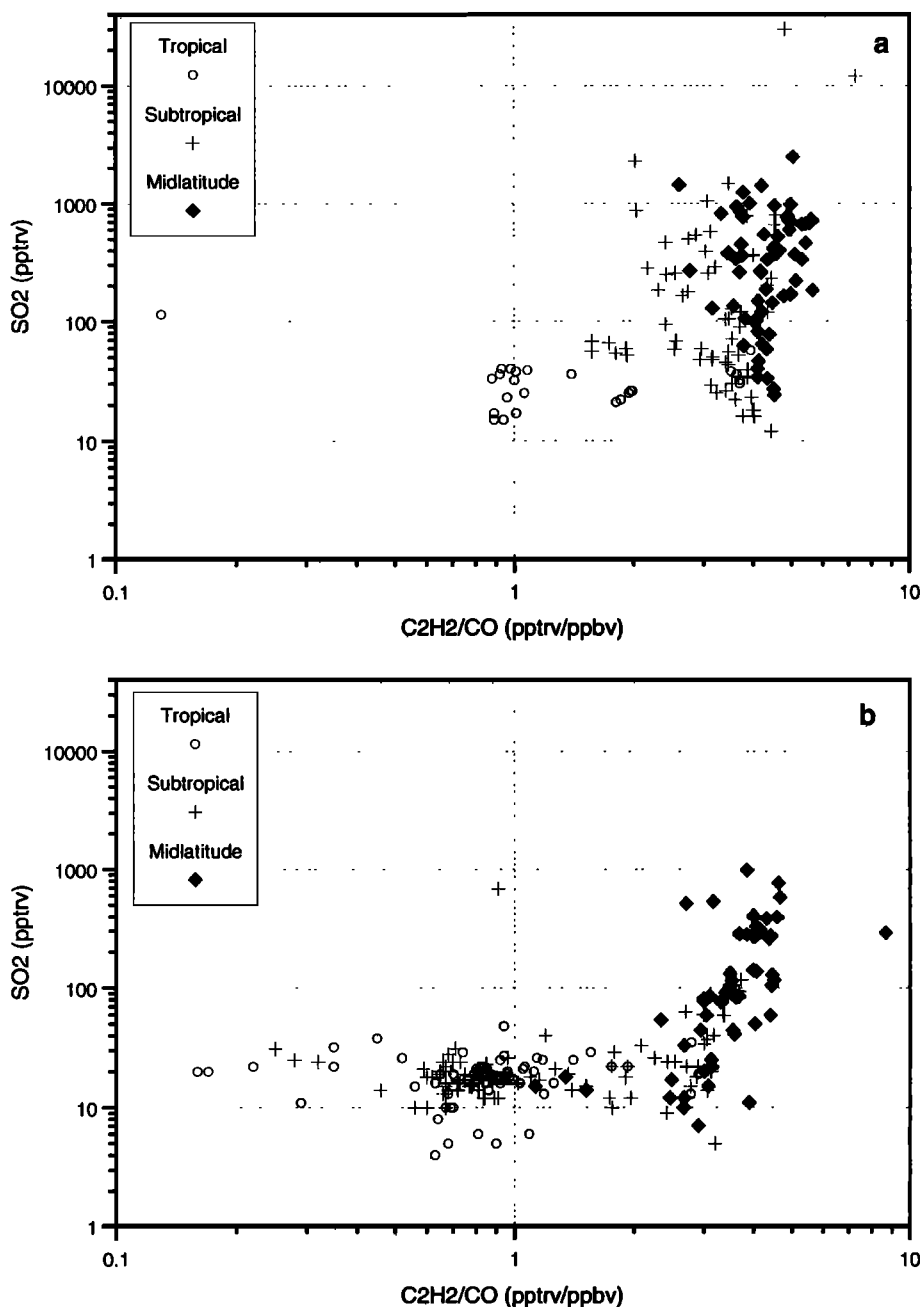


Figure 11. Sulfur dioxide compared to the ratio of acetylene to carbon monoxide as a combustion indicator: (a) altitude <3 km, (b) altitudes of 3-8.5 km, and (c) altitudes >8.5 km.

a significant role because the SO_2 lifetime is relatively short and air outside of a pollution plume with low SO_2 could be mixed with air of much higher SO_2 concentration.

