7-20-1999

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Recommended Citation

Dibb, J. E., R. W. Talbot, L. D. Meeker, E. M. Scheuer, N. J. Blake, D. R. Blake, G. L. Gregory, and G. W. Sachse (1999), Constraints on the age and dilution of Pacific Exploratory Mission-Tropics biomass burning plumes from the natural radionuclide tracer 210Pb, J. Geophys. Res., 104(D13), 16233–16241, doi:10.1029/1999JD900066.

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 104, NO. D13, PAGES 16,233–16,241, JULY 20, 1999

Constraints on the age and dilution of Pacific Exploratory Mission-Tropics biomass burning plumes from the natural radionuclide tracer ^{210}Pb

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Abstract. During the NASA Global Troposphere Experiment Pacific Exploratory Mission-Tropics (PEM-Tropics) airborne sampling campaign we found unexpectedly high concentrations of aerosol-associated ^{210}Pb throughout the free troposphere over the South Pacific. Because of the remoteness of the study region, we expected specific activities to be generally less than 35 μBq m^{-3} but found an average in the free troposphere of 107 μBq m^{-3}. This average was elevated by a large number of very active (up to 405 μBq m^{-3}) samples that were associated with biomass burning plumes encountered on nearly every PEM-Tropics flight in the southern hemisphere. We use a simple aging and dilution model, which assumes that ^{222}Rn and primary combustion products are pumped into the free troposphere in wet convective systems over fire regions (most likely in Africa), to explain the elevated ^{210}Pb activities. This model reproduces the observed ^{210}Pb activities very well, and predicts the ratios of four hydrocarbon species (emitted by combustion) to CO to better than 20% in most cases. Plume ages calculated by the model depend strongly on the assumed ^{222}Rn activities in the initial plume, but using values plausible for continental boundary layer air yields ages that are consistent with travel times from Africa to the South Pacific calculated with a back trajectory model. The model also shows that despite being easily recognized through the large enhancements of biomass burning tracers, these plumes must have entrained large fractions of the surrounding ambient air during transport.

1. Introduction

The pervasive influence of long-traveled biomass burning plumes that were advected over the South Pacific from the west was an unexpected finding of the NASA Global Tropospheric Experiment (GTE) Pacific Exploratory Mission-Tropics (PEM-Tropics) airborne sampling campaign conducted in September - October 1996 [*Fuelberg et al.*, 1999; *Talbot et al.*, 1999; *Blake et al.*, this issue; *Fenn et al*, this issue; J. Logan et al., unpublished manuscript, 1999; R. Lusher et al., unpublished manuscript, 1999; H. Singh et al., unpublished manuscript, 1999]. These plumes were manifested as layers up to several kilometers thick with elevated mixing ratios of O_3, CO, PAN, several NMHC combustion tracers, and the soluble acidic gases HNO_3, CH_3COOH, and HCOOH that could be hundreds of kilometers wide in the north-south direction and apparently extended thousands of kilometers to the west. *Dibb et al.* [1999] showed that the mixing ratios of aerosol-associated soluble ions, including NH_4^+ and K^+ which are typically enhanced in biomass burning plumes, were quite low in all of the plumes encountered during PEM-Tropics except for one on the transit between Tahiti and New Zealand. We hypothesized that the absence of strong signals in these aerosol-associated tracers of biomass burning indicated that the air masses must have been efficiently scavenged by precipitation during transit from the source region to the PEM-Tropics study area. Elevated concentrations of ^{7}Be throughout the South Pacific troposphere [*Dibb et al.*, 1999] and very high mixing ratios of HNO_3, CH_3COOH, and HCOOH in many of the plumes [*Talbot et al.*, 1999] indicate that such scavenging could not have occurred in the few days immediately prior to interception of the plumes. We therefore suggested that the soluble ions and their precursors were removed from these air masses in wet convective events, most likely over Africa but perhaps even as far upwind as South America, that provided the vertical lifting that transported the biomass burning emissions into the free troposphere.

Dibb et al. [1999] noted that ^{210}Pb activities in the initial aerosol samples (first 12 flights) analyzed from the PEM-Tropics campaign seemed to be enhanced in the plume-impacted air masses, making this natural radionuclide tracer the only aerosol-associated species to show a plume signal. All PEM-Tropics aerosol samples have now been analyzed for ^{210}Pb, and the enhancement in plume-impacted air masses persisted throughout the campaign. This paper focuses on the distribution of ^{210}Pb over the South Pacific during PEM-Tropics and examines whether the observed ^{210}Pb enhancements provide useful constraints on the age of the biomass burning plumes and the extent to which they have mixed with ambient, or background, air during transport to the South Pacific.

Paper number 1999JD900066.
0148-0227/99/1999JD900066$09.00

2. Methods

Details of our filter sampling for aerosols from the NASA DC-8 airborne laboratory are provided by *Dibb et al.* [1999]. Specific activities of ^{210}Pb were determined in 280 samples (which had first been analyzed for ^{7}Be by direct gamma counting) by alpha spectrometric determination of ^{210}Po after allowing 10-15 months for in-growth of this ^{210}Pb daughter. Samples were counted in groups of four until the uncertainty due to counting statistics for the least active sample in each group was ≤20%. In most cases this required counting times of 3-4 days.

