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Asian influence over the western North Pacific during the fall season: Inferences from lead 210, soluble ionic species and ozone

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Abstract. Aerosol samples collected over the western Pacific during the NASA/Global Tropospheric Experiment Pacific Exploratory Mission (PEM-West A) expedition (September - October 1991) revealed mean ^{210}Pb concentrations in the free troposphere in the 5 - 10 fCi m^{-3} STP range. Most soluble ionic aerosol-associated species were near detection limits [<< 40 parts per trillion by volume (pptv)] in these same samples. The altitude distribution of O_3 near Asia closely resembled that of ^{210}Pb, while no relationship was found between the concentrations of O_3 and ^{7}Be. Free tropospheric air over the western Pacific was depleted in soluble aerosol-associated species but enriched in ^{210}Pb and O_3, indicative of deep wet convection over the Asian continent. The influence of Asian air on the composition of the free troposphere over the western Pacific was evident on most of the PEM-West A flights. However, evidence of continental influence was largely restricted to those species that are relatively insoluble (or have insoluble precursors), hence escape scavenging during vertical transport from the boundary layer into the free troposphere by wet convective activity.

Introduction

It is well established that Asian air transported eastward in the free troposphere causes peak concentrations of mineral aerosols at a number of remote Pacific island sites, especially in the spring [e.g., *Prospero et al.*, 1985; *Merrill et al.*, 1989; *Gao et al.*, 1992]. This transport pattern, combined with increasing industrialization in the Asian region, suggests that anthropogenic emissions in Asia may play an increasing role in the composition of the atmosphere over the western North Pacific. The objective of the Pacific Exploratory Mission (PEM-West A) airborne sampling campaign in September - October 1991 was to characterize the composition of the Pacific atmosphere near Asia during the fall season, when the outflow of Asian dust was expected to be near the low point in its seasonal cycle. The NASA Ames DC-8, with an extensive load of remote and in situ atmospheric chemistry instrumentation, flew 17 missions, totaling 120 hours, over the Pacific Ocean toward this end (see overview by *Hoell et al.* [this issue]). The follow-up mission, PEM-West B, was flown in the same regions in February - March 1994 to characterize the spring period when the continental influence was expected to be stronger. Analyses of results from PEM-West B are in progress and will be reported in later papers.

This paper discusses the composition of aerosol samples collected during PEM-West A. Concentrations of a suite of water-soluble ionic species (Cl$^-$, NO$_3^-$, SO$_4^=$, MSA, C$_2$O$_4^-$, PO$_4^{3-}$, Na$^+$,

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NH$_4^+$, K$^+$, Mg^{2+}, and Ca^{2+}) and the natural radionuclides ^{210}Pb and ^{7}Be were determined. Lead 210 and ^{7}Be have well-defined sources and simple atmospheric chemistry, making them valuable tracers of continental and upper troposphere/lower stratosphere air, respectively [see *Dibb et al.*, 1992, and references therein]. We focus on the spatial and altitudinal distribution of ^{210}Pb and its relationship to the distributions of other aerosol-associated and gaseous species measured during PEM-West A, in order to assess the influence of Asian air on the composition of the Pacific atmosphere. Several companion papers address this same question with additional tracers and meteorological analyses [*Browell et al.*, this issue; *Gregory et al.*, this issue; *Smyth et al.*, this issue; *Talbot et al.*, this issue]; these independent approaches validate the utility of ^{210}Pb as a tracer of continentally influenced air over the Pacific.

Methods

Sampling

Aerosol samples for radionuclide and soluble ionic analyses were collected on separate 90-mm-diameter, 2-μm pore size, Zefluor filters. Two sampling systems (see below) were operated in parallel, so that exposure times for the radionuclide and ionic samples were identical. Sampling was restricted to flight legs at constant altitude. During the intensive flights this resulted in filter exposure periods generally between 20 and 45 min in duration. On transit flights with long constant altitude legs, aerosol filters were changed at 45- to 60-min intervals. The volume of sampled air thus ranged 1.4 - 17.5 m^3 STP. Two to eight samples were collected on each of the 17 flights during PEM-West A.

Collecting aerosol samples without altering the characteristics of the ambient aerosol population is never a trivial problem; high-speed airborne platforms present additional challenges in this regard [e.g., *Huebert et al.*, 1990; *Porter et al.*, 1992]. As a participant in NASA's Global Tropospheric Experiment (GTE) since 1983, RWT has continuously refined sampling systems to reduce differences between the ambient and sampled aerosol

populations (R.W. Talbot et al., Improvements in aerosol inlet performance in airborne applications, submitted to *Journal of Geophysical Research*, 1995 hereinafter referred to as T95). Two identical aerosol sampling probes were employed during PEM-West A. These consisted of curved leading edge nozzles (0.7-cm diameter) positioned on the centerline of a 15.2-cm diameter by 40.6-cm-long shroud. The leading edge of the inlet nozzle was 19.0 cm back from the leading edge of the shroud. Nozzles with a curved leading edge design have been shown to reduce aerosol losses due to turbulence within the inlet when compared to nozzles with sharp leading edges [*Porter et al.*, 1992; T95]. Locating the nozzle within a shroud results in air streamlines that are more nearly parallel to the nozzle's long axis, again helping to reduce aerosol losses from flow-separation induced turbulence inside the inlet just downstream of the nozzle's leading edge [*McFarland et al.*, 1989; *Cain et al.*, 1993; T95]. The nozzle ID increased from 0.7 to 5.0 cm over a length of 23.0 cm and then attached to 5.0-cm ID seamless stainless steel inlet tubing. This tubing bent 45° with a 46-cm radius of curvature to penetrate the fuselage.

Both aerosol probes were mounted on the same 62° port on the upper left side of the DC-8, 1194 cm from the nose of the plane. Air velocity within the shrouds was monitored with pitot tubes within the shroud and the static air temperature measured by GTE project instrumentation and was found to be essentially equal to the true air speed. Sampling flow rates were adjusted to ensure that air velocities through the nozzles were within 5 - 10% of true air speed at all altitudes. Integrating linear mass flow meters (Teledyne-Hastings Radist) were used to measure flow rates and the volume of air sampled.

Analysis

The filters for soluble ionic analyses were extracted in the field within 12 hours of each flight, following procedures that have been previously described [*Talbot et al.*, 1986, 1992]. These extracts were analyzed for anionic species by ion chromatography immediately after extraction. Aliquots preserved with chloroform were subsequently analyzed for cationic species, again by ion chromatography, in the laboratory at the University of New Hampshire (UNH) after completion of the mission.

All filters for radionuclide analyses were subjected to nondestructive gamma spectrometry at UNH within 2 - 4 weeks of collection to quantify ^{7}Be activities [*Dibb*, 1990a; *Dibb et al.*, 1992]. (Groups of filters were express mailed to New Hampshire from the field sites at weekly intervals.) Uncertainties in ^{7}Be activity due to counting statistics were below 20% for 16-hour counting periods when the activity exceeded 100 fCi m^{-3} but increased for samples with lower activity. The small air volumes sampled precluded quantification of ^{210}Pb by direct gamma counting. We determined ^{210}Pb activities by alpha spectrometric determination of ^{210}Po (with ^{208}Po tracer added and plating onto Ag planchets) [*Flynn*, 1968; *Dibb*, 1990b] after allowing 1 year for ^{210}Po ingrowth. The ^{210}Po/^{210}Pb ratio will be 85-90% of its value at secular equilibrium after 12 - 14 months (the last samples were processed 2 months after the first), assuming that the aerosols were so young at collection that no ^{210}Po was present. We did not correct the ^{210}Pb activities reported below for this departure from equilibrium, hence they may be as much as 10 - 15% low. The sensitivity of this technique is quite good and can be improved simply by accumulating counts for a longer time period, provided the background count rate is low and stable. (In theory, the same is true for gamma spectrometry, but the short half-life of ^{7}Be precludes very long counting periods, particularly when there is a

sample backlog.) For this study, four samples were counted concurrently until the uncertainty due to counting statistics of the least active sample in each group dropped below 15%, or 8 days had passed. Most samples were counted 3 - 6 days, with 1/4 having uncertainties of 14 - 15% and the rest lower.

Detection limits for the aerosol-associated species were defined as 2 times the standard deviation of the concentration of each analyte determined in 40 blank filters, generated at a rate of at least 2 for each flight, divided by the volume of air collected for a particular sample. For the mean volume of air sampled during PEM-West A (8.9 m^{-3} STP per sample), detection limits would be 0.5 fCi ^{210}Pb m^{-3} STP, 10 fCi ^{7}Be m^{-3} STP, 30 pptv Cl$^-$, 5 parts per trillion by volume (pptv) NO$_3^-$, 9 pptv SO$_4$=, 1 pptv MSA, 2 pptv C$_2$O$_4$=, 20 pptv PO$_4^{3-}$, 40 pptv Na$^+$, 25 pptv NH$_4^+$, 17 pptv K$^+$, 6 pptv Mg^{2+}, and 14 pptv Ca^{2+}. Analytical details for other species discussed in this paper are provided in companion papers in this issue. All of the data are archived at and available from the NASA/GTE project office.

