JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 102, NO. D23, PAGES 28,287–28,302, DECEMBER 20, 1997

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Distributions of beryllium 7 and lead 210, and soluble aerosol-associated ionic species over the western Pacific: PEM West B, February - March 1994

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Abstract. Aerosol sampling for the determination of the concentrations of soluble ionic species and the natural radionuclides ^{7}Be and ^{210}Pb was conducted from the NASA DC-8 over the western Pacific as part of GTE/PEM-West B during February - March 1994. Concentrations of most soluble ionic species in the free troposphere were higher in samples collected on flights originating from Hong Kong and Japan than those collected further east over the open ocean. In both regions the measured concentrations were higher than those found during PEM-West A (fall 1991). Activities of ^{210}Pb, a tracer of air masses influenced by sources on the Asian continent, showed the same patterns. These data indicate the effect of stronger continental outflow from Asia over the western Pacific during the spring compared to fall season. For readily scavenged aerosol-associated species and soluble acidic gases the strongest indications of Asian outflow were restricted to altitudes below 6 km. The distribution of the continental tracer ^{210}Pb was also compared to those of a large number of gas phase species measured on the DC-8. Relatively strong correlations were found with O_3 and peroxyacetylnitrate (PAN), but only during the flights over the remote Pacific. During PEM-West A, similar correlations were seen, but they were stronger near Asia. We believe that these correlations are a signature of continental air that has been processed by deep wet convection over land before being advected over the ocean. One flight over the Sea of Japan provided the opportunity to sample upper troposphere/lower stratosphere air in and around a tropopause fold. Concentrations of ^{7}Be reached 7 pCi m^{-3} STP, and peak O_3 mixing ratios of 480 ppb were encountered at 10.7 km. The ^{7}Be data are used to estimate the fraction of stratospheric air mixed down into the troposphere by circulation in the fold.

Introduction

The NASA DC-8 flew 16 flights over the western Pacific during February - March 1994. The Global Tropospheric Experiment/Pacific Exploratory Mission-West B (GTE/PEM-West B) mission was designed to allow characterization of the influence of continental outflow from Asia on the composition of free tropospheric air over the ocean. In particular, PEM-West B was intended to complement the PEM-West A mission, which was flown in the same region in September - October 1991, thus allowing comparison between the spring (much outflow expected) and fall seasons (when outflow events are less common) [e.g., *Prospero et al.*, 1985; *Merrill et al.*, 1989] (see also the special issue of the *Journal of Geophysical Research* on PEM-West A, volume 101 (D1), 1996). Descriptions of the GTE instrumentation on board the DC-8, and the specific scientific objectives of each flight, are given by *Hoell et al.* [this issue].

This paper focuses on the spatial and vertical distributions of the natural radionuclide tracers ^{7}Be and ^{210}Pb. Beryllium 7 can provide information about stratospheric influence on the composition of tropospheric air, while ^{210}Pb is considered to be an indicator of air masses that have been influenced by ^{222}Rn emissions over continental regions. The distributions of these tracers are compared to those of aerosol-associated soluble ionic species and several gas phase species measured from the DC-8 during PEM-West B. Comparisons are also made to the corresponding distributions observed during PEM-West A.

Methods

The aerosol sampling systems (identical probes operated in parallel for the collection of radionuclide and ionic species samples) and analytical techniques were unchanged from PEM-West A [*Dibb et al.*, 1996]. As during PEM-West A, aerosol collection was restricted to flight legs at constant altitude. Sample integration time was reduced to 20-30 min for all flights, resulting in the collection of 140 sample pairs. Improved sensitivity of the custom ion chromatographs used on board the DC-8 during PEM-West B resulted in comparable, or lower, detection limits for all ionic species relative to our results for PEM-West A, despite the smaller sample volumes. Detection limits are dominated by variability in the loadings on "blank" filters and are inversely related to the volume of air filtered. For the mean sample volume during PEM-West B our detection limits were approximately 0.5 fCi ^{210}Pb m^{-3} STP, 15 fCi ^{7}Be m^{-3} STP, 30 parts per trillion by volume (pptv) Cl^-,

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Paper number 96JD02981.
0148-0227/97/96JD-02981$09.00

Table 1. Concentrations of Aerosol-Associated Species and Selected Gas Phase Species in Eight Geographic/Altitude bins over the western Pacific in February-March 1994.

	Cl^-	NO_3^-	$C_2O_4^=$	$PO_4^=$	$SO_4^=$	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	^{7}Be	^{210}Pb	O_3	HNO_3	HCOOH	CH_3COOH
							Remote Pacific									
							< 1 km (Six Samples)									
n	6	6	5	1	6	6	6	3	6	6	5	6	6	6	6	6
Mean	753	64.0	14.7	4.1	174	239	683	28.1	22.2	37.9	125	6.5	29.9	127	100	147
Std. error	132	15.4	2.7	--	50	68	110	2.8	3.0	9.8	54	1.7	6.3	12	29	45
Median	718	48.7	15.8	--	141	243	625	25.4	21.7	25.0	62	6.7	26.3	129	95	133
							1 - 6 km (Eight Samples)									
n	1	4	5	4	8	6	1	0	5	3	6	8	8	8	8	8
Mean	640	24.4	5.8	4.1	51	79	546		15.8	44.9	66	5.6	47.5	149	108	127
Std. error	--	16.9	1.1	0.1	18	22	--		3.0	19.2	18	0.6	3.3	26	26	32
Median		9.2	5.6	4.1	27	83			17.5	30.5	61	5.8	50.1	125	96	117
							6 - 9 km (Eleven Samples)									
n	0	2	5	2	10	3	0	0	3	0	10	11	11	11	11	11
Mean		6.6	4.5	5.6	12	22			17.0		125	3.5	43.3	108	107	119
Std. error		0.1	0.9	1.8	1	2			2.8		26	0.5	3.4	11	15	24
Median		6.6	4.5	5.6	12	20			16.8		151	3.5	46.9	109	96	102
							> 9 km (19 Samples)									
n	0	6	6	5	15	6	0	1	5	2	16	19	19	18	18	18
Mean		17.1	3.3	6.6	13	27		33.3	9.8	288.0	370	2.1	34.0	133	99	131
Std. error		7.5	0.6	1.9	3	3		--	6.0	256.7	102	0.4	4.7	15	15	18
Median		9.2	2.8	5.2	11	25			3.5	288.0	232	1.4	24.1	128	78	130
							Near Asia									
							< 1 km (16 Samples)									
n	15	15	15	13	15	15	15	13	14	12	12	16	15	16	16	16
Mean	715	128.0	39.0	14.0	500	646	703	74.0	69.0	83.0	158	17.9	40.5	509	602	625
Std. error	135	23.0	9.8	4.4	66	113	135	10.8	11.2	13.0	24	2.7	2.3	172	162	228
Median	520	100.0	19.0	9.0	392	567	432	62.0	55.0	75.0	181	16.6	41.3	324	277	282
							1 - 6 km (25 Samples)									
n	9	21	24	15	25	22	8	14	21	18	19	25	25	23	22	22
Mean	300	73.0	19.0	8.0	242	394	357	98.0	69.0	164.0	277	12.8	46.4	253	399	346
Std. error	130	13.3	4.9	1.6	38	71	169	22.2	17.2	42.2	30	1.3	1.1	50	124	111
Median	157	60.0	10.0	5.0	232	298	169	61.0	30.0	93.0	246	13.3	44.3	157	141	102
							6 - 9 km (22 Samples)									
n	4	13	14	4	22	10	4	5	12	6	22	22	22	20	21	21
Mean	124	28.0	6.4	4.3	47	129	144	42.0	24.0	66.0	372	6.9	48.2	150	113	112
Std. error	40	7.2	1.4	0.7	13	35	58	8.1	5.8	15.9	73	0.9	3.2	12	13	14
Median	108	16.0	4.3	4.4	18	114	99	39.0	20.0	63.0	272	6.2	47.2	147	114	102
							> 9 km (Nine Samples)									
n	0	1	4	2	8	4	0	0	3	1	8	9	9	9	7	9
Mean		55.0	3.8	4.3	126	55			9.7	21.0	3207	5.4	187.0	615	65	52
Std. error		--	1.0	0.3	36	34			3.0	--	853	0.5	56.0	255	17	11
Median			3.4	4.3	132	22			11.7		2700	5.2	81.0	163	66	50

Here, *n* equals the number of samples where each constituent was above our detection limit; std. error equals standard deviation/square root of *n*. Activities of ^{7}Be and ^{210}Pb given in fCi m^{-3} STP. O_3 mixing ratio in ppbv, all others are pptv.