All of the ^{210}Pb data is presented below, but much of the discussion will focus on those samples that were impacted by biomass burning plumes. We use the compilation of plume encounters based on CO and O_3 enhancements presented by J. Logan et al. (unpublished manuscript, 1999) to filter our data set. In some cases we collected two or three filter samples during a single plume encounter, but more often our samples integrate over intervals that include time within a plume and also in the surrounding ambient air. If an aerosol sample overlapped at all with a defined plume encounter, it was considered to be plume-impacted. As a result, our sampling can result in artifact dilution of the plumes, with some 10-15 min long plume-impacted samples including as little as 15 s within an identified plume.

Our ^{210}Pb activities are compared to the mixing ratios of various trace gases measured by other investigators on the DC-8. In all cases the integration period for these analyses is shorter than our sample collection intervals. A merged data product created at Harvard University, wherein all other measurements are averaged over the aerosol sample collection interval, is used exclusively in this paper. Details of the other instruments and higher-resolution versions of the resulting data sets are presented in companion papers in this issue and in the first special issue of *Journal of Geophysical Research* on the PEM-Tropics campaign (in press). All original data and several different merged products are archived, and available, at the Langley Distributed Active Archive Centre (DAAC).

Table 1. Activity of ^{210}Pb in Aerosol Samples Collected During PEM-Tropics

Altitude, km	n[a]	Mean	Standard Deviation	Median
		(μBq m^{-3} STP)		
		>15 °N, 120 °-170 °W		
0-2	6	56	53	38
2-8	7	154	128	119
>8	12	144	54	152
		0 °-15 °N, 120 °-170 °W		
0-2	2	128	36	128
2-8	0			
>8	1	80		80
		0 °-15 °N, 120 °-170 °W		
0-2	8	49	56	18
2-8	12	99	44	107
>8	10	81	33	70
		0 °-35 °S, E of 120 °W		
0-2	18	67	44	67
2-8	45	129	88	104
>8	40	90	58	72
		0 °-35 °S, 120 °-170 °W		
0-2	12	74	50	61
2-8	31	96	61	80
>8	19	126	73	87
		>35 °S, W of 120 °W		
0-2	3	32	6	36
2-8	3	69	11	75
>8	4	112	55	93
		>35 °S, 120 °-170 °W		
0-2	15	48	26	45
2-8	23	121	100	91
>8	9	98	60	85

Geographic and altitude bins correspond to those used by *Dibb et al.* [1999] to summarize the distribution of aerosol-associated soluble ions and ^{7}Be during this mission.
[a] n is number of samples collected; ^{210}Pb was above detection limit in all samples

3. Results

Activities of ^{210}Pb above 2 km averaged 70 to 130 μBq m^{-3} in all of the South Pacific regions sampled during PEM-Tropics (Table 1), with an overall mean of 107 μBq m^{-3}. Considering the distances to major land masses, we expected to encounter levels generally < 35 μBq m^{-3}. Such low values were frequently measured, but the averages were elevated by the numerous samples with activities between 75 and 405 μBq m^{-3} (Figure 1). The geographical and altitudinal distribution of these samples with high ^{210}Pb activities mirrors those of plume encounters, being most frequent between about 3 and 10 km and increasing toward the west [*Fuelberg et al.*, 1999; *Talbot et al.*, 1999; *Blake et al.*, this issue; *Fenn et al.*, this issue; J. Logan et al., unpublished manuscript, 1999; R. Lusher, unpublished manuscript, 1999; H. Singh et al., unpublished manuscript, 1999].

Scatterplots of ^{210}Pb in plume-impacted samples versus several trace gases enhanced in the plumes reinforce the impression that high ^{210}Pb activities were associated with the transport of biomass burning emissions, and photochemical products of these emissions, from the west (Figure 2). Correlations between ^{210}Pb and the combustion tracers in Figure 2 (r^2 = 0.5, 0.7, and 0.4 for C_3H_8, C_2H_6, and CH_3Cl, respectively) were not very tight, but they were comparable to or higher than those found between the soluble acidic gases apparently produced in the plumes and several plume tracers. (*Talbot et al.* [1999] reported r^2 values near 0.4 for correlations of HNO_3, CH_3COOH, and HCOOH versus CH_3Cl, PAN, and O_3.) Relatively strong relationships were also found for ^{210}Pb versus O_3, CO, and PAN in plume-impacted samples (r^2 = 0.5, 0.5, and 0.6, respectively). The correlation between ^{210}Pb and C_2H_2 in plume-impacted samples (not shown) was also quite strong (r^2 = 0.5), in contrast to the case for HNO_3 and C_2H_2 where any relationship was restricted to just a few of the plumes [*Talbot et al.*, 1999].