Results

A total of 98 aerosol samples were collected during PEM-West A. All of the samples had ^{210}Pb activities that could be quantified by our techniques, while ^{7}Be and SO$_4$= were quantified in 82 and 90 samples, respectively. Nitrate and NH$_4^+$ mixing ratios were also high enough to quantify in more than 1/2 the samples, but all other soluble ionic species were below our detection limits more often than not (Table 1). Mean concentrations of all aerosol-associated species, except ^{7}Be, were higher in the 0- to 2-km altitude range than at higher elevations. This difference would be accentuated for most of the ionic species if all samples below detection limit were included in the averaging process (Table 1).

We expected ^{210}Pb activities to decrease rapidly with altitude and ^{7}Be activities to increase. However, the observed contrasts between boundary layer and free tropospheric activities of ^{7}Be and ^{210}Pb were quite small. Nearly 1/2 of the samples above 2 km were collected between 6 and 13 km where ^{210}Pb activities near or below 2 fCi m^{-3} STP were expected [e.g., *Moore et al.*, 1973; *Lambert et al.*, 1982], yet the PEM-West A mean was 4 fCi m^{-3} STP (Table 1). Middle and upper troposphere mean ^{7}Be activities in the 400 - 1000 fCi m^{-3} range have been previously reported for several regions [*Bhandari et al.*, 1966; *Dutkiewicz and Husain*, 1979, 1985; *Dibb et al.*, 1992]; the mean measured over the western Pacific is more than twofold lower than these values (Table 1). This aggregated overview suggests "too much" ^{210}Pb and "too little" ^{7}Be were present in the free troposphere over the western Pacific.

Many of the PEM-West A flights were characterized by vertical separation of marine and continental air masses. Similar layering has also been reported for the eastern Pacific [*Paluch et al.*, 1992]. *Talbot et al.* [this issue] and *Gregory et al.* [this issue] use a combination of meteorological analyses and chemical tracers to identify periods when the DC-8 was clearly sampling air that had been over land within 5 days before it was encountered (continental) or had not passed over land in the previous 10 days (marine), respectively. We adopt the same air mass classifications to stratify the aerosol composition data (Table 2). Nitrate, SO$_4$=, and NH$_4^+$ were the only soluble ionic species detected above the boundary layer in this subset of the data. These three species plus Na$^+$ and Mg^{2+} were slightly enhanced in northern versus southern hemisphere marine boundary layer air. Free-tropospheric marine air in the northern hemisphere showed NH$_4^+$ enhancement relative to that from the southern hemisphere. Not surprisingly, continen-

Table 1. Summary of the Radionuclide Activities and Soluble Ionic Concentrations in all Aerosol Samples Collected During PEM-West A

^{210}Pb	^{7}Be	Cl$^-$	NO$_3^-$	SO$_4^=$	MSA	C$_2$O$_4^-$	PO$_4^{3-}$	Na$^+$	NH$_4^+$	K$^+$	Mg^{2+}	Ca^{2+}
					0 – 2 km							
5.6	112	313	52	266	3.2	6.1	92	390	402	40	54	72
(5.9)	(83)	(73)	(66)	(368)	(2.0)	(5.4)	(41)	(584)	(565)	(63)	(67)	(92)
25	*17*	*23*	*23*	*24*	*8*	*17*	*3*	*22*	*21*	*14*	*21*	*8*
					2 – 13 km							
4.1*	218*	132	25	51	11	4.1	83	144	67	10	17	38
(3.4)	(160)	(104)	(24)	(71)		(6.0)	(46)	(108)	(113)	(11)	(11)	(35)
65	*59*	*4*	*34*	*66*	*1*	*17*	*6*	*18*	*32*	*30*	*13*	*14*
					Detection Limits							
0.2	10	30	5	9	1	2	20	40	25	17	6	14

Activities of ^{210}Pb and ^{7}Be are reported in fCi m^{-3} STP, all ionic concentrations in parts per trillion by volume. Simple arithmetic means (with standard deviation) are given for all samples above detection limits. The number of such samples is shown in italics; ^{210}Pb was detected in all samples, but all other species were below detection limits in at least one sample.

*A total of 73 filters were collected at altitudes above 2 km. Eight of these were on the transit flights at altitudes between 9.8 and 11 km, in the lower stratosphere or upper tropospheric air with large stratospheric influence. These filters were not analyzed for ^{210}Pb, nor were the ^{7}Be concentrations included in the averages above. Including the mean ^{7}Be concentration on these eight filters (2134 fCi m^{-3} STP) raises the overall mean above 2 km to 428 fCi m^{-3} STP.

tally derived air showed large enhancements of all soluble ionic species except Cl$^-$ and MSA. However, this impact was largely restricted to the boundary layer. Sulfate, NH$_4^+$, and perhaps NO$_3^-$ concentrations were also elevated in continental outflow between 1 and 7 km (Table 2).

Activities of ^{210}Pb and ^{7}Be were lowest in southern hemisphere marine air at all elevations (Table 2), suggesting a lengthy aging period since any continental influence and efficient removal of submicron aerosols. Comparing ^{210}Pb concentrations in aged

marine air between hemispheres suggests a diffuse continental influence at all altitudes in the north. Concentrations of ^{210}Pb were higher in continental outflow than northern aged marine air, but this was hardly unexpected since ^{210}Pb was one of the tracers used to define continental influence [*Talbot et al.*, this issue]. In the northern hemisphere, ^{210}Pb activities in the 1- to 7-km altitude range were higher than the mean below 1 km in both aged marine and clearly continentally influenced air, in contrast to the anticipated rapid decrease with height. Similarly, ^{7}Be distributions

Table 2. Composition of Aerosols in Air Masses Characterized As Marine Versus Continental [see *Talbot et al.*, this issue] for Discussion of Criteria Used to Define Air Mass Types

n*	Alt km	^{210}Pb	^{7}Be	Cl$^-$	NO$_3^-$	nss-SO$_4^-$	MSA	NH$_4^+$	Na$^+$	K$^+$	Mg^{2+}	Ca^{2+}
				Southern Hemisphere Aged Marine								
2	<1	0.4	27	224	<5	20	<1	33	66	<17	15	<14
		(0.4)	(23)	(59)		(12)		(11)	(9)		(2.1)	
2	1-7	0.7	43	<30	17	18	<1	<25	<40	<17	<6	<14
		(0.3)	(46)		(9)	(13)						
4	7-13	0.6	95	<30	21	22	<1	<25	<40	<17	<6	<14
		(0.2)	(98)		(28)	(9)						
				Northern Hemisphere Aged Marine								
9	<1	4.0	43	157	17	142	1.4	103	246	<17	35	<14
		(1.7)	(71)	(69)	(9)	(98)	(0.7)	(43)	(249)		(31)	
8	1-7	5.4	218	<30	10	45	<1	30	<40	<17	<6	<14
		(2.7)	(97)		(12)	(31)		(15)				
25	7-13	2.4	151	<30	15	21	<1	35	<40	<17	<6	<14
		(1.6)	(135)		(18)	(17)		(15)				
				Asian Continental Outflow								
2^b	<1	23.0	121	263	239	1363	<1	1938	1053	156	101	51
		(0.7)	(89)	(174)	(51)	(219)		(446)	(957)	(121)	(64)	(19)
8	<1	5.5	101	140	61	325	2.3	489	149	26	65	<14
		(3.3)	(95)	(108)	(37)	(159)	(1.2)	(192)	(81)	(28)	(93)	
7	1-7	11.5	235	<30	38	104	<1	273	<40	<17	<6	<14
		(3.1)	(103)		(46)	(101)		(387)				
7	7-13	7.7	222	<30	13	32	<1	30	<40	<17	<6	<14
		(3.4)	(226)		(15)	(15)		(10)				

The mean activities (and standard deviations) for the radionuclides are given in fCi m^{-3} STP, soluble ionic concentrations (and standard deviations in parts per trillion by volume. For the cases when an ionic species was not quantifiable, the concentration is reported as less than the mean detection limit.