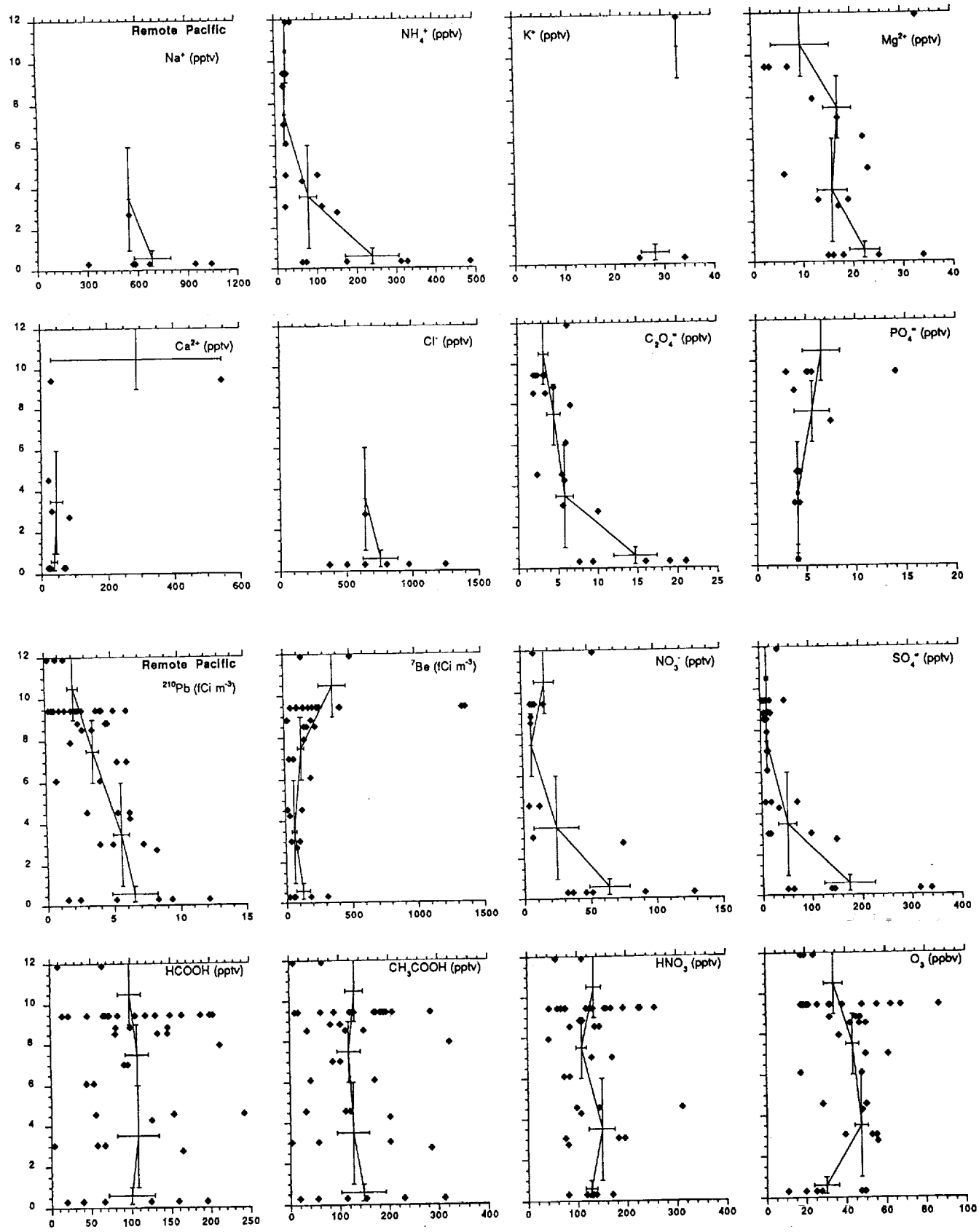

Figure 1. Mean concentrations of soluble aerosol-associated species, soluble acidic gases and ozone versus altitude (km) over the western Pacific during PEM-West B. All samples with concentrations above detection limits in the "remote Pacific" and "near-Asia" regions are plotted. The horizontal arms of the crosses represent the standard error of the mean for each species in the eight region/altitude bins presented in Table 1, while the altitude range is encompassed by the vertical arms.

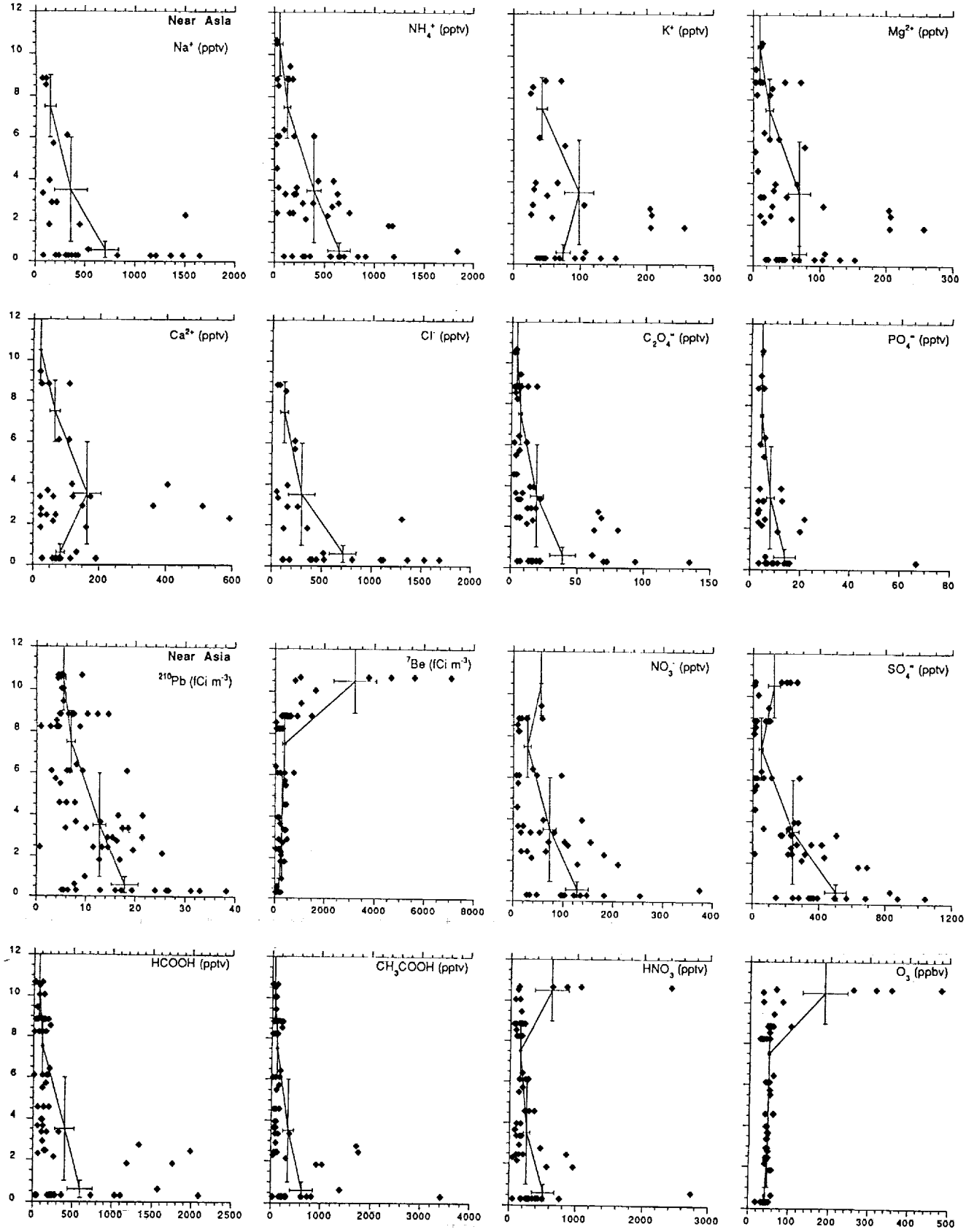

Figure 1. (continued)

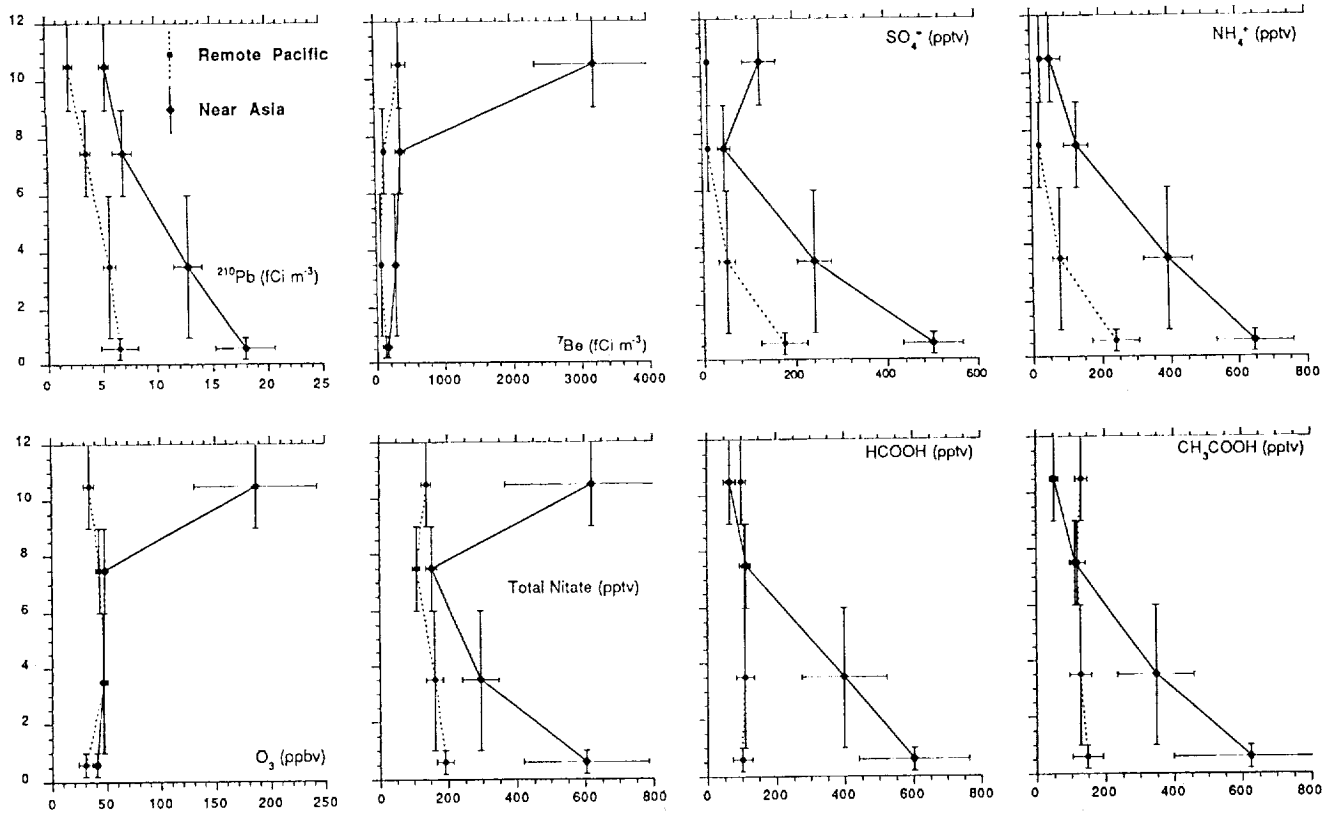

Figure 2. Comparison between the mean concentrations of selected species (those quantified in the most samples) in the two geographic regions. The crosses have the same meaning as in Figure 1.