4. Discussion

The associations between ^{210}Pb and various biomass burning tracers in plumes over the South Pacific do not necessarily imply that ^{210}Pb is a product of combustion. It has been shown that very young fire plumes can be greatly enriched in Rn daughters including ^{210}Po and ^{210}Pb, reflecting volatilization of these tracers both within the plants and dry deposited onto their surfaces [*Lambert et al.*, 1991; *Le Cloarec et al.*, 1995]. However, these researchers have shown that the Po and Pb rapidly recondense when temperatures drop, returning them to the aerosol phase. In general, a large fraction is scavenged onto other particulates in the plume and does not travel far, though submicron aerosols formed in the free troposphere could be transported long distances. In the case of PEM-Tropics plumes transported to the South Pacific it is unlikely that this process is a significant source of aerosol ^{210}Pb (or ^{210}Po)

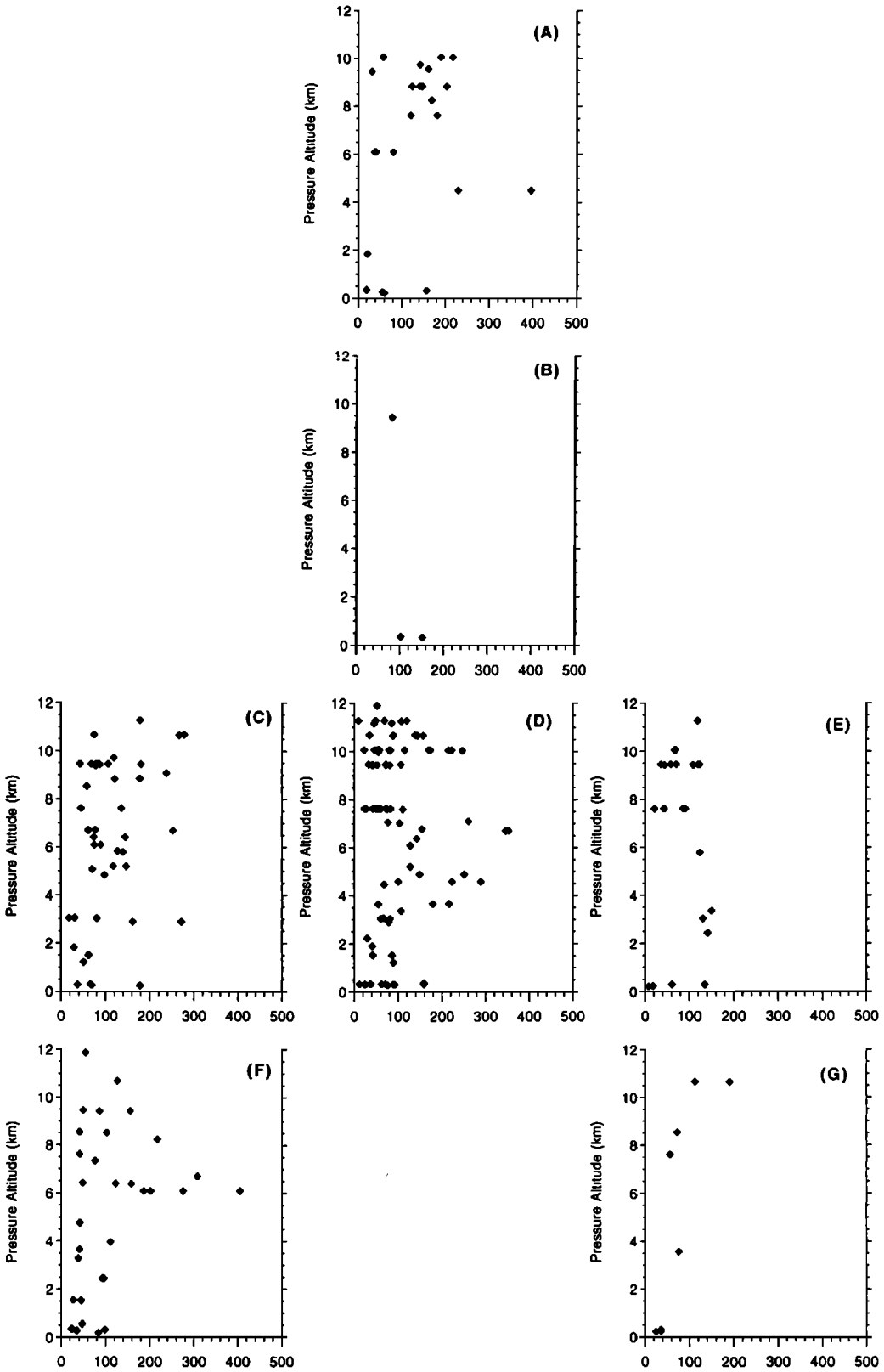

Figure 1. Vertical profiles of ^{210}Pb activity ($\mu Bq\ m^{-3}$) in seven regions sampled during PEM-Tropics. The regions are the same as those used by *Dibb et al.* [1999] and for Table 1. The geographic boundaries are: (a) >15°N, 120°-170°W, (b) 0°-15°N, 120°-170°W, (c) 0°-35°S, W of 170°W, (d) 0°-35°S, 120°-170°W, (e) 0°-35°S, E of 120°W, (f) >35°S, W of 170°W, and (g) >35°S, E of 120°W.