*n, Number of samples used to derive these average values.
^{b}Very strong outflow at low altitude on flight 13 was separated from other low-altitude samples impacted by continental outflow.
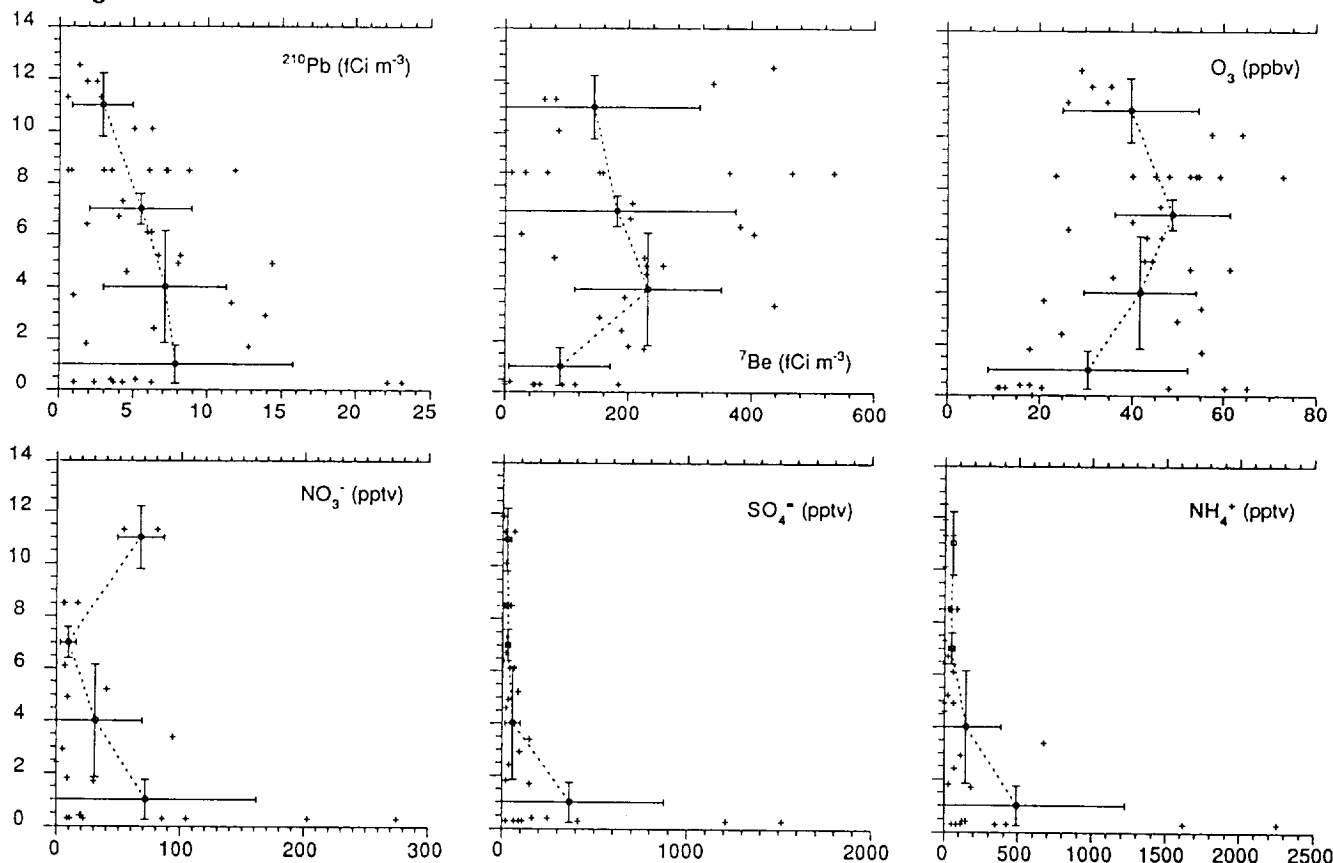
Figure 1. Altitude distributions of the concentrations of all aerosol species that were detected in more than 1/2 the samples. Average O_3 concentrations during the period when each aerosol sample was collected are also shown. Average concentrations were calculated for four altitude bins, these are shown as pluses, with the horizontal arms representing standard deviations and vertical arms the altitude range. Results have been separated on the basis of location into a near-Asia group (a) and those over more remote regions of the western Pacific (b).

departed from expectations, showing little or no increase with height in the free troposphere in the northern hemisphere, and only a twofold to threefold increase between the boundary layer and free troposphere in both continental and aged marine air masses (Table 2).

Discussion

Binning the aerosol data by altitude band and air mass type (Table 2) suggests that the free troposphere in the PEM-West A study area was depleted in all aerosol-associated species except ^{210}Pb. Such binning also highlights the scarcity of soluble ionic species data. The very low ambient concentrations of most of these species limits quantitative interpretation or discussion of the composition of the soluble fraction of the aerosol. We will thus emphasize the results for the radionuclides, particularly ^{210}Pb, and their relation to other observations made from the DC-8. We will also abandon the air mass classifications discussed above in favor of dividing the data into two geographic regions; near Asia and over the remote Pacific. All samples collected during flights 6 -13 when the plane was based in Yokota and Hong Kong are considered near Asia. Flights 14 - 19 sampled a broad region over the remote western Pacific, mainly around Guam but including the transit flights to Wake Island and Honolulu [see *Hoell et al.*, this issue]. It should be noted that this division introduces a southward shift in latitude in addition to the eastward shift farther from the

Asian continent, as flights 14 - 19 were mainly conducted in tropical and subtropical regions.

Continental Influence, Lead-210 and Ozone Relationships

Altitude distributions of ^{210}Pb over the western Pacific are shown in Figure 1, with the distributions of all other aerosol-associated species that were detected in at least 1/2 the samples. Average in situ O_3 concentrations during each aerosol collection interval are also shown. The low concentrations of ^7Be and soluble ionic species in the free troposphere are clearly evident in this figure, both near Asia and farther east. Ozone mixing ratios in the free troposphere near Asia ranged 1.5- to threefold higher than in the corresponding altitude ranges over the remote Pacific, with the largest enhancements observed between 2 and 8.5 km (Figure 1). Mean concentrations of ^{210}Pb near Asia in the 2- to 8.5-km altitude range were comparable to those in the boundary layer; if the two boundary layer samples with ^{210}Pb concentrations > 23 fCi m^{-3} STP are ignored, the concentrations in the 2- to 7 and 7- to 8.5-km bins generally exceeded those in the boundary layer (Figure 1a).

Much of the scatter within altitude bins in Figure 1 is the result of combining data from all flights in each of the respective regions. Profiles for individual flights are data sparse but indicate that air masses with elevated concentrations of ^{210}Pb and O_3 were generally restricted to narrow altitude ranges on any given flight.

B Flights 14 - 19

Figure 1. (continued)

Occurrence of such layers at different heights on different days causes the general enhancement of ^{210}Pb and O_3 between 2 and 8.5 km near Asia (Figure 1a).

The samples collected on flight 12 provide a clear example of the vertical layering encountered offshore of the Asian continent (Figure 2). Ozone and ^{210}Pb concentrations increased substantially in the two samples collected above 8 km. In contrast, ^{7}Be concentrations dropped in this altitude range, to levels > twofold lower than those measured between 1.5 and 6.5 km. Nitrate and NH_4^+ concentrations were only above detection limits in the bottom 2 km of the profile, while $SO_4^=$ concentrations decreased more than tenfold between the boundary layer and all higher elevations. Meteorological and trajectory analyses indicate that the air masses sampled at the top of this profile had been recently advected from the Asian continent, while the air masses intercepted at lower levels had originated farther east over the Pacific [*Bachmeier et al.*, this issue; *Merrill*, this issue].

Scatterplots of O_3 versus ^{210}Pb for each altitude/location bin provide a closer look at the apparent similarity of the variation with altitude of these two species (Figure 3). Near Asia there was a tendency for covariation of ^{210}Pb and O_3 at all altitudes. Below 8.5 km a 1 fCi m^{-3} STP increase of ^{210}Pb was associated with an unexpectedly consistent 2.4 parts per billion by volume (ppbv) increase in the O_3 mixing ratio. Similar trends were found over the remote Pacific in the boundary layer and in the 7- to 8.5-km range (Figure 3). Ozone mixing ratios decrease less than ^{210}Pb activities between 7 and 8.5 km and higher altitudes in both regions, but the two species continue to covary (Figures 1 and 3).

The statistical significance of the relationships between ^{210}Pb and O_3 (Figure 3) is limited by the small number of observations, but consideration of atmospheric dynamics over Asia and the western Pacific suggests they are real. Specifically, deep convection over the Asian continent has been shown to rapidly transport ^{222}Rn to the middle and upper troposphere, where it can then be advected eastward over much of the northern Pacific [*Kritz et al.*, 1990; *Balkanski et al.*, 1992]. Recent measurements in the lower stratosphere north of Australia have shown that large tropical cyclones with heavy precipitation can rapidly transport boundary layer ^{222}Rn up to, and through, the tropopause [*Kritz et al.*, 1993; *Danielsen*, 1993]. Efficient scavenging of aerosols and soluble gases in deep wet convection would provide a source of middle to upper tropospheric air with low concentrations of aerosol-associated species [*Kleinman and Daum*, 1991]. Decay of the ^{222}Rn lifted by such convection would constitute a source of ^{210}Pb at higher elevations where precipitation scavenging is greatly reduced. Sparingly soluble O_3 and O_3 precursors as well as other gases like CO would also survive processing through wet convective updrafts [e.g., *Newell et al.*, 1988; *Kleinman and Daum*, 1991; *Pickering et al.*, 1992].