For the upper troposphere, SO_2 was near background levels for all regions over the range of 0.4 to 4 $\text{C}_2\text{H}_2/\text{CO}$ ratios. At low $\text{C}_2\text{H}_2/\text{CO}$ ratios (<0.3) the air mass was relatively photochemically old and extensively processed by dynamics. The volcanic sources of SO_2 were clearly associated with low acetylene (Figure 11c). The New Britain volcanoes contributed all the data above 80 pptv in Figure 11c. The <30 pptv levels of SO_2 for the tropical and subtropical regions were probably related to the cross equatorial flow at high altitude during the PEM-West B period [Merrill *et al.*, this issue]. These air masses were outflow of the monsoon over northern

Australia. The lower SO_2 concentrations at high-altitude south of 23°N were typical of southern hemisphere air masses [Thornton *et al.*, 1993; unpublished PEM Tropics data].

For the midlatitude region when $\text{C}_2\text{H}_2/\text{CO}$ was high in the upper troposphere SO_2 was reduced to background levels. If convection over the combustion sources on land has produced the high $\text{C}_2\text{H}_2/\text{CO}$, it is likely that SO_2 has been removed by cloud processing. However, the very high wind speeds above 8.5 km [Merrill *et al.*, this issue] made it likely that the high-altitude air masses may be more related to the Eurasian border than east Asia. The stratospheric SO_2 observed during flight 17 over the Sea of Japan was about 50% greater than the apparent background levels of 30-40 pptv above 8.5 km during PEM-West B.

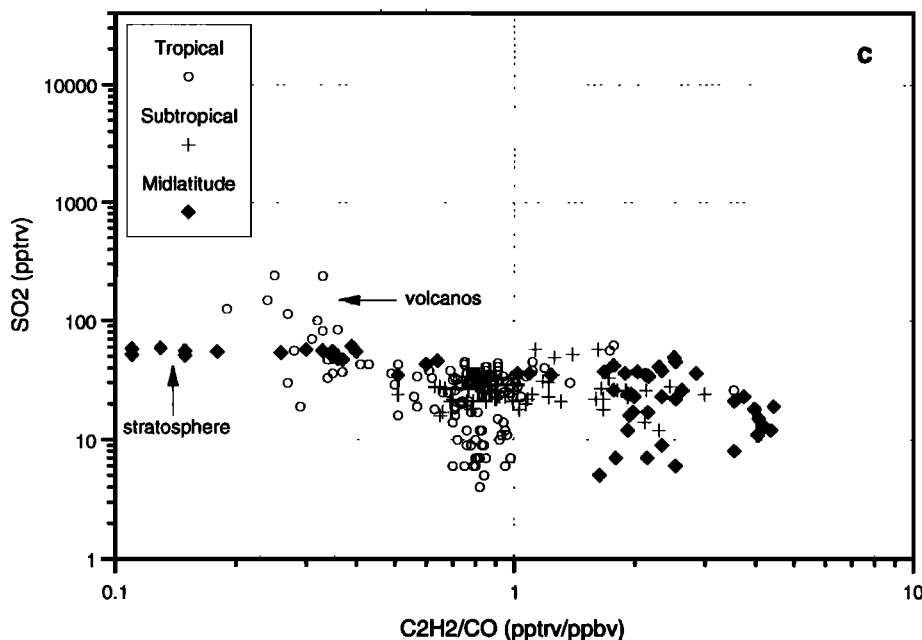


Figure 11. (continued)

Radionuclides as Oxidized Sulfur Tracers

The radionuclide data for beryllium-7 (⁷Be) and lead-210 (²¹⁰Pb) are generally associated with submicron sulfate aerosol [Moore et al., 1980; Sanak et al., 1981]. These radionuclides provide complementary tracers with ⁷Be having its source in the stratosphere via spallation and ²¹⁰Pb as an end product of the decay of ²²²Rn, whose flux from the Earth's land masses is about 2 orders of magnitude greater from than the oceans [Balkanski et al., 1993]. The use of ²¹⁰Pb as a tracer for aerosol sulfate from the surface is not completely rigorous since transport of insoluble ²²²Rn by deep convection [Kritz et al., 1993] can occur which would skew the correlation of sulfate and ²¹⁰Pb.