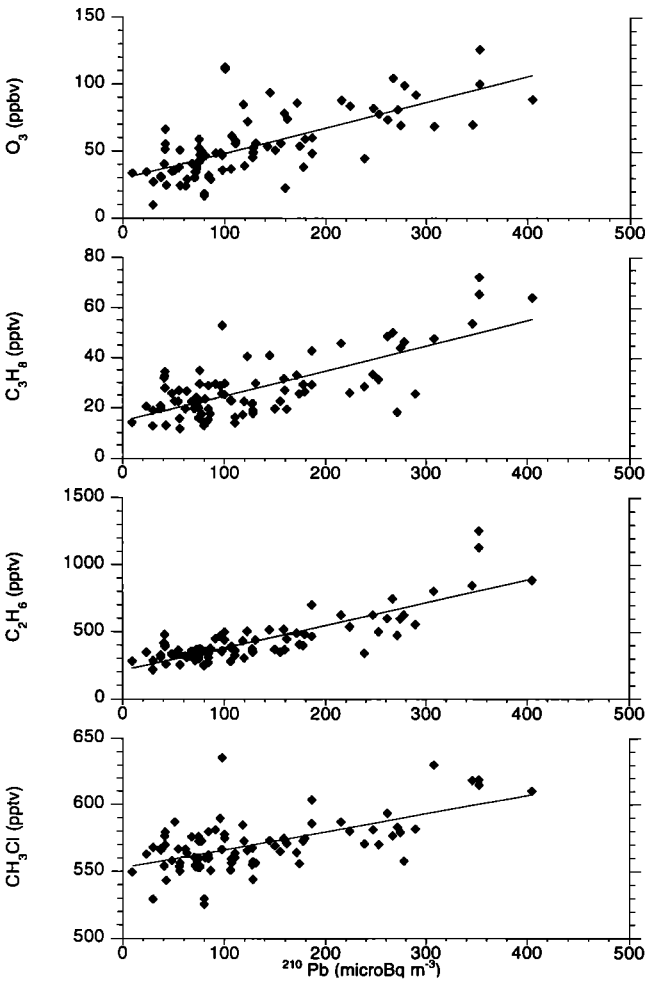

Figure 2. Scatterplots of O_3, C_3H_8, C_2H_6, and CH_3Cl as a function of ^{210}Pb activity in all plume-impacted samples collected during PEM-Tropics. The lines are least squares fits.

because we do not see any enhancements of other aerosol-associated species that should also be greatly enriched in the plumes. *Dibb et al.* [1999] suggested that effective scavenging in wet convective systems removed the other aerosol tracers of biomass combustion, and this process would also depress the concentrations of ^{210}Pb in recently uplifted boundary layer air (we will term such air masses "fresh plumes" in the following sections).

We suspect that the observed correlations result from pumping boundary layer air enriched in ^{222}Rn (the precursor of ^{210}Pb), and sparingly soluble trace gases emitted by biomass burning, into the free troposphere. Strong westerlies then advected this lifted boundary layer air into the PEM-Tropics study region [*Fuelberg et al.*, 1999]. Because Rn is a noble gas, it would not be depleted by the precipitation scavenging associated with wet convective uplift that we invoked to explain the low mixing ratios of aerosol-associated soluble ions in the plumes over the South Pacific [*Dibb et al.*, 1999; *Talbot et al.*, 1999].

Consider a hypothetical tropospheric air mass with very low levels of ^{210}Pb, but high levels of ^{222}Rn and biomass burning emissions, that experiences no loss of aerosols by scavenging and does not mix at all with surrounding air. Over timescales of hours to weeks, concentrations of ^{210}Pb would increase due to ^{222}Rn decay, while mixing ratios of primary combustion products would decrease, largely due to attack by OH. Given different OH reactivities, the various primary combustion products will be depleted at different rates, and the ratio of shorter/longer lived tracers (S/L) should decrease, while ratios of longer/shorter lived tracers (L/S) should increase.

We examined two S/L ratios (C_3H_8/CO and C_2H_2/CO) and two L/S ratios (C_2H_6/CO and CH_3Cl/CO) as a function of ^{210}Pb activity in all plume-impacted samples. Three of the four cases show trends opposite to those expected in an idealized, isolated, air mass. Both S/L ratios increase (rather than decrease) as ^{210}Pb increases, with a tighter trend for C_2H_2/CO ($r^2 = 0.4$) than that for C_3H_8/CO ($r^2 = 0.1$) (Figure 3). Given the much longer lifetime of CH_3Cl than CO, their ratio should increase as ^{210}Pb grows in over time, yet the ratio in plume-impacted samples sharply decreases with increasing ^{210}Pb ($r^2 = 0.4$) (Figure 3). In our data set, C_2H_6/CO is the only ratio to show the expected trend, increasing with ^{210}Pb activity ($r^2 = 0.3$). These relationships indicate that we cannot consider the plumes to be isolated air masses, but must consider dilution of the plumes with ambient air during transport.

4.1. A Simple Aging and Dilution Model

It has been shown that mixing between two different air masses generally does not result in linear mixing lines when one considers ratios of species (usually ratios of hydrocarbons (HC) or HC/CO or