4 pptv NO_3^-, 4 pptv $SO_4^=$, 2 pptv $C_2O_4^=$, 40 pptv Na^+, 20 pptv NH_4^+, 20 pptv K^+, 3 pptv Mg^{2+}, and 14 pptv Ca^+. We use pptv concentration units (mol^{-12} of analyte (mol of sampled air)$^{-1}$) for aerosol-associated species to facilitate comparison to all of the gas phase measurements made concurrently on the DC-8.

The sample integration times on board the DC-8 for all other species discussed herein are shorter than those for the collection of aerosols (see companion papers in this issue for details of other measurements). A merged data set, where all other measurements were averaged over the collection time of each aerosol sample, was produced at the Georgia Institute of Technology. This merged product is used exclusively in this paper. The complete PEM-West B data set and several different merged products are available through the Langley Distributed Active Archive Center.

Results

Following the lead of *Dibb et al.* [1996], we separate the PEM-West B aerosol samples into "remote Pacific" and "near Asia" regional groups. The first group includes 44 samples collected on flights 5 through the first half of flight 10 (Guam to Hong Kong), and the near Asia subset includes 72 samples from the end of flight 10 through flight 17. An additional 24 samples were collected during the transit flights from California to Hawaii (flight 4), Japan to Alaska (flight 18), and Alaska to California (flight 19). These samples were predominantly collected at cruise altitiudes (> 8 km) and are not discussed herein, but are included in the archived data set.

Further division of the data set into altitude bins considers the marine boundary layer (< 1 km) and three free tropospheric intervals (Table 1). An attempt was made to select the free tropospheric bin altitude intervals so that they contained nearly equal numbers of samples when both regions are considered. However, proportionally more time was spent at the highest altitudes in the remote region than near Asia. Table 1 also summarizes the concentrations of soluble acidic gases and O_3, averaged over the integration time of each pair of aerosol samples. All samples with concentrations above our detection limits are plotted against altitude in Figure 1. It is apparent that data coverage is sparse (concentrations often near or below detection limits) in the free troposphere, particularly over the remote Pacific, for most aerosol-associated species except ^{210}Pb (100% of samples above detection limit), $SO_4^=$ (94% > detection limit), and ^{7}Be (84% > detection limit) (Table 1). However, near Asia, all of the soluble ionic species except Na^+ and Cl^- were readily quantified in most (60-100%) of the samples collected between 1 and 6 km, with the low end of the range dropping to 18% ($PO_4^=$) for the 22 samples collected in the 6 - 9 km altitude bin (Figure 1, Table 1). In contrast, during PEM-West A, NO_3^-, $SO_4^=$ and NH_4^+ were the only soluble ionic species we were able to quantify in any samples collected above 2 km altitude [*Dibb et al.*, 1996]. In this light, even the low concentrations measured in the free troposphere over the remote Pacific suggest enhanced concentrations of soluble aerosol-associated species over much of the western Pacific in early spring relative to fall.

Discussion

Comparisons Between Remote Pacific and Near Asia Regions

Continental Influence. Concentrations of ^{210}Pb range from 2.0 to 2.7 times higher in all altitude bins near Asia, but a steady decrease with altitude is apparent in both regions (Figure 2). Below

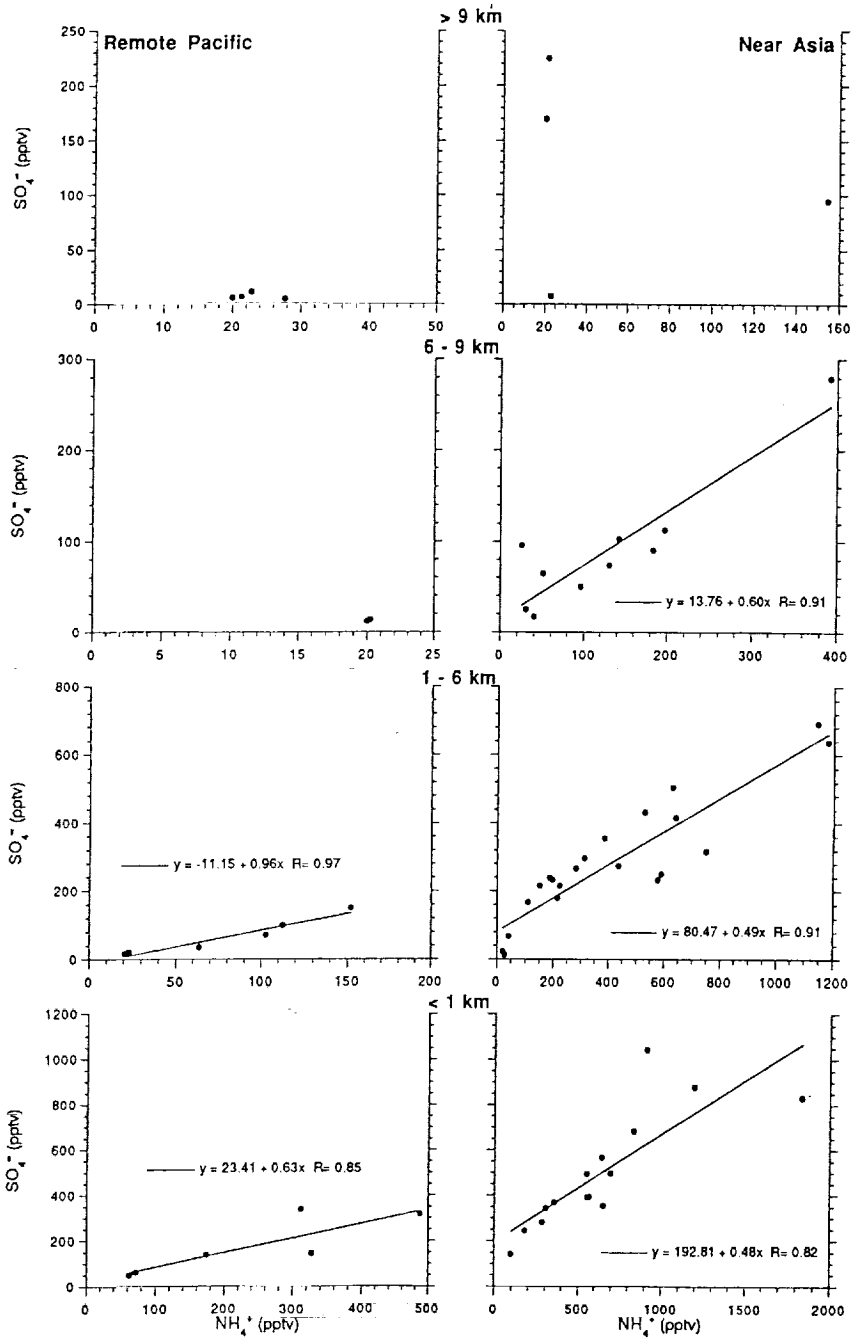

Figure 3. Scatterplots of $SO_4^=$ versus NH_4^+ in the eight data bins. Correlation coefficients for all bins without regression lines plotted (and more than three sample pairs) were ≤ 0.25.

9 km the trends in $SO_4^=$ and NH_4^+ concentrations are similar, but the near Asia region has mean concentrations that are 2.7- to 5.9-fold higher than those over the remote Pacific, with the largest differences in the two lowest altitude bins (0 - 6 km) (Figure 2). Sulfate tends to be nearly completely neutralized by NH_4^+ ($(NH_4)_2SO_4$) near Asia while NH_4HSO_4 appears to be more prevalent further east, particularly in the 1-6 km bin (Figure 3). These profiles suggest that strong Asian sources of $SO_4^=$ and particularly NH_4^+ are impacting air masses advecting over the Pacific. Comparisons between air masses stratified into continental versus marine on the basis of back trajectory analyses reinforce this hypothesis [*Talbot et al.*, this issue (a)]. Recent results from several flights southward from Tokyo during the summer season also suggest nearly complete neutralization of $SO_4^=$ by NH_4^+ close to land [*Yamato and Tanaka*, 1994]. However, these same flights found H_2SO_4 to be the dominant form of sulfate aerosol at latitudes below 30°S, or more than 1000 km from land, while our winter samples even further from Asia contained significant amounts of NH_4^+ (Figure 3).