We hypothesize that frequent wet convection over Asia during the autumn season characterized in PEM-West A was the mechanism responsible for the free tropospheric aerosol distributions and ^{210}Pb-O_3 relationships described above. On the other hand, stratospheric air is also enriched in O_3 and depleted in aerosols, suggesting that injection of stratospheric air into the middle troposphere could account for the altitude distributions we observed.
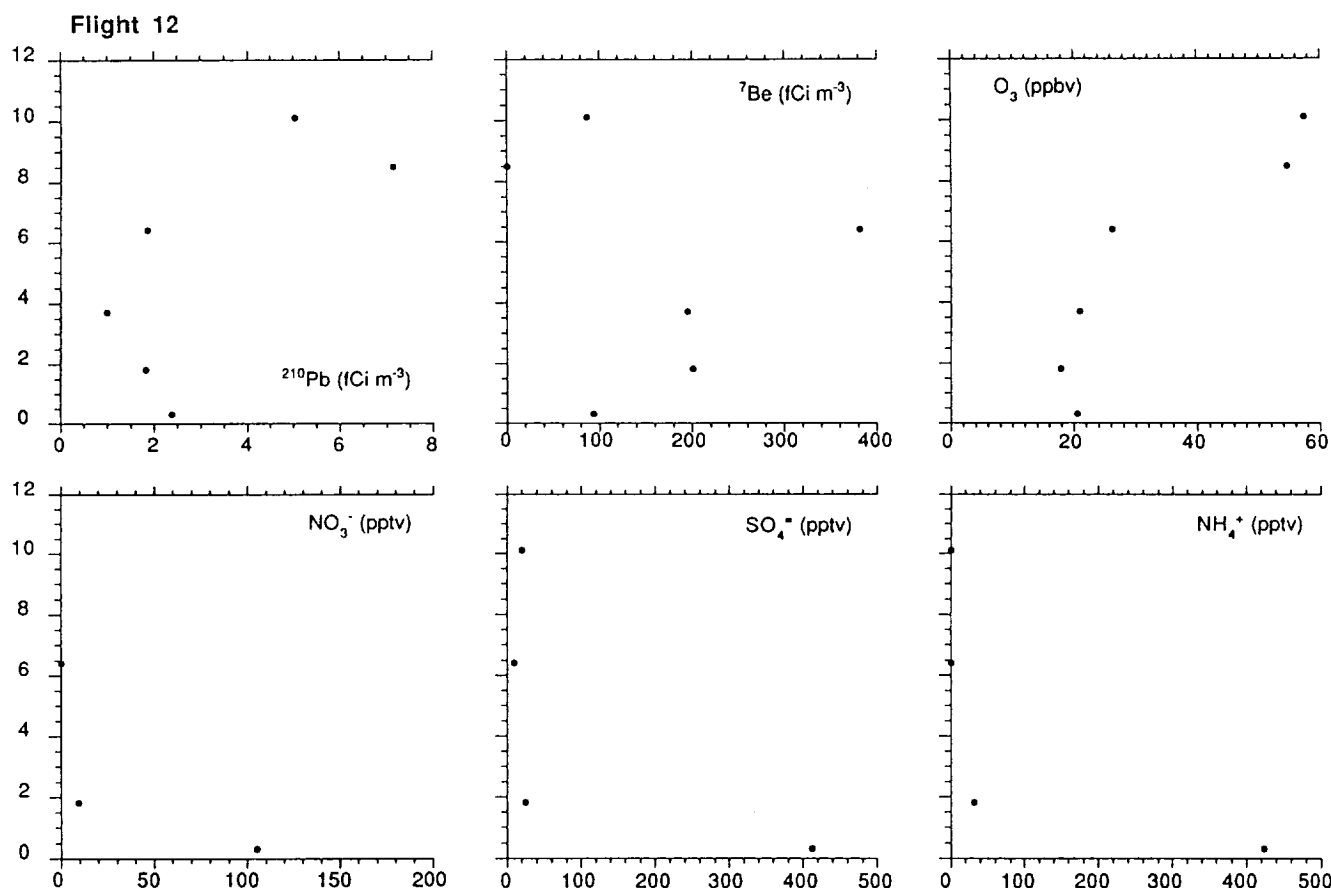
Figure 2. Results for aerosol-associated species and O_3 on flight 12, plotted in the same format as Figure 1.

However, stratospheric ozone should be accompanied by ^7Be [*Dutkiewicz and Husain*, 1979, 1985]. Strong correlations were seen between ^7Be and O_3 on three of the transit flights during PEM-West A (flights 4, 5, and 21) but were notably lacking on the flights over the western Pacific (Figure 4)

Enhanced ^{210}Pb concentrations below 2 km altitude, both near Asia and over the remote Pacific, were accompanied by elevated NO_3^-, $SO_4^=$, and NH_4^+ concentrations (Figure 1). We interpret these cases as low-level transport of continental boundary layer air over the ocean with minimal precipitation, a view that is supported by the meteorological analyses [*Talbot et al.*, this issue; *Merrill*, this issue; *Bachmeier et al.*, this issue]. These cases were identified as "plumes" in the lidar and potential vorticity air mass characterization described by *Browell et al.* [this issue] and were clearly distinquished from continental outflow that had been processed through convecting clouds ("convective outflow-continental" in the Browell et al. classification scheme).

A recent three-dimensional modeling experiment also implicates vertical transport of ^{222}Rn in wet convection as a major factor controlling the distribution of ^{210}Pb in the free troposphere [*Balkanski et al.*, 1993]. The model calculates midtroposphere ^{210}Pb concentrations over northern hemisphere continents during the summer, and in the tropics most of the year, that are only twofold lower than those in the boundary layer. Uplift of ^{222}Rn in deep wet convection is clearly the cause of these ^{210}Pb distributions in the model [*Balkanski et al.*, 1993]. The model calculates September-October mean ^{210}Pb activities for a grid cell in the middle of the near Asia region sampled during PEM-West A of

12.5, 6.5, and 9 fCi m^{-3} STP, in the boundary layer, at 6 km and near 12 km, respectively (D. Jacob, personal communication, 1993). The model results are in accord with our observations up to 6 km (Figure 1a), but do not reflect the observed decrease in ^{210}Pb concentration at higher altitudes. The extent of agreement between the model and observations is encouraging, but it is clear that the PEM-West A data set is not extensive enough to constitute a rigorous test of the model.