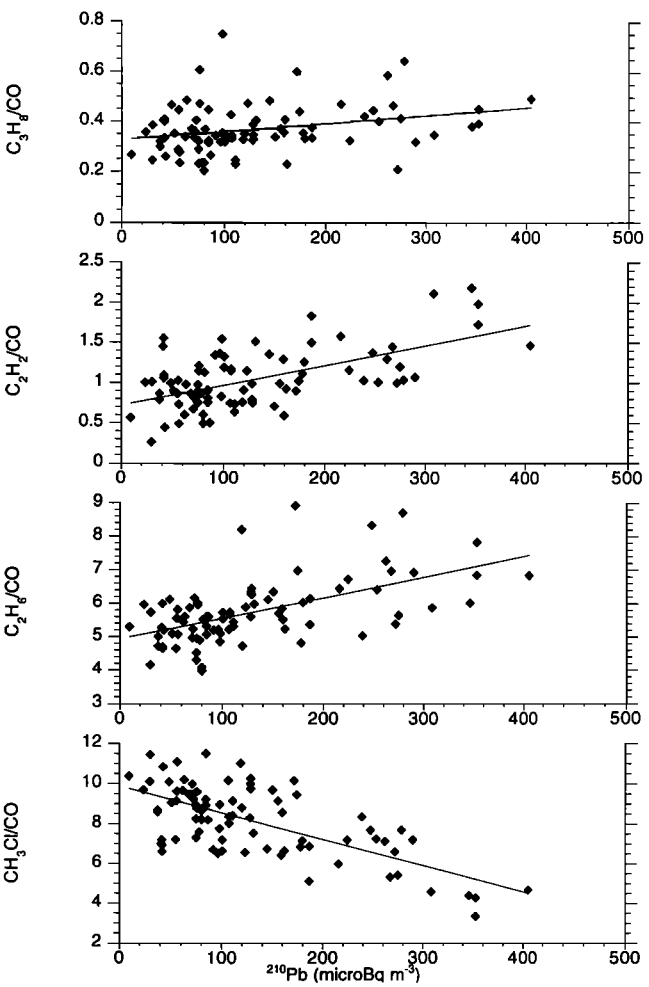

Figure 3. Scatterplots of C_3H_8/CO, C_2H_2/CO, C_2H_6/CO, and CH_3Cl/CO as a function of ^{210}Pb activity in all plume-impacted samples. The lines are least squares fits.

HC/CO_2) [*McKeen and Liu*, 1993; *Mckeen et al.*, 1990, 1996; *Mauzerall et al.*, 1998]. In addition, variations in OH levels over short time scales complicate the use of HC ratios to estimate the age of an air mass. However, the decay of ^{222}Rn to ^{210}Pb is not impacted by the composition of an air mass, and mixing of two air masses with different ^{210}Pb activities should be a simple dilution process. Therefore we used a very simple model to explore the relationships between ^{210}Pb and several primary emission products of biomass burning in plume-impacted samples from PEM-Tropics.

We consider ^{210}Pb and ^{222}Rn activities and the mixing ratios of four HC tracers of biomass burning (C_3H_8, C_2H_2, C_2H_6, and CH_3Cl) plus CO. The evolution of ^{210}Pb concentration in a plume impacted air mass is given by

$$dN_{Pb}/dt = \lambda_{Rn} N_{Rn} - S N_{Pb} - Dpb \quad (1)$$

where λ_{Rn} is the radioactive decay constant (0.18 d^{-1}), S denotes removal by scavenging, and D is dilution by ambient air. Loss of ^{210}Pb by radioactive decay (half-life equal to 22.3 years) is assumed to be insignificant. For ^{222}Rn the expression is similar though loss by scavenging is not a factor;

$$dN_{Rn}/dt = -\lambda_{Rn} N_{Rn} - Drn \quad (2)$$

For the five trace gases we use the simple model for the i^{th} species;

$$dC_i/dt = -k_i(OH)C_i - D_i \quad (3)$$

with the low solubilities of the trace gases again indicating that scavenging can be neglected.

In the atmosphere the details of mixing, and the impact of mixing on the various tracers, are very complex. In our model this complexity is entirely ignored by assuming that each sample represents a linear combination of plume air (which changes composition over time in a manner described shortly) and surrounding ambient air (of fixed composition).

Our aging plume is assumed identical to the hypothetical isolated air mass described in the second paragraph of the discussion. Within the plume we assume that loss of ^{210}Pb by scavenging must be very small on the basis of the high ^{7}Be activities and mixing ratios of soluble acidic gases measured in the South Pacific study area [*Dibb et al.*, 1999; *Talbot et al*,1999]. Neglecting scavenging and mixing within the plume leads to a very simple solution to equation (1):

$$N_{Pb}(t) = N_{Pb}(0) + N_{Rn}(0)\,(1 - \exp(-\lambda_{Rn} t)) \quad (4)$$

For the hydrocarbons and CO an even simpler first-order loss expression results for the mixing ratio of the i^{th} species:

$$C_i(t) = C_i(0) \exp(-K_i t) \quad (5)$$

where $K_i = k_i(OH)$. Estimates for the constant loss rate (equivalent to 1/lifetime) were derived from the Harvard photochemical point model [*Schultz et al.*, 1999]. We binned our samples into four latitude/altitude bins based on where each sample was collected and use averages of all point calculations within these large bins for the model (Table 2). The model calculates the mixing ratios of all five gases in the mixture of aging plume and background air and then finds the HC/CO ratios.