The concentrations of formic, acetic, and nitric acids decrease rapidly from the boundary layer up to 9 km near Asia, while no altitude gradients were found for any of these acids in the more remote region (Figure 2). Again, differences between the two

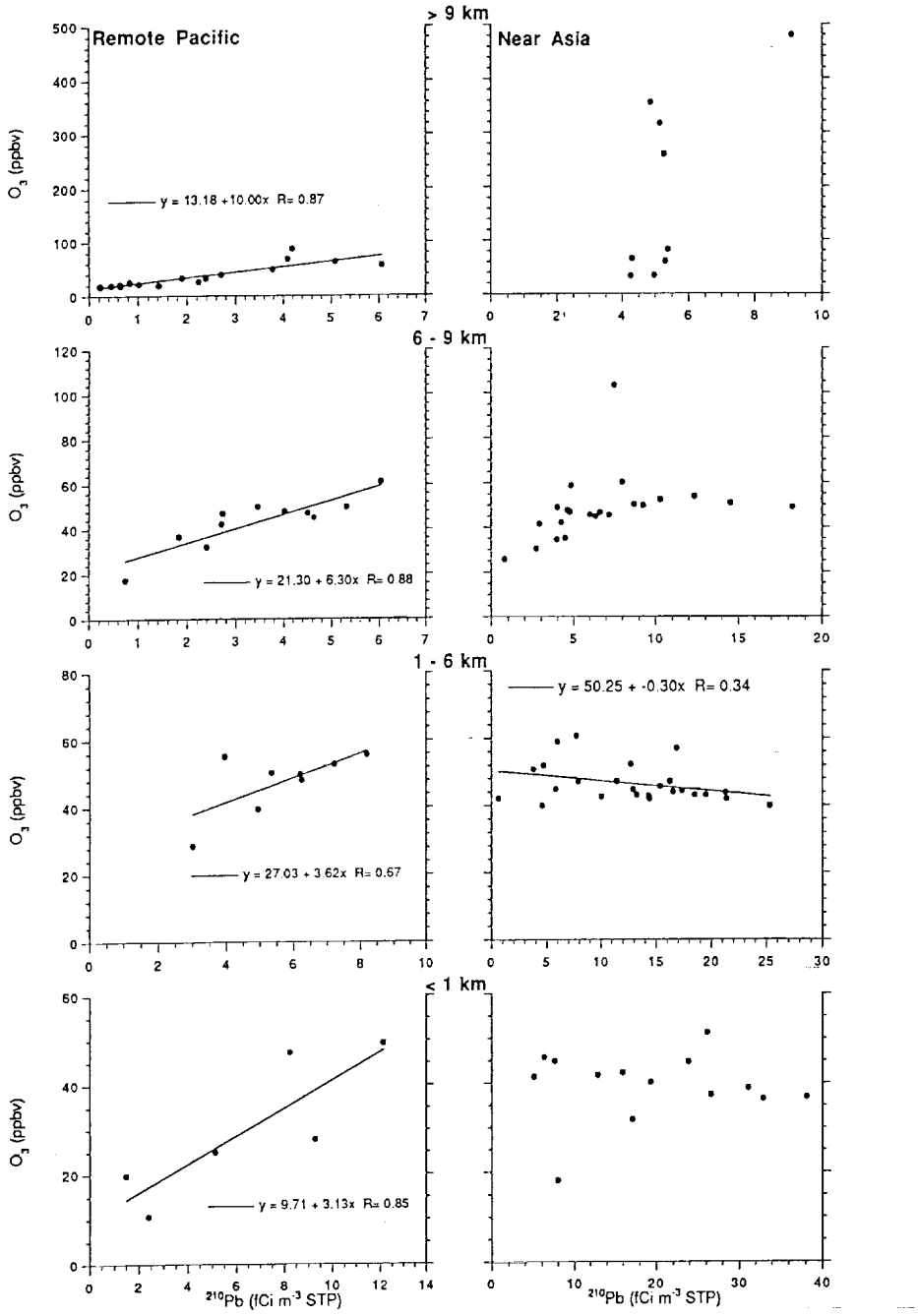

Figure 4. Scatterplots of ^{210}Pb versus O_3 in the eight data bins. Correlation coefficients for all bins without regression lines plotted (and more than three sample pairs) were $\leq$0.34.

regions are most prominent below 6 km, with mean concentrations near Asia 2 - 6 times higher. *Talbot et al.* [this issue (b)] discuss the complete (4 - 8 min sampling resolution) soluble acidic gas data set and suggest that enhancements in Asian air masses reflect combustion and other industrial emissions.

In the same 0 - 9 km altitude range where enhanced concentrations of soluble ionic species indicate the influence of sources on the Asian continent, the mean O_3 concentrations differ by less than 30% between regions in any of the altitude bins (Table 1, Figure 2). Ozone and ^{210}Pb concentrations are correlated ($r \geq 0.67$) in all altitude bins in the remote region (but not near Asia) (Figure 4). This relationship was present in both regions during PEM-West A (stronger near Asia), and was attributed to pumping of Rn and O_3 (and/or O_3 precursors) from the continental boundary layer high into the troposphere by deep wet convective systems [*Dibb et al.*, 1996]. The very low concentrations of soluble aerosol-associated species (readily scavenged) and the constant mean concentrations of soluble acidic gases throughout the depth of the free troposphere (reflecting vigorous vertical mixing) over the remote Pacific during PEM-West B would be consistent with deep wet convection over Southeast Asia and Indonesia, providing modified continental air to the remote free troposphere sampled by the DC-8 [*Talbot et al.*, this issue (a), (b)].

It has been suggested that deep wet convective pumping could

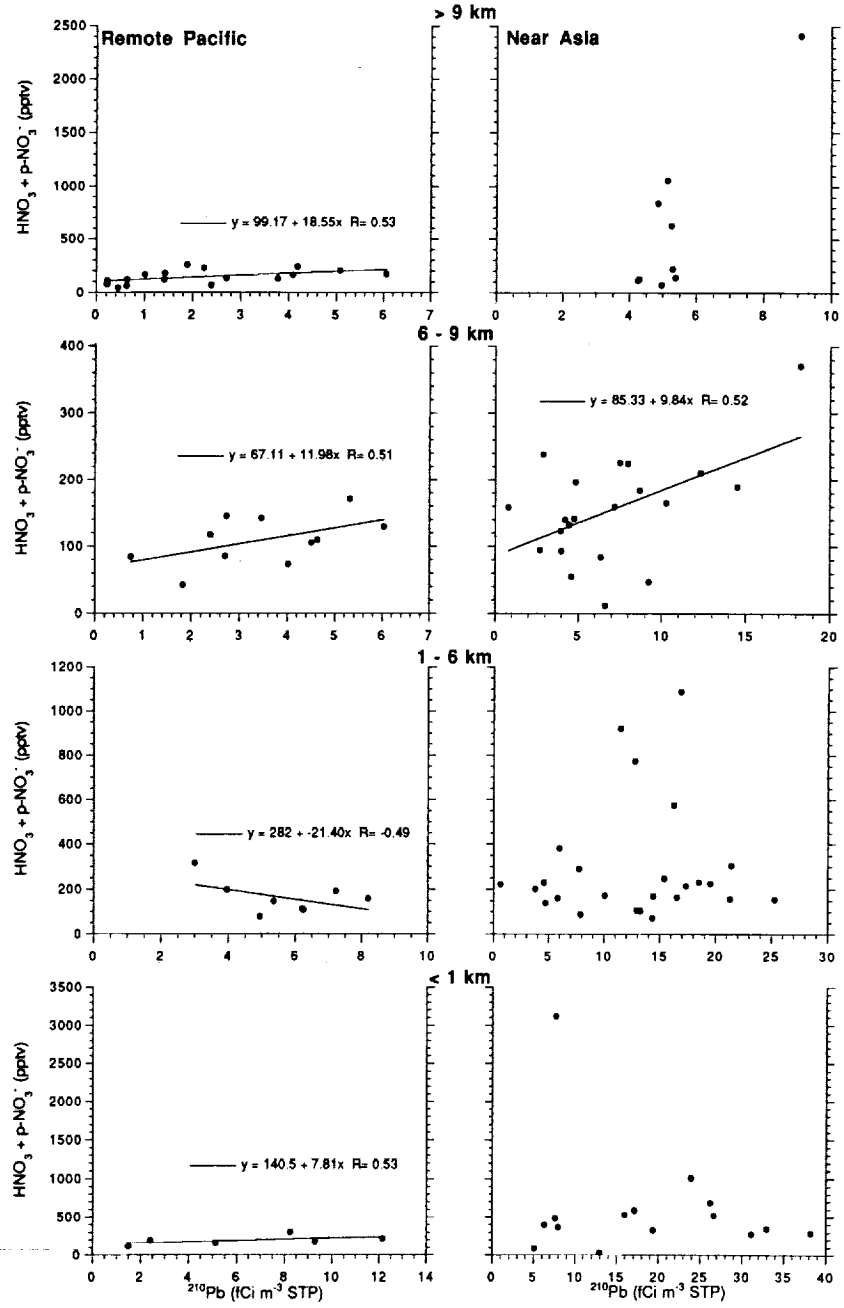

Figure 5. Scatterplots of ^{210}Pb versus HNO_3 plus p-NO_3^- in the eight data bins. Correlation coefficients for all bins without regression lines plotted (and more than three sample pairs) were $\leq$0.30.

also explain the correlation often observed between ^{210}Pb and inorganic nitrate at sampling sites on Pacific Islands, since both the ^{222}Rn and NO_x precursors are only sparingly soluble [e.g., *Savoie et al.*, 1989; *Balkanski et al.*, 1993]. No relationship was found between ^{210}Pb and p-NO_3^-, HNO_3, or their sum during PEM-West A, though a persistent correlation was seen between ^{210}Pb and peroxyacetylnitrate (PAN) [*Dibb et al.*, 1996]. Our PEM-West B samples also fail to reveal any strong relationship between ^{210}Pb and either of the two main inorganic nitrate species (not shown) or their sum (Figure 5). Likewise, no relationships were found between ^{210}Pb and NO (no NO_2 measurements were made during PEM-West B). However, relatively high correlations were found between ^{210}Pb and PAN in all free tropospheric bins over the remote Pacific, with a weaker relationship found only in the 6 - 9 km range closer to Asia (Figure 6). We hypothesize that these ^{210}Pb-PAN relationships during PEM-West B are again reflecting the importance of deep wet convection on the composition of the troposphere over the western Pacific, though the convective activity in spring is more equatorial than during fall, when the storms were mainly over central Asia. Meteorological analyses [*Merrill et al.*, this issue], the large-scale characterization of air masses from the UV-differential absorption lidar (DIAL) records (E.V. Browell et al., unpublished manuscript, 1997), and the distributions of hydrocarbons and halocarbons [*Blake et al.*, this issue] for PEM-West B also lead to the conclusion that deep convective pumping played a major role in the more southern and eastern regions of the western Pacific sampled by the