Deep Wet Convection and Reactive Nitrogen Species

Balkanski et al. [1993] suggest that the separation of ^{222}Rn (not scavenged) from primary aerosols and soluble gaseous species that react to form secondary aerosols (efficiently scavenged) by the mechanism of deep wet convection makes ^{210}Pb a poor tracer of continentally derived aerosols. *Tsunogai et al.* [1988] made the same suggestion on the basis of differing temporal patterns of ^{210}Pb and Al concentrations in aerosol samples from six western Pacific stations. Our results seem to support this conclusion, but they also confirm that ^{210}Pb is a sensitive tracer of continentally influenced air over the Pacific. *Balkanski et al.* [1993] also speculate that the low solubility of NO_x may allow a significant fraction of boundary layer NO_x to survive wet convective transport to the middle and upper troposphere, thereby explaining the strong correlation between ^{210}Pb and nitrate observed at remote islands in the Pacific Ocean [*Savoie et al.*, 1989]. Savoie et al. also invoked convective transport to lift the ^{210}Pb precursor ^{222}Rn into the free troposphere but suggested that lightning provided the midtropospheric source of NO_x that was later converted to NO_3^-.
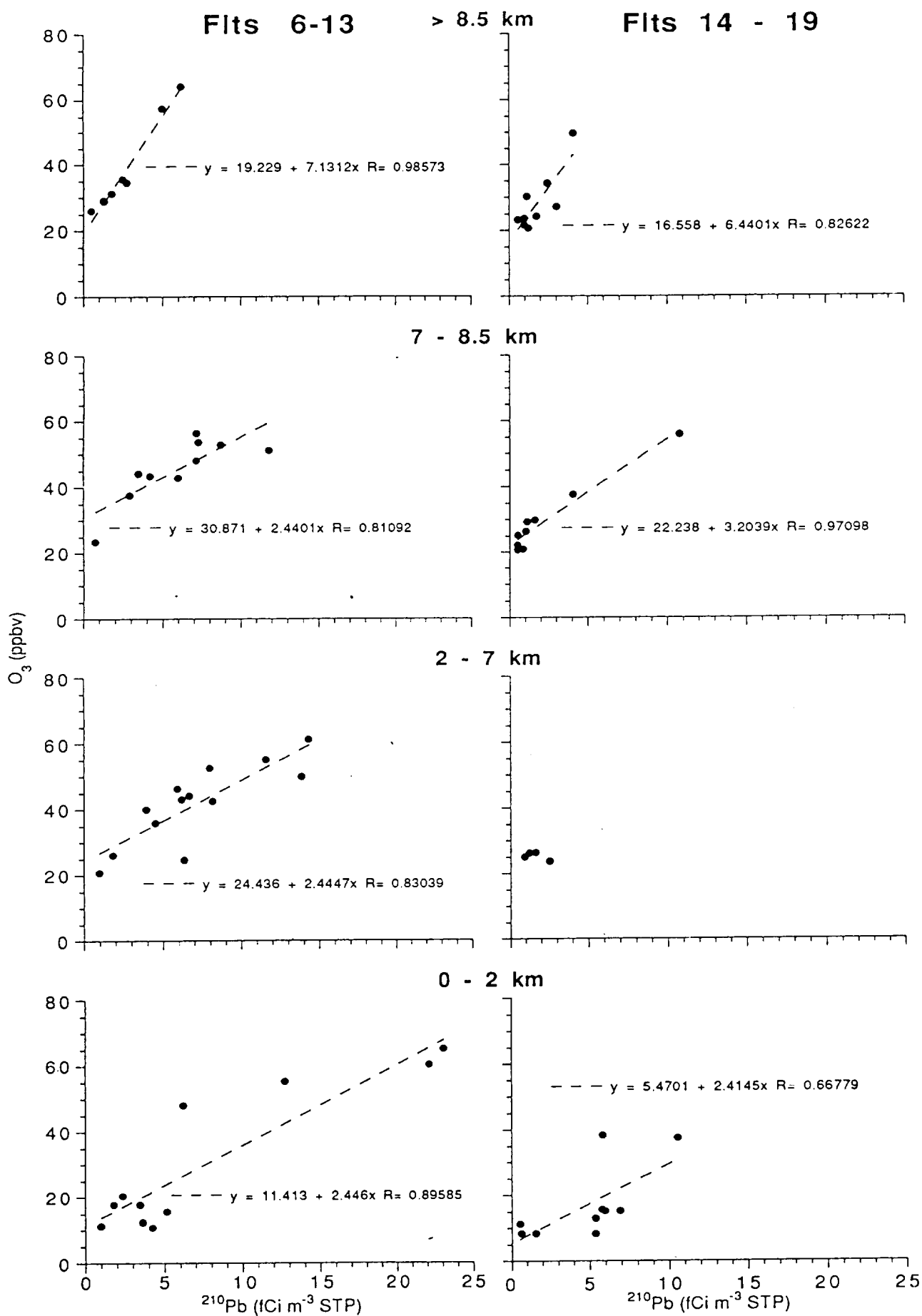
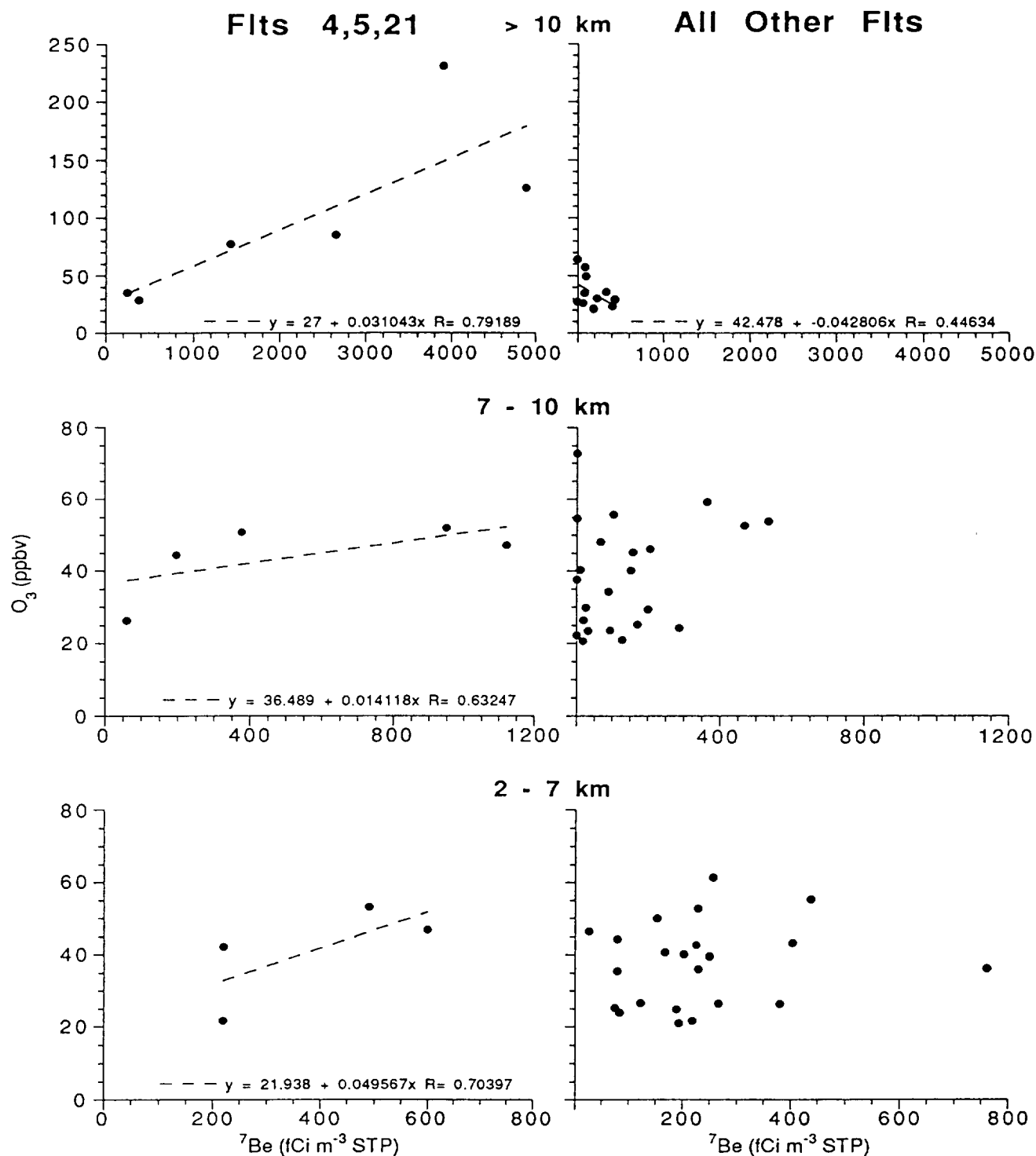**Figure 3.** Scatterplots of O_3 against ^{210}Pb for the eight location/altitude bins depicted in Figure 1.

Figure 4. Scatterplots of O_3 against [7]Be in the free troposphere. The three transit flights (4, 5, and 21) were flown between California and Alaska, Alaska and Japan, and from Hawaii to California. All remaining flights over the western Pacific are compared to these three.
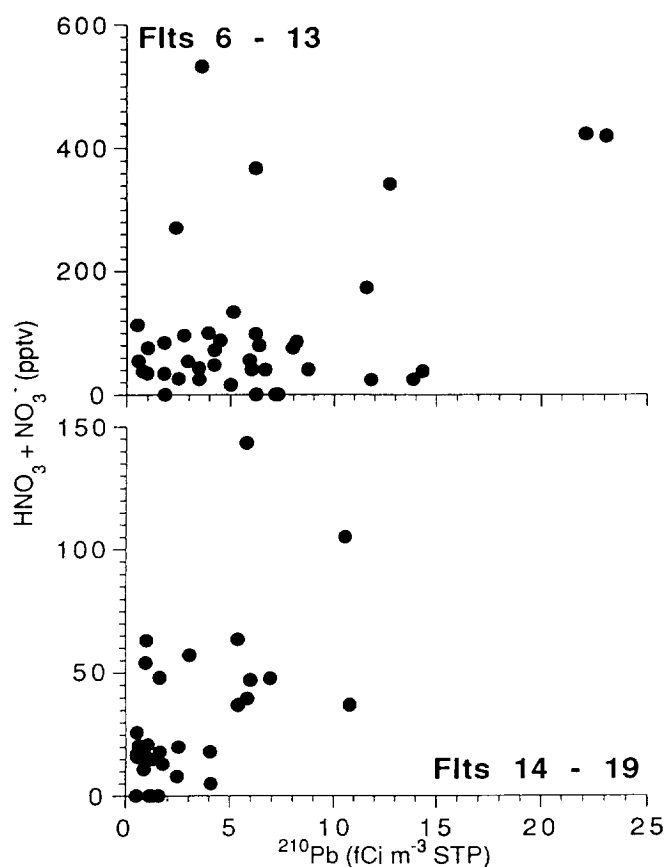
Figure 5. Scatterplots of atmospheric nitrate (aerosol NO_3^- plus HNO_3) against ^{210}Pb. Separate plots are shown for the samples collected near Asia and those from the remote western Pacific.

The PEM-West A data set allows a preliminary assessment of these hypotheses.

The filter sampling technique used at the remote island sites is felt to efficiently collect HNO_3 in addition to aerosol NO_3^- [*Savoie et al.*, 1989]. If atmospheric nitrate is considered to be the sum of NO_3^- and HNO_3, the PEM-West A atmospheric nitrate data show little or no relationship with ^{210}Pb when results from all altitudes are considered (Figure 5). It may be that the previously noted stratification of the free troposphere during PEM-West A is obscuring any relationships that are present.