The radionuclide data were segregated by altitude, and the distribution of the samples with respect to the fraction SO₂/SO_x was determined (Figures 12 and 13). If there was a significant amount of SO₂ in the stratosphere near Asia, it should have been correlated

with ⁷Be. The flight legs in the stratosphere for PEM-West B encountered relatively low SO₂ and SO_x levels (<325 pptv), which was 2-4 times lower than during PEM-West A for comparable ⁷Be levels. In the stratosphere over the Sea of Japan, ⁷Be was over 2000 fCi/m³ and corresponded to ozone levels over 200 ppbv. For those stratospheric samples SO₂ ranged from 46 - 73 pptv and contributed <25% of the SO_x compared to the SO₂/SO_x of 40-60% during PEM-West A. In the instances where the upper troposphere was significantly influenced by stratospheric air (800 <⁷Be <2000 fCi/m³), SO₂ was half or more of SO_x only when SO_x was <100 pptv. On the basis of these data it appeared that the stratosphere may have been a source of sulfate for the upper troposphere. Dibb et al. [this issue] estimated from the ⁷Be that approximately 50% of the air near 11 km may have been from the stratosphere between 15 and 20 km.

Other than in the stratosphere or in upper tropospheric air strongly influenced by stratospheric air (⁷Be <800 fCi/m³), SO₂

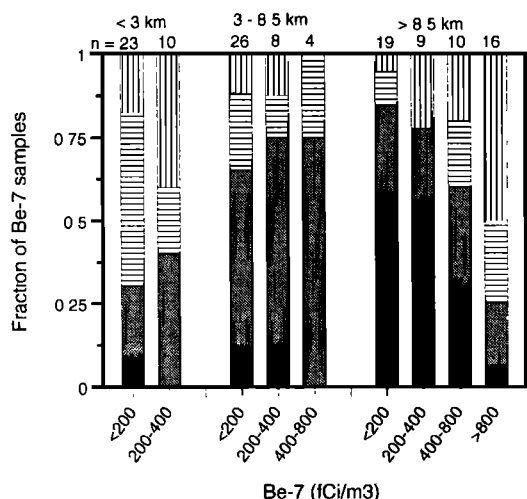


Figure 12. Fraction of oxidized sulfur that is SO₂ as a function of ⁷Be concentration and altitude.