We specify a constant initial composition for the fresh plumes that is based on low-altitude sampling over Africa during GTE TRACE- A [*Blake et al.*, 1996; *Mauzerall et al.*, 1998], since back trajectory calculations point to this region as a likely source of the PEM-Tropics plumes [*Fuelberg et al.*, 1999; R. Lusher et al., unpublished manuscript, 1999]. The mixing ratios of C_3H_8, C_2H_2, C_2H_6, and CH_3Cl are set at 700, 2000, 3600, and 860 ppt, respectively, with 600 ppb of CO. We must also specify initial activities of ^{222}Rn and ^{210}Pb. We are not aware of any airborne measurements of these tracers over Africa during austral spring, but *Ramonet et al.* [1996] report ^{222}Rn results for 10 samples collected on three flights in late January 1991. These ranged from below detection limit to 1.7 Bq m^{-3} with 3/10 samples > 1 Bq m^{-3} and half > 0.3 Bq m^{-3}. All of these elevated samples were clearly traced to strong wet convective uplift. The output of a global 3-D model suggests values of 3.7-7.4 Bq ^{222}Rn m^{-3} (100-200 pCi m^{-3}) in the boundary layer and 1.1-1.9 Bq m^{-3} (30-50 pCi m^{-3}) in convective outflow over Africa during spring (Y. Balkanski, personal communication, February 1998), so we tested the range 1.1-7.4 Bq m^{-3} (30-200 pCi m^{-3}). If wet convection is the process pumping boundary layer air into the free troposphere, ^{210}Pb activities should be quite low. However, this is an unproven hypothesis, so we tested sensitivity to initial ^{210}Pb activities over the range 0-93 μBq m^{-3} (0-2.5 fCi m^{-3}).

It is also necessary to assume a fixed composition of background air to mix into the aging plume. We use PEM-Tropics measurements outside of plumes to define the composition of this air: 15, 19, 230, and 540 ppt of C_3H_8, C_2H_2, C_2H_6, and CH_3Cl, respectively, 50 ppb of CO and 19 μBq ^{210}Pb m^{-3}. Each sample is then considered to be a mixture of aged plume and ambient air. With plume fraction f and plume age a this expresses the concentration of species i in the sample, $C_{i,S}$, in terms of the aged plume concentration and the ambient concentration of the species, $C_{i,A}$, as an estimated "theoretical" quantity, $C_{i,T}(f, a)$, depending on the estimated age and plume fraction,

$$C_{i,S} \text{ Å } f\,C_i(a) + (1 - f)\,C_{i,A} = C_{i,T}(f, a) \quad (6a)$$

Similarly, for ^{210}Pb (from equation (4)),

$$N_{Pb,S} \text{ Å } f\,N_{Pb}(a) + (1 - f)\,N_{Pb,A} = N_{Pb,T}((f, a) \quad (6b)$$

The observed ratio of hydrocarbon species i to CO, denoted by species 0, for a sample with theoretical plume fraction f and age a is

Table 2. Lifetimes in Days of the Hydrocarbons and CO Used in the Aging/Mixing Model

Sample Bin	C_3H_8	C_2H_2	C_2H_6	CH_3Cl	CO
0°-30°S, <6 km	8.6	12.4	42.8	302.9	38.1
0°- 30°S, >6 km	16.0	21.6	101.6	874.0	57.6
>30°S, <6 km	23.0	32.4	122.1	911.7	92.3
>30°S, >6 km	22.4	30.5	135.4	1121.6	82.0