The vertical distribution of ^{210}Pb in the two regions over the western Pacific is compared to those of all measured reactive N species in Figure 6. Near Asia, all of the N species except PAN are enhanced in the boundary layer relative to the free-tropospheric air just above (Figure 6a), but we do not consider that the ^{210}Pb enhancement in the boundary layer is related to wet convection (see above). Aerosol NO_3^-, NO_x, and NO_y also increase in the highest-altitude bin near Asia, where ^{210}Pb concentrations are the lowest of the entire profile. High-altitude aircraft traffic may be an important source of reactive N in this region [e.g., *Kasibhatla*, 1993]. Over the remote western Pacific, modest enhancement of ^{210}Pb concentrations in the boundary layer are accompanied by slightly elevated NO_3^- concentrations, but concentrations of the other N species are quite low (Figure 6b). Relatively large enhancements of NO_x and NO_y near 8.5 km over the remote western Pacific correspond to proportionally smaller increases in ^{210}Pb and PAN concentrations. Overall, the correspondence between ^{210}Pb and NO_3^- or HNO_3 appears to be weak.

Scatterplots of atmospheric nitrate versus ^{210}Pb for each latitude/region bin reinforce the impression that no consistent strong relationships exist in the PEM-West A data set. Atmospheric nitrate and ^{210}Pb concentrations only covaried in the boundary layer over the remote western Pacific (Figure 7). It is possible that ^{222}Rn decay to ^{210}Pb occurs more quickly than the conversion of NO_x (from the boundary layer or lightning) to nitrate, but similar plots of NO_x and NO_y against ^{210}Pb (not shown) also indicate little or no correspondence. However, PAN concentrations tended to covary with those of ^{210}Pb at all altitudes near Asia and in the 7- to 8.5-km bin over the remote western Pacific (Figure 8).
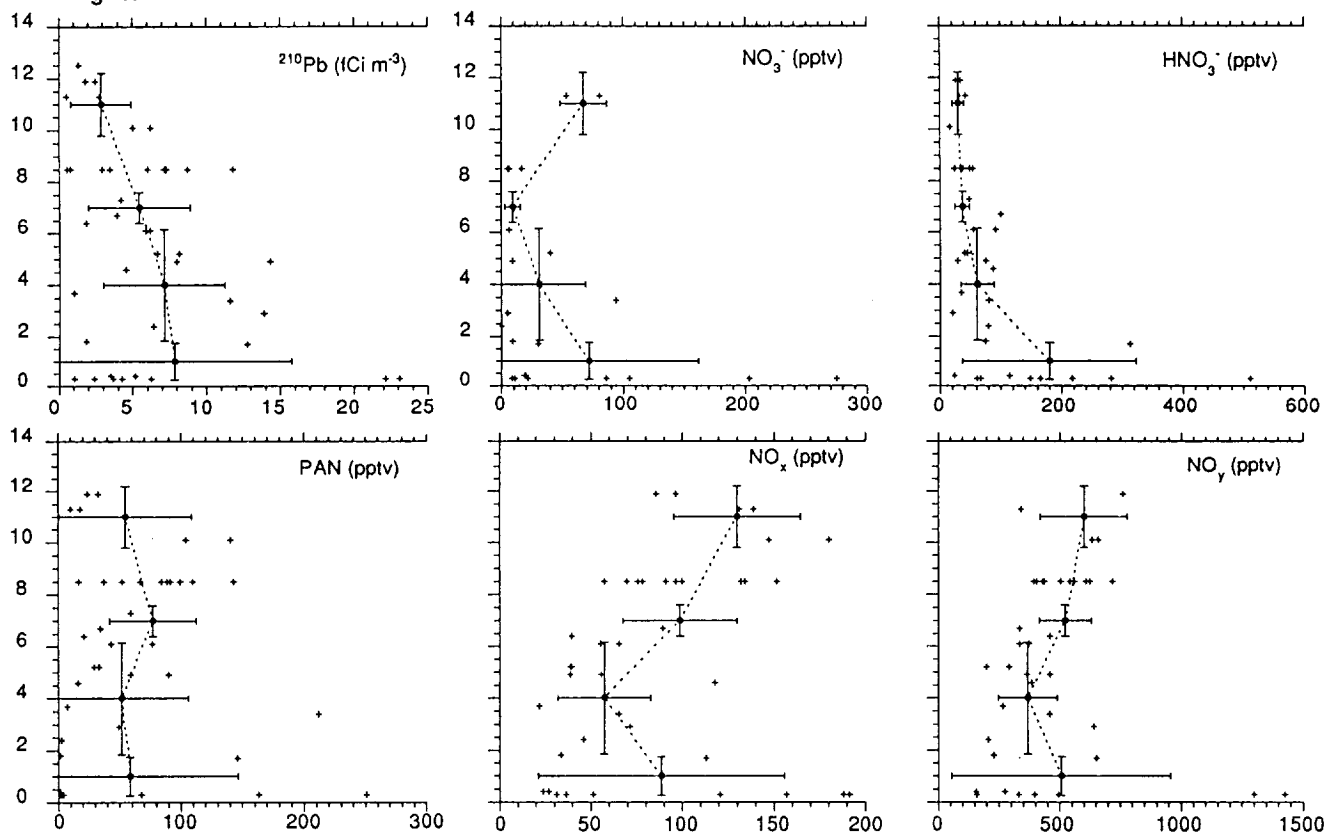
The observed correlation between ^{210}Pb and PAN, alone of the reactive N species, may be consistent with wet convection of NO_x and ^{222}Rn from the continental boundary layer resulting in strong ^{210}Pb-NO_3^- relationships in remote oceanic regions. We hypothesize that the modified boundary layer air that passed through the deep wet convection cycle retained NO_x and NMHC in proportions that favored the formation of PAN over inorganic forms of nitrate. As middle to upper tropospheric air over Asia enriched in ^{210}Pb (and/or ^{222}Rn) and PAN is advected eastward and subsides somewhere over the Pacific, thermal decomposition of PAN will generate NO_x far from its initial source [*Singh et al.*, 1987; *Singh et al.*, 1992a, b; this issue]. This NO_x may then be converted to NO_3^- and/or HNO_3, creating an air mass enriched in both ^{210}Pb and atmospheric nitrate. If PAN is the initial product of most NO_x lifted to the free troposphere over Asia, the time lag required for its decomposition could account for the ^{210}Pb rich, but nitrate poor, free-tropospheric air sampled over the western Pacific during PEM-West A. Trajectory analyses indicate that the continental air masses encountered by the DC-8 had generally been over Asia as little as 2 days previously [*Talbot et al.*, this issue]. Older continental air, presumably more prevalent farther from the Asian continent, might be expected to shower tighter relationships between ^{210}Pb and atmospheric nitrate. Flight 20, the Mauna Loa flyby conducted during PEM-West A [see *Atlas et al.*, 1995; *Hoell et al.*, this issue] provides some support for this hypothesis.

Older Continental Air Case Study, Flight 20

The primary objective of the Mauna Loa flyby was intercomparison with ground-based measurements conducted by the MLOPEX team. Sampling from the DC-8 was restricted to altitudes below 5 km. Surface level winds were easterly and back trajectories at low levels indicated transport from near the North American west coast (all meteorological analyses were provided by the GTE project office and are available from the PEM-West A data archive). A midtroposphere ridge of high pressure over Hawaii caused weak subsidence and relatively light winds aloft. Trajectories at the maximum sampling altitudes indicate that air had circled Hawaii with anticyclonic curvature for the previous 5 - 7 days. None of these trajectories ventured more than 10° away from Hawaii, so it is unclear whether any continentally influenced air in the free troposphere originated over Asia or North America.

Lead 210 concentrations above the boundary layer ranged 3 - 8 fCi m^{-3} STP and decreased toward the surface (Figure 9), indicating long-range transport of continental air in the free troposphere. In this case the altitude profiles of all reactive N species were quite similar to that of ^{210}Pb. It should be noted that PAN mixing ratios were nearly fivefold lower than those observed in younger continental outflow near Asia (compare Figures 6a and 9). The much higher ^7Be concentrations at 5 km over Hawaii relative to the majority of PEM-West A flights (compare Figures 1 and 9) appear to reflect the input of upper tropospheric/lower stratospheric air during high-level transport, with little subsequent