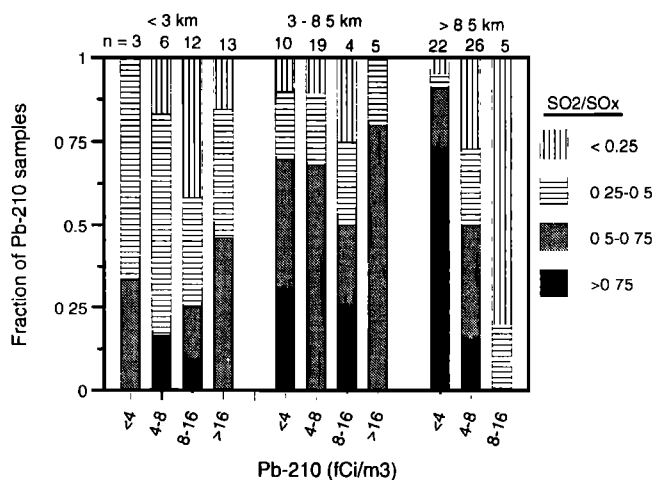
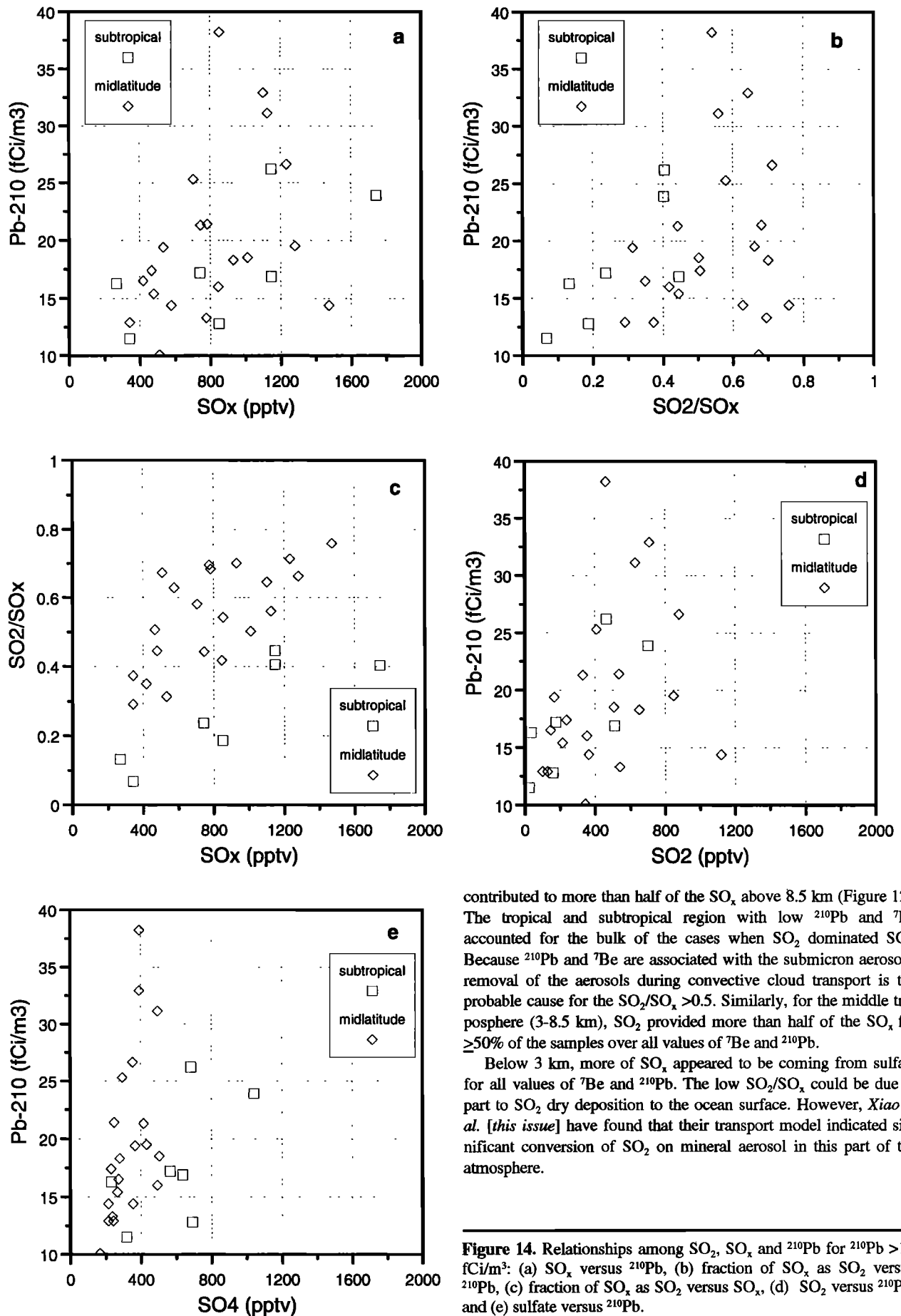


Figure 13. Fraction of oxidized sulfur that is SO₂ as a function of ²¹⁰Pb concentration and altitude.



contributed to more than half of the SO_x above 8.5 km (Figure 12). The tropical and subtropical region with low ^{210}Pb and ^7Be accounted for the bulk of the cases when SO_2 dominated SO_x . Because ^{210}Pb and ^7Be are associated with the submicron aerosols, removal of the aerosols during convective cloud transport is the probable cause for the $\text{SO}_2/\text{SO}_x > 0.5$. Similarly, for the middle troposphere (3–8.5 km), SO_2 provided more than half of the SO_x for $\geq 50\%$ of the samples over all values of ^7Be and ^{210}Pb .

Below 3 km, more of SO_x appeared to be coming from sulfate for all values of ^7Be and ^{210}Pb . The low SO_2/SO_x could be due in part to SO_2 dry deposition to the ocean surface. However, *Xiao et al. [this issue]* have found that their transport model indicated significant conversion of SO_2 on mineral aerosol in this part of the atmosphere.

Figure 14. Relationships among SO_2 , SO_x and ^{210}Pb for $^{210}\text{Pb} > 10$ fCi/m³: (a) SO_x versus ^{210}Pb , (b) fraction of SO_x as SO_2 versus ^{210}Pb , (c) fraction of SO_x as SO_2 versus SO_x , (d) SO_2 versus ^{210}Pb , and (e) sulfate versus ^{210}Pb .