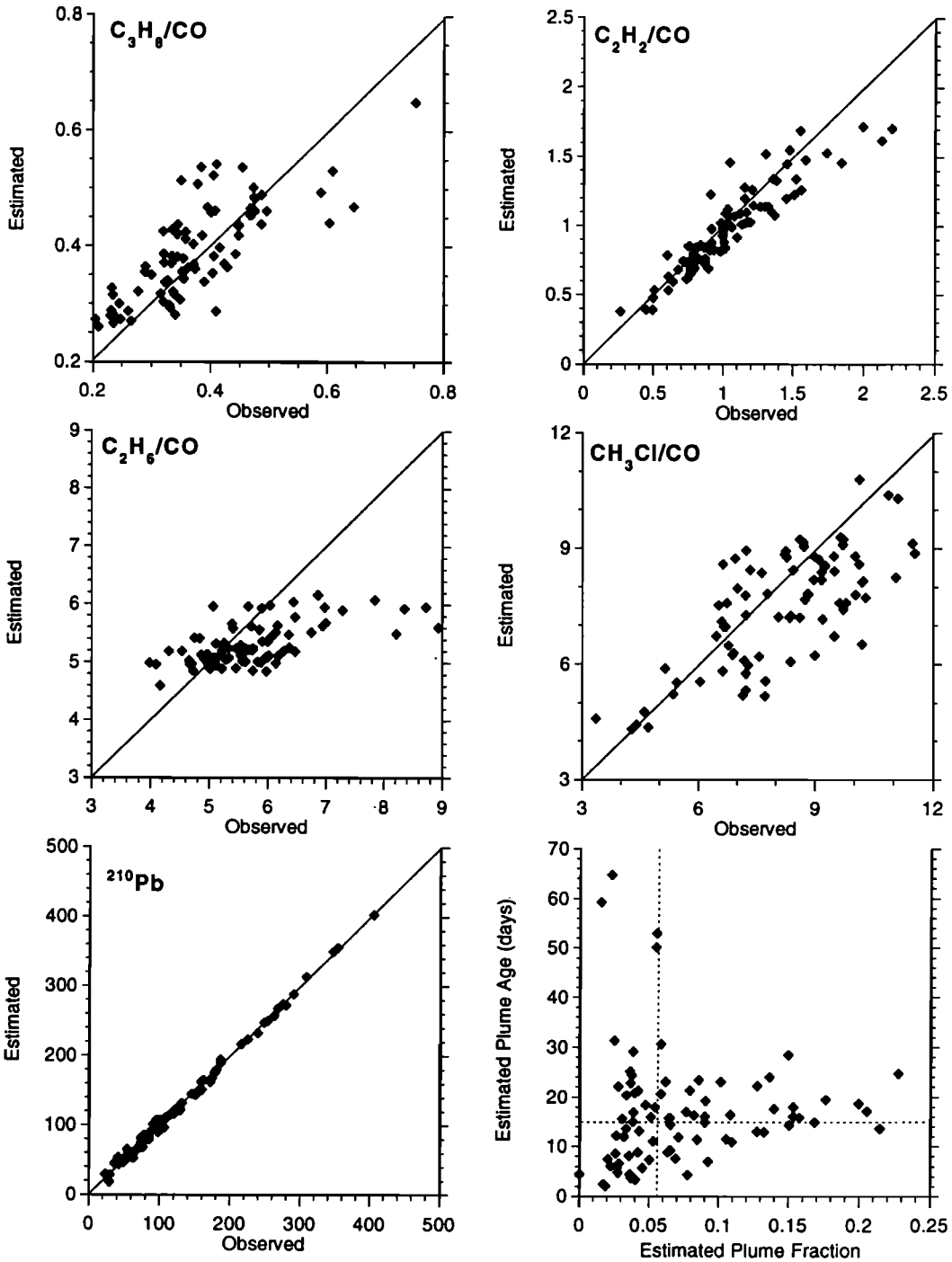

Figure 4. Comparison between model-predicted and observed values of four HC/CO ratios and ^{210}Pb activities in all plume-impacted samples. Activities of the radionuclide tracers in the fresh plume for this run were set at 3.7 Bq ^{222}Rn m^{-3} and 19 μBq ^{210}Pb m^{-3}. The model estimate of plume age and fraction of aged plume in each sample is also shown, with the median values for each shown as dashed lines.

$$R_{i,S} = C_{i,S}/C_{0,S} \text{ Å } C_{i,T}(f, a) / C_{0,T}(f, a) = R(f, a) \quad (7)$$

Equation (7) provides an approach to estimating the plume fraction and age of a sample. We define the "residual error" for the i^{th} species ratio as

$$E_i(f, a) = R_{i,S} - R_{i,T}(f, a) \quad (8)$$

and for ^{210}Pb,

$$E_{Pb}(f, a) = N_{Pb,S} - N_{Pb,T}(f, a) \quad (9)$$

and form the "sample error sum of squares,"

$$Q_S(f, a) = E_1(f, a)^2 + E_2(f, a)^2 + E_3(f, a)^2 + E_4(f, a)^2 + E_{Pb}(f, a)^2 \quad (10)$$

Our estimates of the plume fraction and age of the plume are determined for each sample independently by minimizing $Q_S(f, a)$ under the constraints, $0 \le f \le 1$ and $0 \le a$.

4.2. Model Results

4.2.1. A selected run. Since we use low-altitude measurements of CO and the HC to initialize the fresh plume, we suspect that

using estimates for ^{222}Rn activity in the boundary layer may be more internally consistent. The agreement between model results and observations when initial ^{222}Rn and ^{210}Pb activities are set at 3.7 Bq m^{-3} and 19 μBq m^{-3}, respectively, are shown in Figure 4. These results are typical in that the model does extremely well predicting ^{210}Pb activities and not as well with the reactive trace gases. However, the model-predicted HC/CO ratios are generally within 20% of the measured values (Figure 5), a finding which also applies to all of the other runs. Given the drastic simplifications made in the treatment of CO and the HC, we are quite pleased with the model performance. In particular, recall that a constant initial plume composition, based on a few samples from a single flight over Africa 4 years earlier, was assumed to be a valid representation of the composition of all of the plumes advected to the South Pacific during PEM-Tropics.

4.2.2. Sensitivity to initial Rn and Pb. The model is much more sensitive to the value of initial ^{222}Rn than to that of ^{210}Pb over the ranges of these parameters that we explored (Figure 6). Increasing initial ^{222}Rn from 1.1-3.7 Bq m^{-3} reduces the median estimated plume age by about a week, with the higher HC mixing