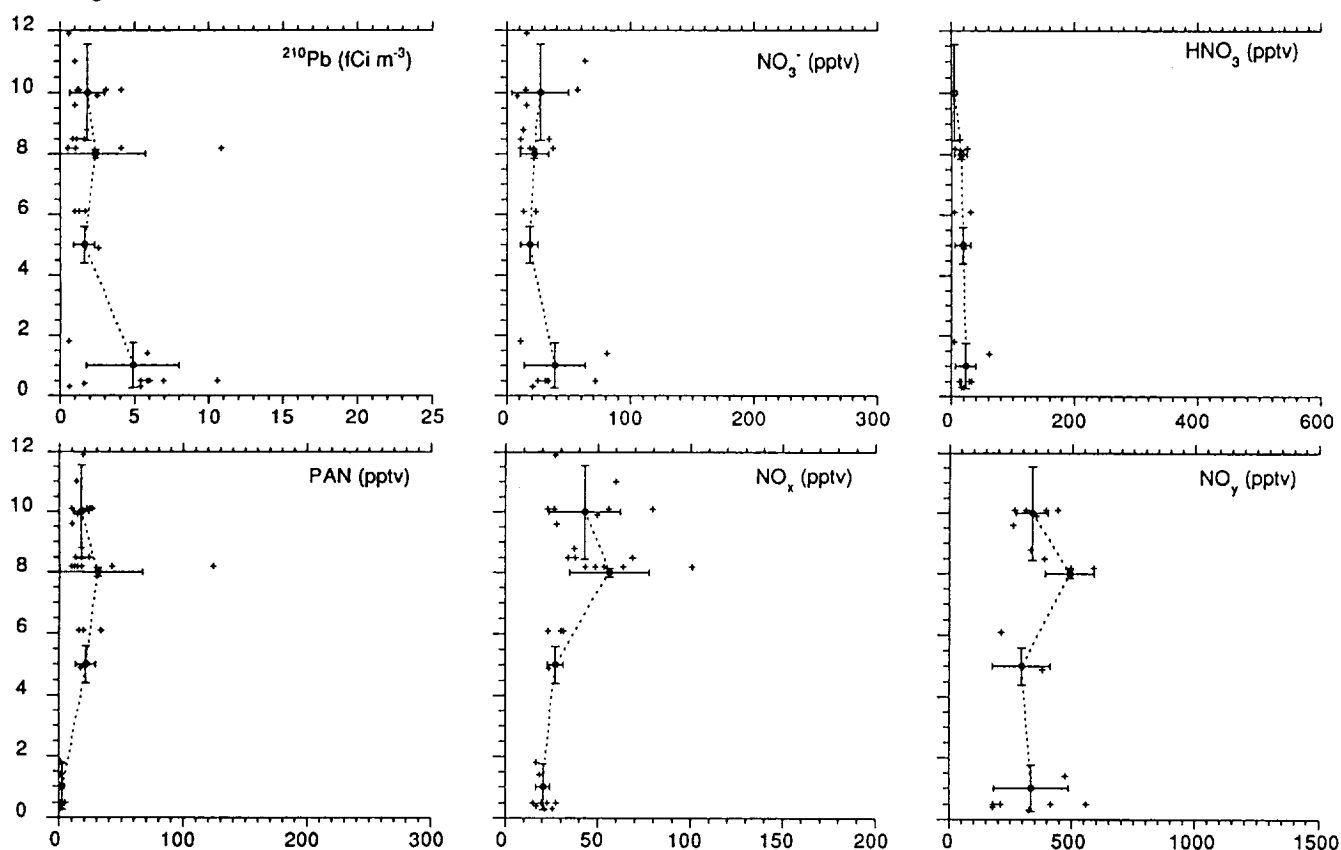**A** **Flights 6 - 13**

B **Flights 14 - 19**

Figure 6. Comparison of the altitude distributions of ^{210}Pb and the major reactive nitrogen species measured during PEM-West A. Sampling frequencies for the nitrogen species are much higher than the aerosol sampling; data shown here have been averaged to correspond to the intervals represented by each aerosol sample. Geographic separation into near Asia (a) and remote western Pacific (b) subsets has been maintained.
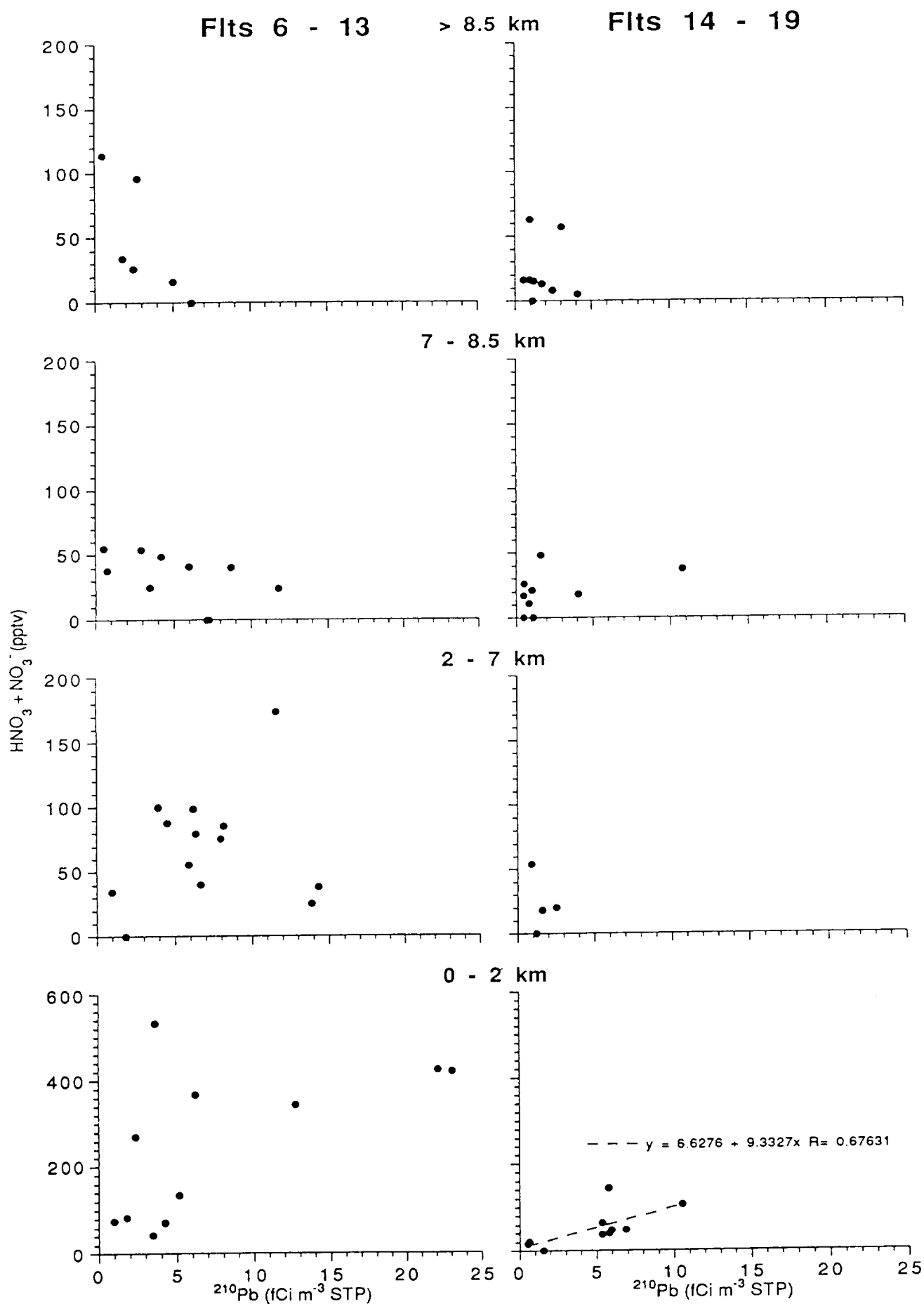
Figure 7. Scatterplots of atmospheric nitrate (NO_3^- plus HNO_3) against ^{210}Pb for the eight location/altitude bins depicted in Figure 6.
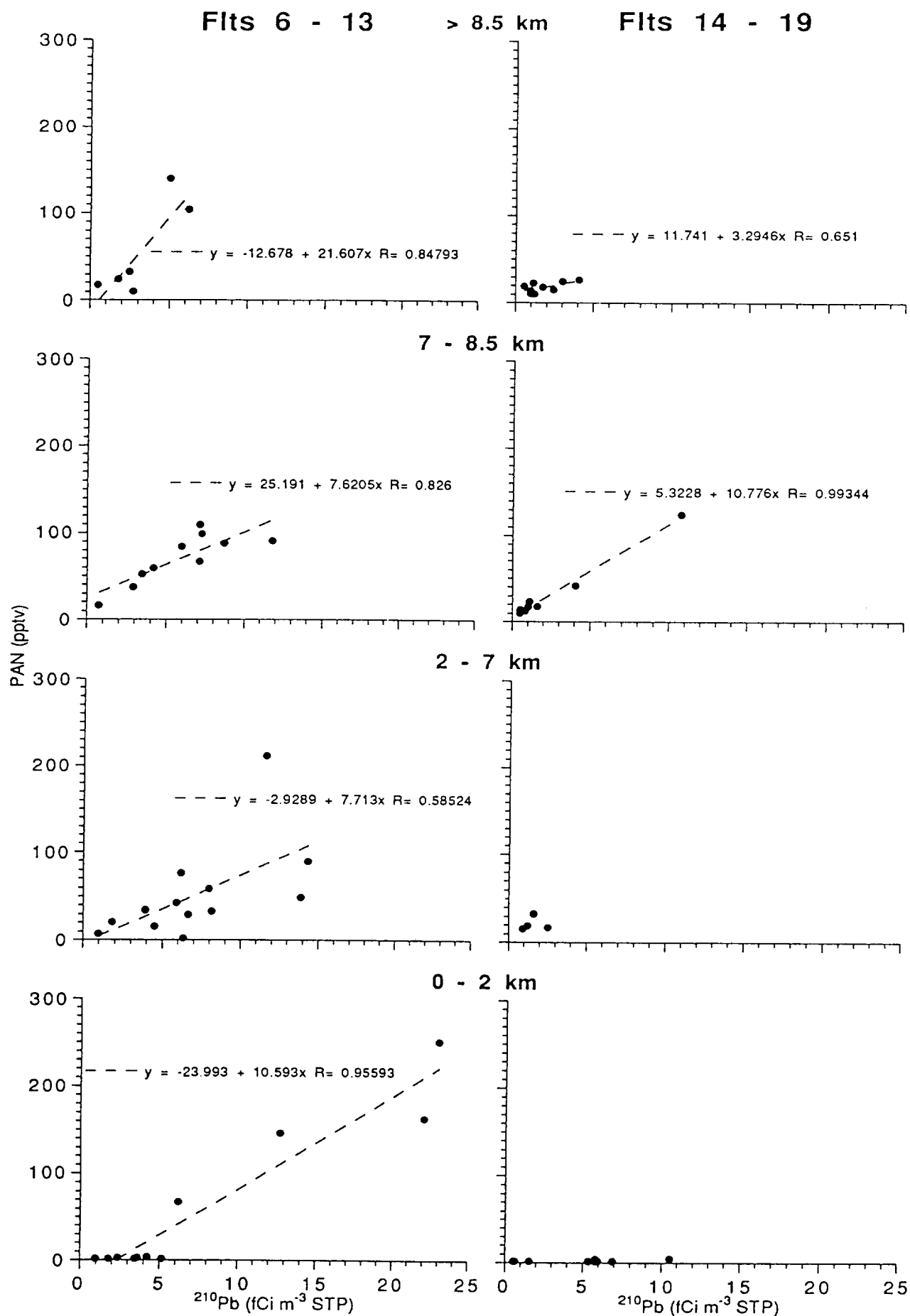
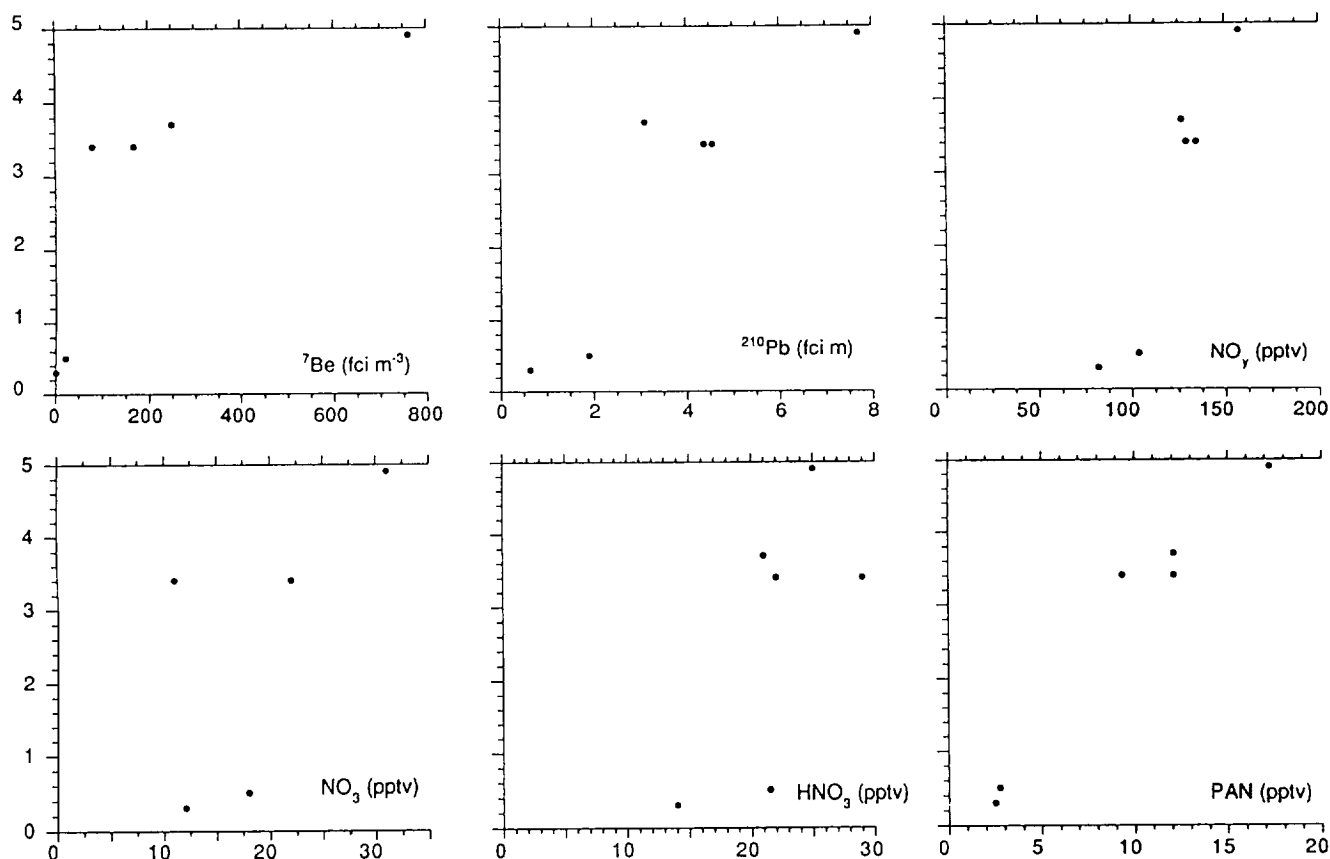**Figure 8.** As in Figure 7 but for peroxyacetylnitrate against ^{210}Pb.