To further understand the relationship of SO_2/SO_x and ^{210}Pb , the subset where $^{210}\text{Pb} > 10 \text{ fCi/m}^3$ was examined because these data were from altitudes $< 4 \text{ km}$ and were all from the subtropical and midlatitude regions where the ^{210}Pb source strength should be greatest. This analysis showed that ^{210}Pb increased with increasing SO_x and SO_2/SO_x , but SO_2/SO_x also increased as SO_x increased (Figure 14a, 14b, and 14c). The correlation of ^{210}Pb with SO_x was more related to the SO_2 component than to sulfate (Figure 14d and 14e). This implies that ^{210}Pb was not a very good tracer for sulfate aerosol in this data set. Dibb *et al.* [this issue] also found no relationship for particulate nitrate with ^{210}Pb for the near-Asia samples.

Conclusions

Transport of oxidized sulfur from eastern Asia has had a considerable impact on the western Pacific both near the continent and to the south and east for more than 1500 km. However, the oxidized sulfur was primarily below 4 km under the meteorological conditions encountered in the late winter. Often the oxidized sulfur was predominantly sulfur dioxide compared to aerosol sulfate. Near Asia, ^{210}Pb was better correlated to SO_2 than to aerosol sulfate.

The subtropical and tropical regions surveyed from Guam were impacted by transport of anthropogenic trace gases from Asia, although the SO_2 concentrations were near background levels. Both SO_2 and sulfate appeared to have been reduced by cloud processing but more so for aerosol sulfate based on the radionuclide tracers. Relative to the sparingly soluble combustion gases, such as acetylene, sulfur dioxide and sulfate appeared to be rapidly removed from the atmosphere during transport.

During PEM-West B the stratosphere was not a significant contributor of SO_2 near Asia but appeared to be a contributor of sulfate at high altitude. Volcanic contributions of SO_2 were localized but significant where they occurred. The primary impacts from volcanoes were in the equatorial region and south and east of Japan.

Acknowledgment. Support from the NASA Global Troposphere Program under grant NAG-1-1224 is gratefully acknowledged.