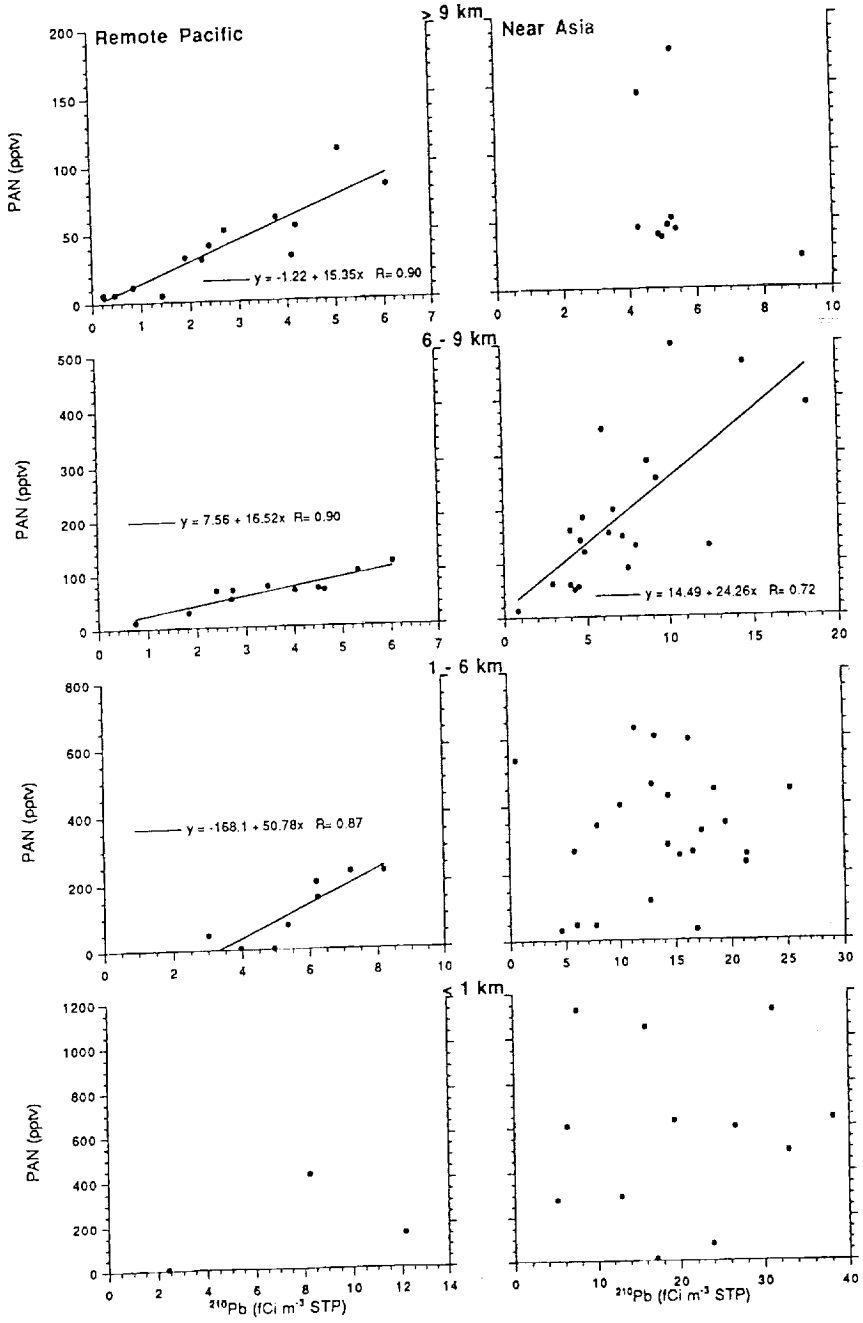

Figure 6. Scatterplots of ^{210}Pb versus PAN in the eight data bins. Correlation coefficients for all bins without regression lines plotted (and more than three sample pairs) were ≤0.32.

DC-8. Also, these other analyses suggest that the air masses encountered near Asia at 6 - 9 km were significantly impacted by northward advection of tropical air that had passed through deep clouds in the Intertropical Convergence Zone (ITCZ), with much of the convective activity near the numerous islands of Indonesia. This bin is the only one near Asia that showed a correlation between ^{210}Pb and PAN (Figure 6).

We speculated that this relationship between ^{210}Pb and PAN, relatively near the presumed continental source, may account for the correlation between ^{210}Pb and inorganic nitrate observed further downwind through thermal decomposition of PAN to NO_x and subsequent formation of HNO_3 and/or p-NO_3^- [*Dibb et al.*, 1996]. These new data from PEM-West B indicate that the association between ^{210}Pb and PAN also occurs during late-winter/early-spring in regions further from Asia. The ratio of $NO_3^-/^{210}Pb$ over the remote Pacific during PEM-West B (15 - 50 pptv/(fCi m^{-3})) (Figure 6) is directly comparable to the $NO_3^-/^{210}Pb$ ratio of 27 reported for Samoa [*Savoie et al.*, 1989], though this southern hemisphere site is felt to be receiving long-range continental influence from South America. We can also estimate the $NO_3^-/^{210}Pb$ ratio at Enewetak during spring as being approximately 20, from Sea-Air Exchange (SEAREX) data reported for 1979 (^{210}Pb [*Turekian and Cochran*, 1981]) and 1981-1982 (NO_3^- [*Prospero et al.*, 1985]). These observations suggest that a large fraction of the nitrate reaching

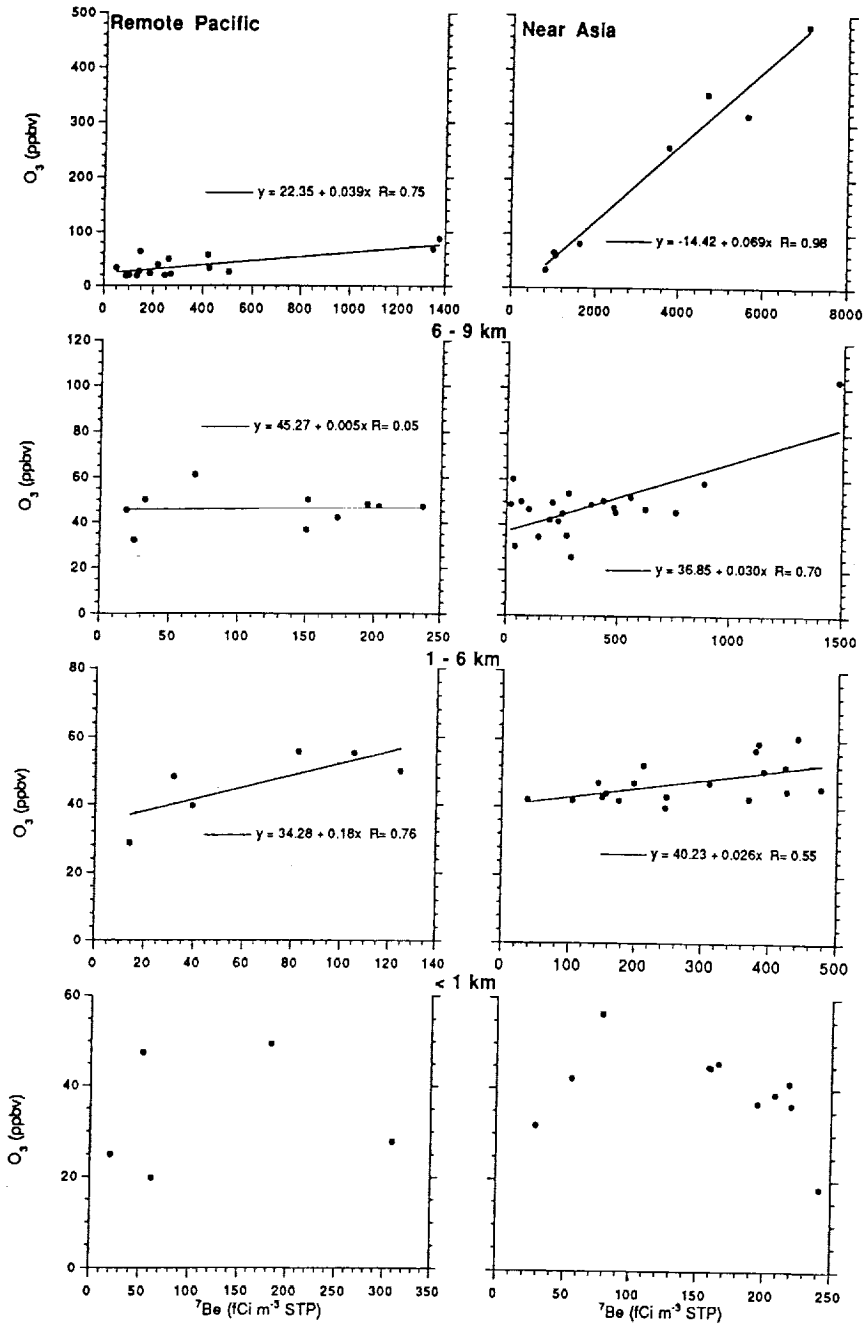

Figure 7. Scatterplots of ^{7}Be versus O_3 in the eight data bins. Correlation coefficients for all bins without regression lines plotted (and more than three sample pairs) were ≤0.20.

remote Pacific islands could originate as PAN (or insoluble precursors of PAN) which are then injected into the upper troposphere, along with high concentrations of ^{222}Rn, by convective pumping. It should be pointed out that the $NO_3^-/^{210}Pb$ ratio at the tropical North Atlantic Atmosphere/Ocean Chemistry Experiment (AEROCE) site on Barbados is also quite constant through the year at about 17, and very similar to those over the remote Pacific, despite much higher concentrations of both species [*Savoie et al.*, 1992]. At Barbados it is clear that the NO_3^- - ^{210}Pb relationship is reflecting transport from continental sources, but the possible role of PAN as an intermediary has not yet been investigated.