Flight 20

Figure 9. Altitude distributions of ^{7}Be, ^{210}Pb, NO_3^-, HNO_3, PAN, and NO_y on flight 20, the Mauna Loa flyby.

scavenging. None of the soluble aerosol-associated species except NO_3^- increased with altitude, suggesting they were scavenged at some point in the history of this air mass when ^{210}Pb and nitrate were still present in the form of insoluble precursors. As we have seen, wet convection over continents appears the most likely mechanism that could enrich ^{210}Pb relative to other aerosol-associated species in free tropospheric air over the ocean. In this particular air mass, greater than one week removed from last direct continental influence, atmospheric nitrate variations with altitude correspond to those of ^{210}Pb.

Summary and Conclusions

The atmosphere over the Pacific Ocean just east of the Asian continent and in a broader region centered on Guam was sampled from the NASA AMES DC-8 in September - October 1991. Only a few weeks were spent in any given region, so the findings must be regarded as a series of snapshots of atmospheric composition that resulted from the specific meteorological conditions prevailing during the period of the PEM-West A mission. This paper has focused primarily on the composition of aerosols. Despite the short-term nature of the investigation the findings appear to be consistent over large geographic regions and with a conceptual model relating deep wet convection over Asia to the composition of the free troposphere downwind over the western Pacific ocean.

Concentrations of ^{7}Be and soluble ionic species were quite low in most aerosol samples collected in the free troposphere, both near Asia and farther east near Guam. In contrast, ^{210}Pb concentrations were higher than expected between 2 and 14 km near

Asia and in a narrower altitude range near 8 km over the more remote western Pacific. Ozone concentration variations in the free troposphere tended to follow those of ^{210}Pb. Concentrations of ^{210}Pb and nearly all of the soluble aerosol-associated ionic species in the boundary layer increased markedly when continental air was advected over the ocean at low altitudes.

Deep wet convection over Asia appears to provide a mechanism to rapidly lift continental boundary layer air to the middle and upper troposphere, where strong zonal winds can subsequently advect it over the Pacific. Intense precipitation in these systems apparently scavenges aerosols and soluble gases from the ascending air without depleting ^{222}Rn and sparingly soluble O_3 precursors. As a result, ^{210}Pb and O_3 tended to be correlated in the free troposphere 2- 5 days downwind of Asia. It has recently been suggested that the solubility of NO_x is low enough that deep wet convection could also lift NO_x rapidly into the free troposphere, which might account for the strong correlations between ^{210}Pb and NO_3^- reported from remote ocean islands. During PEM-West A, no relationships were found between ^{210}Pb and inorganic nitrate in the free troposphere, rather concentrations of PAN correlated strongly with those of ^{210}Pb. We hypothesize that the composition of modified continental boundary layer air after wet convective processing favors production of PAN over inorganic NO_3^-, at least within the short periods of aging represented by the PEM-West A samples. It is likely that subsidence of this ^{210}Pb- and PAN-rich air farther to the east results in thermal decomposition of PAN to NO_x and subsequent production of NO_3^- and HNO_3, thereby accounting for the correlation between ^{210}Pb and nitrate.

It should be borne in mind that PEM-West A was scheduled during the fall in order to characterize atmospheric composition over the Pacific at a time when continental influence should be at its minimum. The results presented herein revealed significant continental influence even during this season, but the impact was largely restricted to those tracers of continental air that are relatively unaffected by precipitation scavenging processes. Even larger Asian influence on the composition of the atmosphere over the western Pacific should be expected during the spring and summer "dust" season.

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