References

- Balkanski, Y. J., D. J. Jacob, G. M. Gardner, W. C. Graustein, and K. K. Turekian, Transport and residence times of tropospheric aerosols inferred from a global three-dimensional simulation of ^{210}Pb , *J. Geophys. Res.*, **98**, 20,573-20,586, 1993.
- Bandy, A. R., D. C. Thornton, R. G. Ridgeway Jr., and B. W. Blomquist, Key sulfur-containing compounds in the atmosphere and ocean: Determination by gas chromatography-mass spectrometry and isotopically labeled internal standards, *Isotope Effects in Gas-Phase Chemistry*, edited by J. A. Kaye, chap. 25, ACS, Washington, D. C., 1992.
- Bandy, A. R., D. C. Thornton, and A. R. Driedger III, Airborne measurements of sulfur dioxide, dimethyl sulfide, carbon disulfide and carbonyl sulfide by isotope dilution gas chromatography/mass spectrometry, *J. Geophys. Res.*, **98**, 23,423-23,442, 1993.
- Danielson, E. F., R. S. Hipskind, S. E. Gaines, G. W. Sachse, G. L. Gregory, and G. F. Hill, Three-dimensional analysis of potential vorticity associated with tropopause folds and observed variations of ozone and carbon monoxide, *J. Geophys. Res.*, **92**, 2103-2111, 1987.
- Dibb, J. E., R. W. Talbot, K. I. Klemm, G. L. Gregory, H. B. Singh, J. D. Bradshaw, and S. T. Sandholm, Asian influence over the western North Pacific during the fall season: Inferences from lead-210, soluble ionic species, and ozone, *J. Geophys. Res.*, **101**, 1779-1792, 1996.
- Dibb, J. E., R. W. Talbot, B. L. Lefer, E. Scheuer, G. L. Gregory, E. V. Browell, J. D. Bradshaw, S. T. Sandholm, and H. B. Singh, Distributions of beryllium-7, lead-210, and soluble aerosol-associated ionic species over the western Pacific: PEM-West B, February-March 1994, *J. Geophys. Res.*, this issue.
- Hoell, J. M., D. D. Davis, S. C. Liu, R. Newell, H. Akimoto, R. J. McNeal, and R. J. Bendura, The Pacific Exploratory Mission-West, Phase B: February-March, 1994, *J. Geophys. Res.*, this issue.
- Kritz, M. A., S. W. Rosner, K. K. Kelly, M. Lowenstein, and K. R. Chan, Radon measurements in the lower tropical stratosphere: Evidence for rapid vertical transport and dehydration of tropospheric air, *J. Geophys. Res.*, **98**, 8725-8736, 1993.
- Maroulis, P. J., A. L. Torres, A. B. Goldberg, and A. R. Bandy, Atmospheric SO_2 measurements of project GAMETAG, *J. Geophys. Res.*, **85**, 7345-7349, 1980.
- McKeen, S. A., S. C. Liu, E.-Y. Hsie, X. Lin, J. D. Bradshaw, S. Smyth, G. L. Gregory, and D. R. Blake, Hydrocarbon ratios during PEM-West A: A model perspective, *J. Geophys. Res.*, **101**, 2087-2109, 1996.
- Merrill, J. T., R. E. Newell, and A. S. Bachmeier, A meteorological overview for the Pacific Exploratory Mission-West, Phase B, *J. Geophys. Res.*, this issue.
- Moore, H. E., S. E. Poet, and E. A. Martell, Size distribution and origin of lead-210, bismuth-210, and polonium-210 on airborne particles in the troposphere, *DOE Symp. Ser.*, **51**, 415-429, 1980.
- Newell, R. E., et al., Atmospheric sampling of supertypoon Mireille with the NASA DC-8 aircraft on September 27, 1991, during PEM-West-A, *J. Geophys. Res.*, **101**, 1853-1871, 1996.
- Sanak, J., A. Gaudry, and G. Lambert, Size distribution of ^{210}Pb aerosols over oceans, *Geophys. Res. Lett.*, **8**, 1067-1069, 1981.
- Smyth, S., et al., Comparison of free tropospheric western Pacific air mass classification schemes for the PEM-West A experiment, *J. Geophys. Res.*, **101**, 1743-1762, 1996.
- Talbot, R. W., A. S. Vijgen, and R. C. Harris, Soluble species in the Arctic summer troposphere: Acidic gases, aerosols and precipitation, *J. Geophys. Res.*, **97**, 16,531-16,543, 1992.
- Talbot, R. W., et al., Chemical characteristics of continental outflow from Asia to the troposphere over the western Pacific Ocean during February-March 1994: Results from PEM-West B, *J. Geophys. Res.*, this issue.
- Thornton, D. C., and A. R. Bandy, Sulfur dioxide and dimethyl sulfide in the central Pacific troposphere, *J. Atmos. Chem.*, **17**, 1-13, 1993.
- Thornton, D. C., A. R. Bandy, B. W. Blomquist, D. D. Davis, and R. W. Talbot, Sulfur dioxide as a source of condensation nuclei in the upper troposphere of the Pacific Ocean, *J. Geophys. Res.*, **101**, 1883-1890, 1996.
- Thornton, D. C., A. R. Bandy, B. W. Blomquist, J. D. Bradshaw, and D. R. Blake, Vertical transport of sulfur dioxide and dimethyl sulfide in deep convection and its role in new particle formation, *J. Geophys. Res.*, this issue.
- Venzke, E., A. Cua, and R. Wunderman, *Bulletin of the Global Volcanism Network*, **18**(10), 2, 1993.
- Xiao, H., G. R. Carmichael, J. Durchenwald, D. Thornton, A. Bandy, Long range transport of SO_2 and dust in East Asia during the PEM-West B experiment, *J. Geophys. Res.*, this issue.

A. R. Bandy and D. C. Thornton, Department of Chemistry, Drexel University, Philadelphia, PA 19104. (e-mail: arb@ac1.chemistry.drexel.edu; dct@ac2.chemistry.drexel.edu)

B. W. Blomquist, Department of Oceanography, School of Ocean and Earth Science Technology, University of Hawaii, Honolulu, Hawaii 96822.
J. E. Dibb and R. W. Talbot, Institute for the Study of Earth, Oceans, and Space, University of New Hampshire, Durham, NH 03824. (e-mail: jack_dibb@grg.sr.unh.edu; rwt@christa.unh.edu)

(Received August 5, 1996; revised June 10, 1997
accepted June 18, 1997.)