Stratospheric Influence. The concentrations of ^{7}Be, O_3, and HNO_3 are all strongly enhanced in the >9 km altitude bin near Asia (Figure 2, Table 1). Concentrations of $SO_4^=$ also increase in this bin, though by a relatively smaller amount. The very high concentrations of ^{7}Be and O_3 in some of the samples (Figure 1) are clear evidence of stratospheric inputs into the air masses sampled [e.g., *Dutkiewicz and Husain*, 1979, 1985]. Stratosphere to troposphere exchange has long been known to reach its annual peak in spring at midlatitudes [e.g., *Staley*, 1982; *Dutkiewicz and Husain*, 1985], so evidence of stratospheric influence on the composition of the troposphere was expected during PEM-West B. However, ^{7}Be - O_3 relationships in the eight region/altitude bins suggest that any stratospheric influence was quite weak outside of the highest near

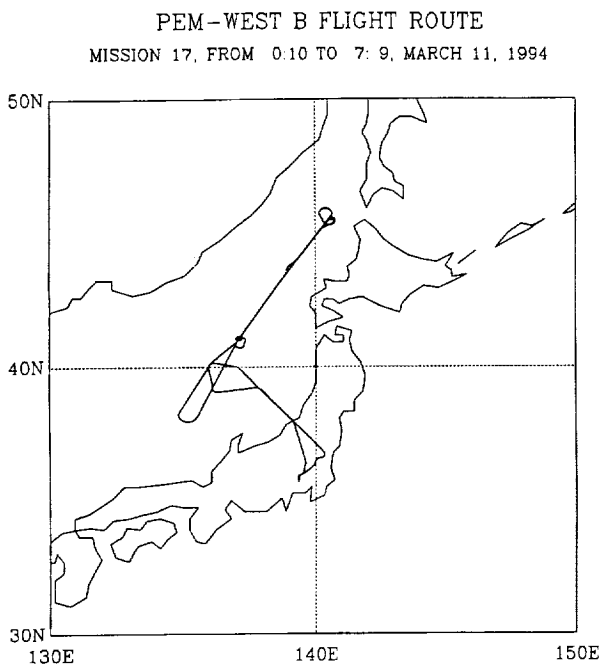

Figure 8. Flight track for flight 17, 0010-0709, March 11, 1994, over the Sea of Japan. The vertical wall was flown along the south west to north east trending "line" between about 38°N and 45°N.

Asia bin (Figure 7). In fact, all of the samples with O_3 concentrations >110 ppbv and ^{7}Be > 1.7 pCi m^{-3} were collected on a single flight.

This particular flight (17) provided a unique opportunity to characterize stratosphere to troposphere exchange through a tropopause fold [e.g., *Danielsen*, 1968, 1980; *Danielsen and Mohnen*, 1977; *Danielsen et al.*, 1987]. The flight track included long constant-altitude legs at five levels along a SW-NE line over the Sea of Japan (Figure 8). The highest altitude leg (10.7 km) was flown twice, first from SW to NE, and then back. Aerosol and O_3 vertical profiles measured with the UV-DIAL instrument on the 3.4 km leg of the wall clearly captured the structure of the fold the plane had flown through earlier (Plate 1). Concentrations of the stratospheric tracers ^{7}Be and O_3 are significantly higher on the southern half of both 10.7 km legs, decreasing to the north of the fold axis (Figure 9). These results are consistent with the dynamic mixing around the jet causing the tropopause fold, as such mixing has been described by Danielsen and coworkers.

Kritz et al. [1991] reported O_3 and ^{7}Be measurements through a similar tropopause fold near 35°N over the southwestern United States as part of the Stratosphere-Troposphere Exchange Project (STEP) program. In this earlier study, measurements were made in the stratosphere (12.5 - 20.7 km), and peak concentrations reached 13.5 pCi m^{-3} STP ^{7}Be and 3.8 ppmv O_3. However, eight samples collected between 12.5 and 15.2 km ranged 3.1 - 7.7 pCi ^{7}Be m^{-3} STP and 193 - 537 ppbv O_3, values that are comparable to our measurements at 10.7 km (Figures 7 and 9). Regression analysis indicates very similar relationships, with 1 pCi ^{7}Be m^{-3} STP associated with 59 ppbv O_3 at the lower levels we sampled, while the slope found in the subset of the STEP data set was 67 ppbv/(pCi m^{-3} STP). *Kritz et al.* [1991] observed a further steepening of slope between their lowest sampling altitudes and 20 km.

The fraction of stratospheric air in the samples we collected at 10.7 km can be roughly estimated from the ^{7}Be concentrations. If we assume equilibrium ^{7}Be concentrations at 40°N of about 8 pCi m^{-3} STP at 15 km, or 12 pCi m^{-3} STP at 20 km [*Bhandari et al.*, 1966], and take 0.5 pCi m^{-3} STP as a good estimate of the concentration at the top of the troposphere [*Kritz et al.*, 1991 and references therein], we calculate that a 43 - 88% contribution of 15 km stratospheric air could account for the measured ^{7}Be. If the stratospheric air originated as high as 20 km, the fraction required would drop to 22 - 45% for the 3.8 - 7.1 pCi ^{7}Be m^{-3} STP in these 4 samples. It should be noted that ^{7}Be data from the stratosphere to confirm the assumption of equilibrium are relatively sparse and that the dynamic processes associated with mixing around tropopause folds can be quite complex, potentially making simple linear mixing calculations suspect. However, *Kritz et al.* [1991] found good agreement for 3 different tracers with this approach, in a dynamically more complex fold than the lidar image (Plate 1) indicates we encountered, suggesting that the ^{7}Be observations should provide reasonable constraints on stratospheric influence in this case.

As a test of the validity of the assumed ^{7}Be end members and validity of the linear mixing assumption, we can use the calculated fractions of stratospheric air to estimate concentrations of other stratospheric tracers in the presumed stratospheric source. The mean O_3 mixing ratio in the highest altitude bin near Asia was 187 ppbv (Table 1), but this drops to 55 ppbv if the four samples from flight 17 are excluded. Using 55 ppbv O_3 as the tropospheric end-member yields estimated concentrations of 440 - 600 ppbv if the stratospheric air is assumed to have come from 15 km, or 640 - 883 if the source of the stratospheric air was at 20 km. The levels estimated for the 15 km source are consistent with O_3 profiles from sondes in April 1989 [*Austin and Midgley*, 1994], while measured levels at 20 km were three- to four-fold higher than our estimates. The suggestion of a lower stratospheric origin for the air transferred into the troposphere through the fold is in accord with the dynamics of this mixing process [e.g., *Danielsen*, 1968, 1980; *Danielsen and Mohnen*, 1977; *Danielsen et al.*, 1987].

The similar pattern of HNO_3 concentrations indicates a strong stratospheric source for this species as well. As was the case for O_3, excluding the four samples from flight 17 reduces the mean HNO_3 concentration above 9 km near Asia considerably, from 615 to 122 pptv. This estimate for an upper tropospheric end-member and the ^{7}Be-based estimates of stratospheric fraction yield estimated HNO_3 concentrations at 15 km in the lower stratosphere from 1.9 to 4.1 ppbv, in harmony with our measurements and model results that predict HNO_3 should be the dominant reactive N species in the lower stratosphere. *Talbot et al.* [this issue (b)] discuss the relationships between HNO_3, other measured reactive N species, O_3 and N_2O observed over the Sea of Japan and in several other less extensive encounters with stratospherically impacted air during PEM-West B and compare them to the limited number of previous in situ measurements of this suite of species in stratospheric air.

The concentrations of ^{210}Pb in the four samples from this flight averaged 6.1 fCi m^{-3} STP, slightly higher than the overall mean for all samples in this bin (Table 1). Similar calculations suggest that concentrations in the lower stratosphere are in the range of 5.3 - 9.7 fCi ^{210}Pb m^{-3} STP. These concentrations would be in very good agreement with the mean of 8 fCi m^{-3} STP for the 15-19 km range (Krey as cited by *Lambert et al.*, [1982]), but the small difference between the assumed tropospheric end-member and estimated stratospheric end-member suggests that the latter may be quite uncertain.

Comparisons Between Spring and Fall Seasons. The spring timing of PEM-West B was selected to allow sampling of air

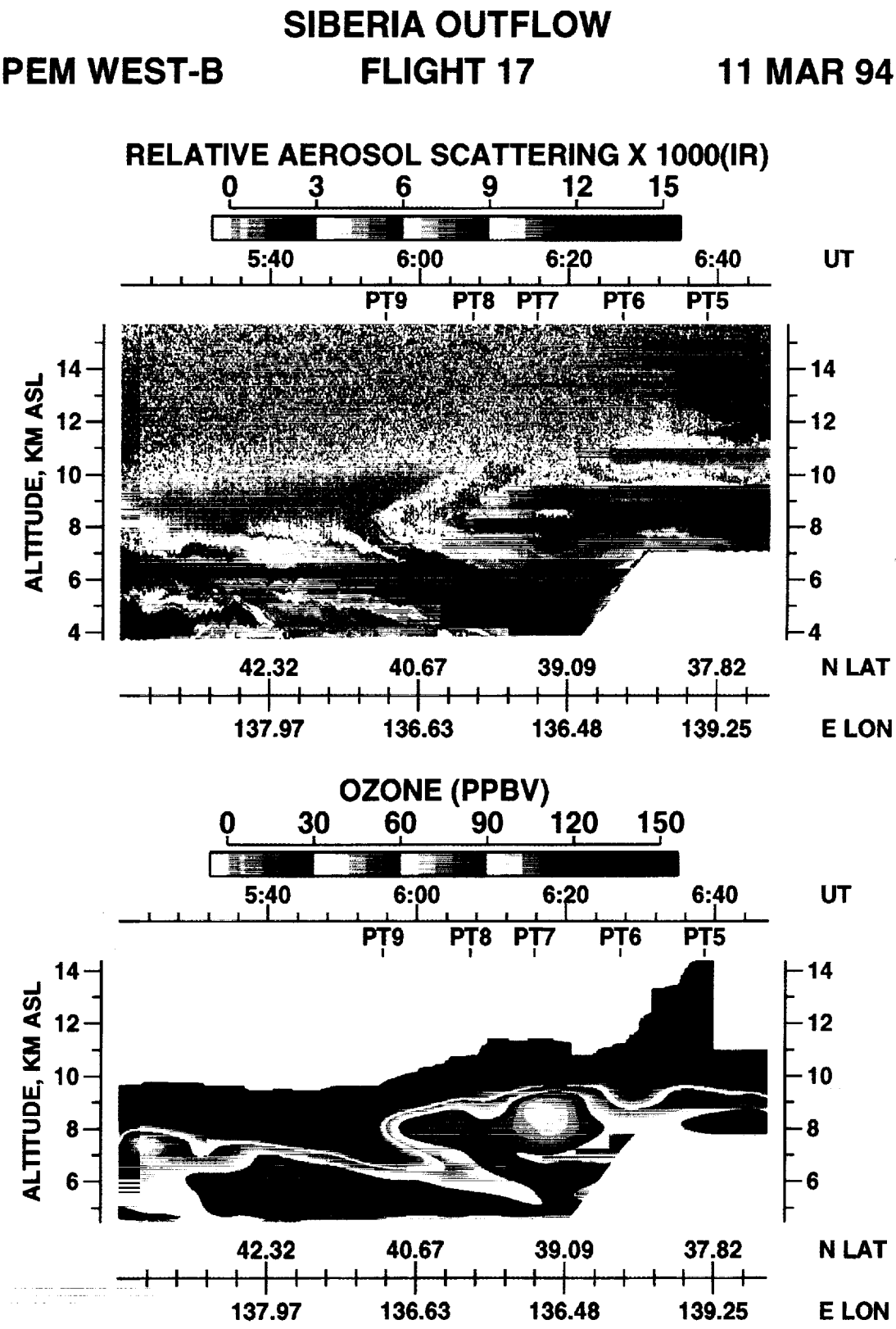

Plate 1. Zenith profiles of O_3 and aerosol scattering from the UV-DIAL instrument. These data were collected during the 3.4 km leg of the vertical wall, looking upward at the air masses the DC-8 had earlier flown through. A tropopause fold is clearly outlined in both sets of data.

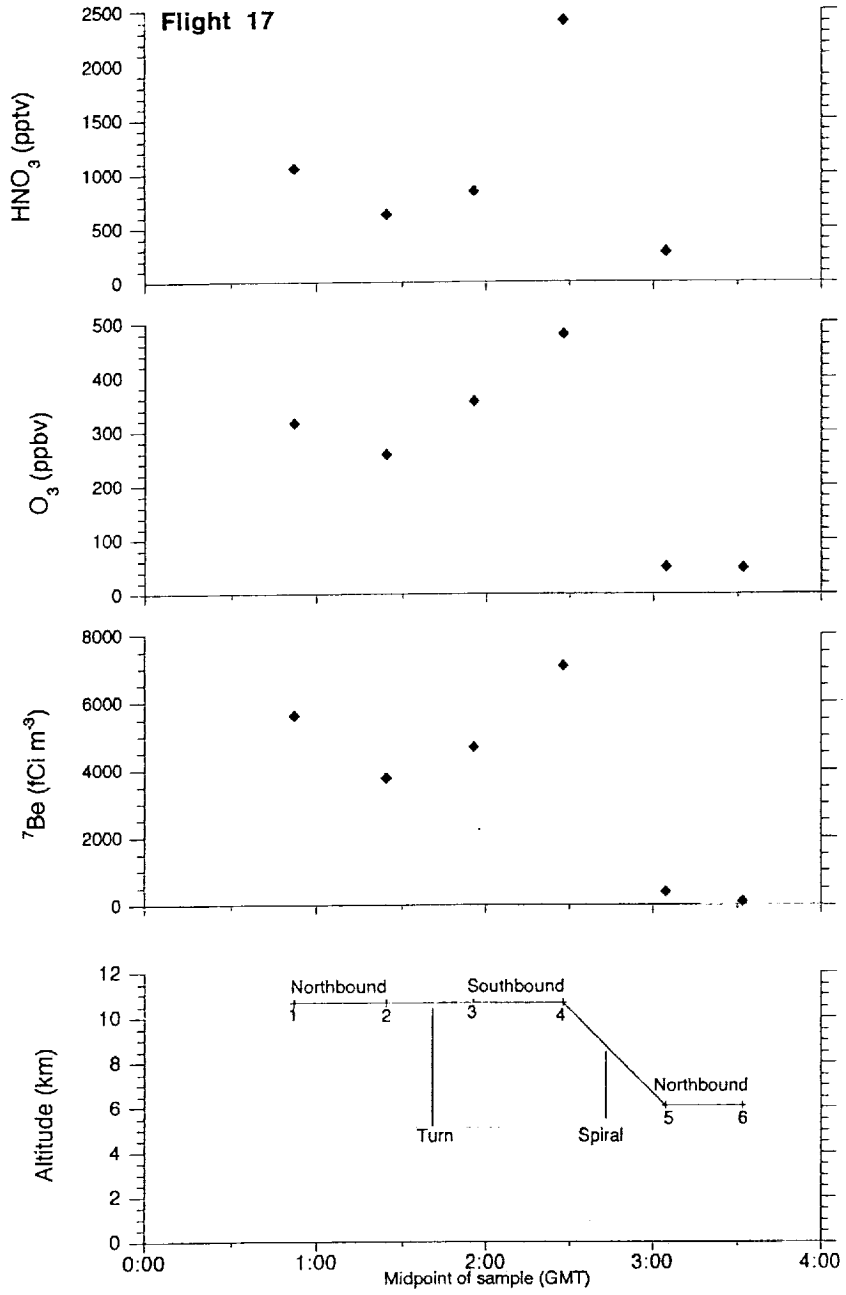

Figure 9. Mean concentrations of HNO_3, O_3 and ^{7}Be in the first six aerosol sampling intervals of flight 17. As depicted in the lower panel, the first four aerosol samples were all collected during the 10.7 km leg of the wall, with five and six from the 6.1 km leg.

masses over the Pacific during the period of peak Asian dust outflow [e.g., *Prospero et al.*, 1985; *Merrill et al.*, 1989; *Gao et al.*, 1992]. Comparisons to PEM-West A results (conducted in the fall) should reflect the expected seasonal contrast. We noted that most soluble aerosol-associated species were not detected above the boundary layer during PEM-West A [*Dibb et al.*, 1996]; thus there was general enhancement of these species during PEM-West B (Table 1).

The largest difference in the binned data for aerosol-associated species and O_3 near Asia reflects the intrusion of stratospheric air into the upper troposphere (discussed in the preceding section) (Figure 10). Enhancements of ^{210}Pb, NO_3^-, $SO_4^=$, and NH_4^+ are apparent throughout the tropospheric column near Asia in spring, but they do not exceed a factor of 3. Over the remote Pacific, ^{210}Pb and O_3 are the only species to show large concentration differences between the seasons, with the 1-9 km region containing at least twice as much of both species during spring (Figure 11). Given the previously noted widespread influence of Asian dust throughout the Pacific during the spring, larger enhancements between PEM-West A and B might have been expected.

These observations may be partially explained by the fact that there was a considerable Asian influence on tropospheric composition over the western Pacific even in the fall season sampled in PEM-West A [e.g., *Dibb et al.*, 1996; *Talbot et al.*, 1996]. *Talbot*

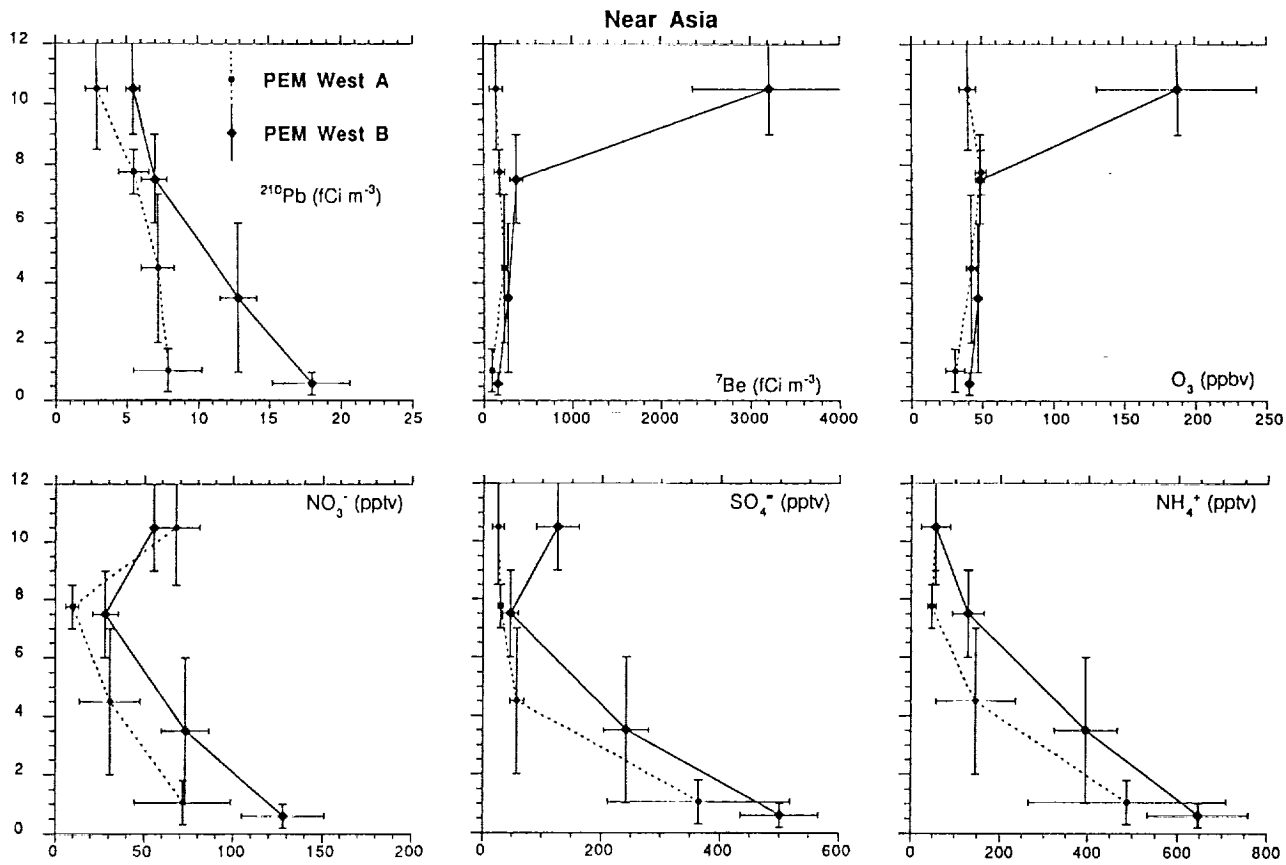

Figure 10. Comparisons between the mean concentrations of selected aerosol-associated species and O_3 in four altitude bins near Asia during PEM-West A and PEM-West B.

et al. [this issue (a)] and *Blake et al.* [this issue] point out that concentrations of sparingly soluble tracers with continental sources (e.g., CO and several nonmethane hydrocarbons (NMHC)) show more pervasive enhancements, up to higher altitudes, over much of the region sampled in PEM-West B than are apparent in easily scavenged constituents like aerosols or the acidic gases. These observations suggest that wet convective pumping of material from the continental boundary layer into the free troposphere may be an important step for transport of Asian signatures over the Pacific during spring, as we have hypothesized for fall [*Dibb et al.*, 1996]. It is also possible that the February-March timing of PEM-West B was too early to capture the peak episodes of dust (and other readily scavenged species) transport from Asia eastward over the Pacific.

Conclusions

Comparison of the concentrations of aerosol-associated species measured during PEM-West B and A confirmed the expectation that Asian outflow should be stronger in spring than fall, though the enhancement in binned concentrations of the most abundant continentally derived species did not exceed a factor of 3. The largest enhancements in concentrations of aerosol-associated species were restricted to low (< 6 km) altitudes. In contrast, *Talbot et al.* [this issue (a)] demonstrate that a strong springtime increase of Asian influence is evident through much of the troposphere if gas phase tracers of combustion and industrial emissions that are less easily scavenged are considered.

Correlations between the concentrations of ^{210}Pb and O_3 in the region sampled on flights out of Guam, where concentrations of anthropogenic aerosols and their soluble gaseous precursors were quite low, reflect the role wet convective pumping of continental-boundary-layer air to the free troposphere plays in the export of pollutants to remote regions. Similar correlations during PEM-West A were limited to the near-Asia region, reflecting a seasonal shift in the occurrence of deep, wet convection from central Asia in summer and fall to Southeast Asia and Indonesia in spring. In the same remote Pacific region, ^{210}Pb concentrations were also correlated with PAN mixing ratios. During PEM-West A, ^{210}Pb-PAN correlations were seen mainly in the near-Asia region. The wet convective pumping mechanism appears to result in free tropospheric air masses which favor the production of PAN over inorganic nitrates, at least during the first few days of transport eastward from the Asian continent that we were able to characterize during the two PEM-West missions. Subsequent decomposition of PAN when these air masses subside over the central Pacific could provide significant amounts of NO_x and allow production of the inorganic nitrates in ^{210}Pb-rich air far from the continental sources.

The distribution of ^{7}Be, and its relationship to O_3, suggests that stratospheric influence on the composition of the troposphere over the western Pacific was relatively weak, with strongest impacts restricted to the highest latitudes sampled. However, one flight provided the opportunity to sample below and through a well-defined tropopause fold near 40°N. The peak ^{7}Be concentration measured in the center of the fold at 10.7 km (7 pCi m^{-3}) was

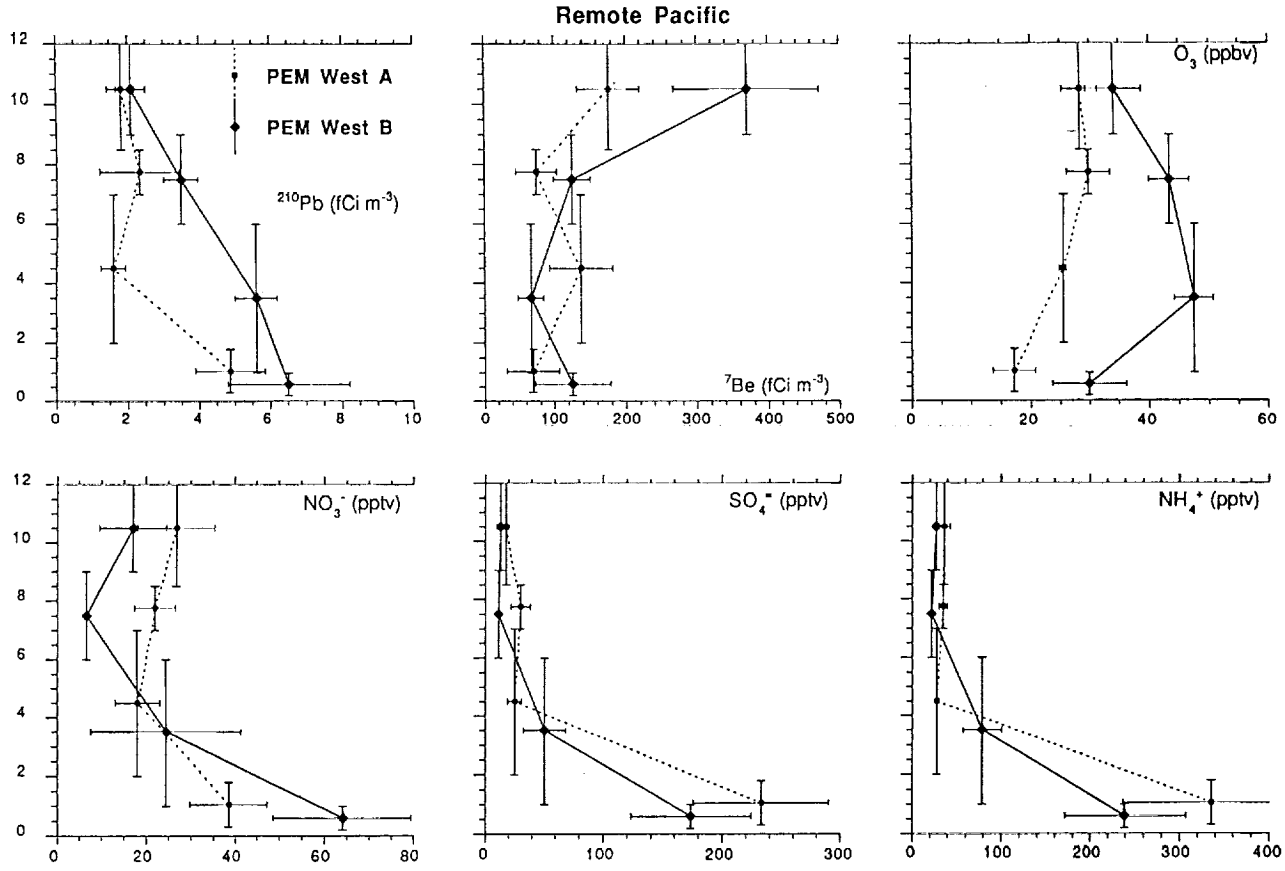

Figure 11. Comparisons between the mean concentrations of selected aerosol-associated species and O_3 in four altitude bins over the "remote" Pacific during PEM-West A and PEM-West B.

consistent with a two-component mixture of stratospheric air from 15 km (88%) and upper tropospheric air (12%). Three other samples collected in and near the fold at the same latitude required greater than 43% contributions from the same stratospheric source to account for their elevated ^{7}Be concentrations. The next highest ^{7}Be concentration measured on all other PEM-West B flights was only 1.6 pCi m^{-3}, or nearly 2.5 times lower than the lowest concentration measured near the fold, implying a maximum stratospheric fraction well below 20% in the upper troposphere air masses that were sampled over the western Pacific in February - March 1994.

Acknowledgements. We would like to thank the NASA Ames DC-8 flight and ground crews for their excellent support throughout PEM-West B. Also, the efforts of S. I. Whitlow to ensure that the radionuclide aerosol samples were promptly processed while we were still on deployment are much appreciated. The comments of W. Graustein and an anonymous reviewer improved this paper, and we thank them for their time. This research was supported by the NASA Global Tropospheric Chemistry program.

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(Received September 6, 1995; revised August 12, 1996; accepted August 20, 1996.)