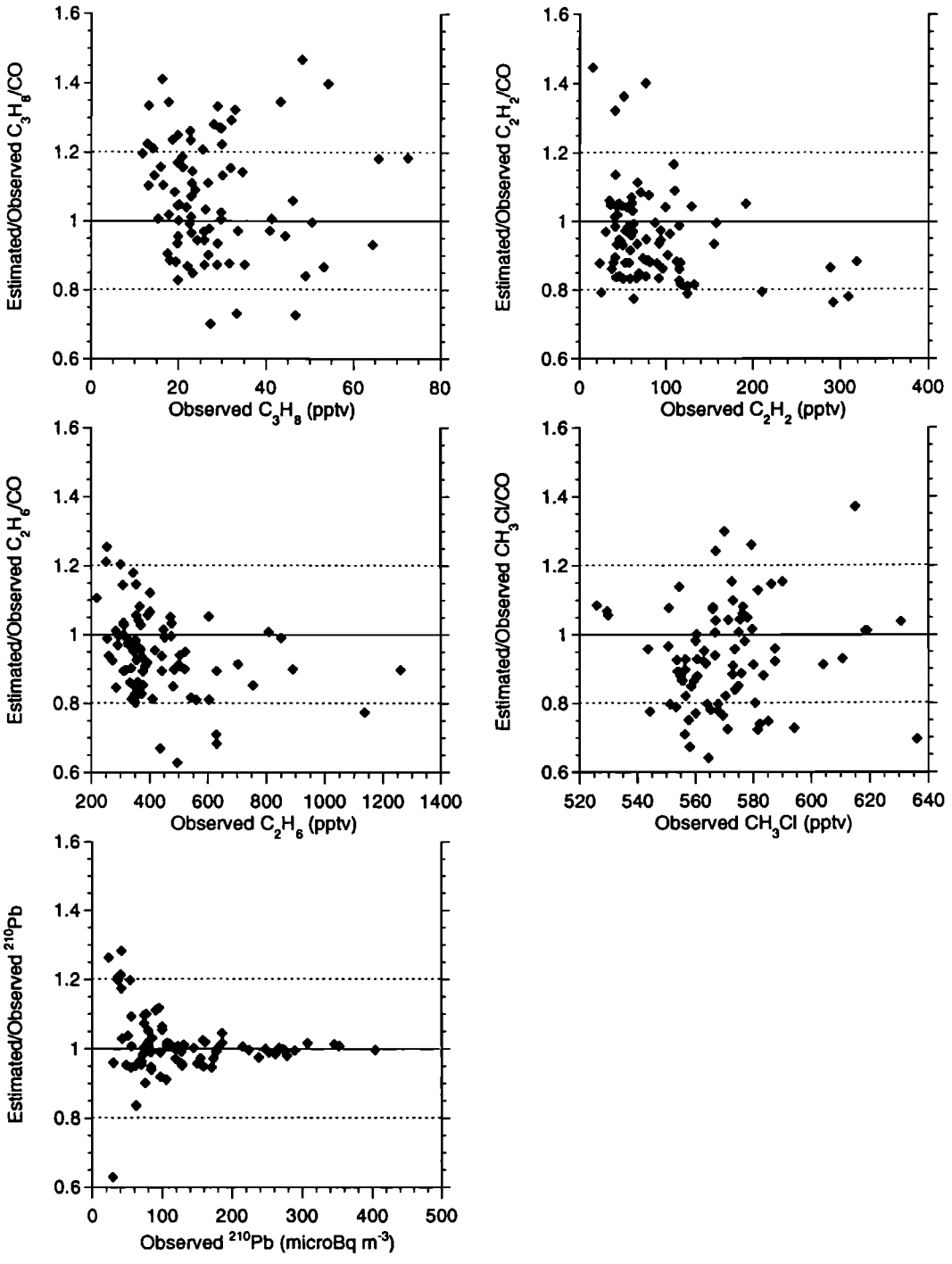

Figure 5. Ratios of model-predicted HC/CO and ^{210}Pb activities over observations, plotted against the observed mixing ratios of the tracer species.

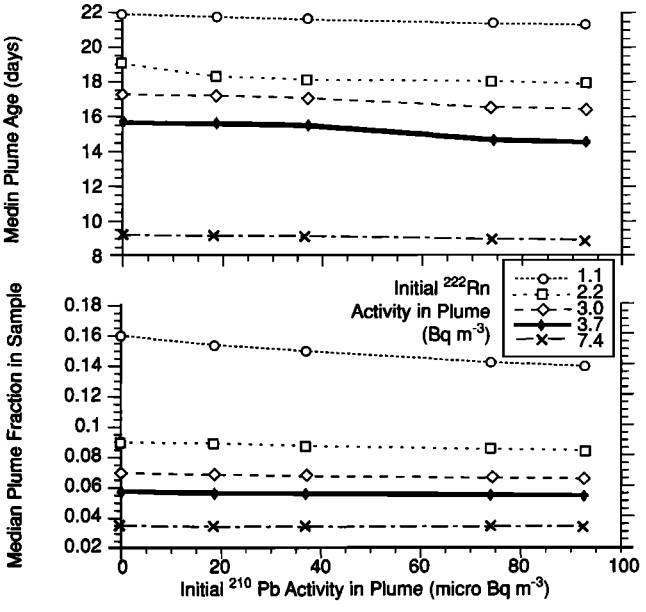

Figure 6. Median values of model-estimated plume ages and fractions of aged plume in each sample plotted as a function of prescribed initial ^{210}Pb activity. Each line/symbol combination corresponds to a different prescribed initial ^{222}Rn activity.

ratios in the younger plume compensated for by increased "entrainment" of background air (about 95% background with the younger plumes compared to roughly 85%). At 7.4 Bq ^{222}Rn m^{-3} in the fresh plume the median age when encountered over the South Pacific drops to about 9 days, and the samples are estimated to be 97% background air. In contrast, the age and dilution estimates vary only a few percent for a given value of initial ^{222}Rn as initial ^{210}Pb is allowed to vary from 0-93 μBq m^{-3} (Figure 6). This reflects the fact that production of ^{210}Pb from ^{222}Rn decay quickly overwhelms the initial value, with 1 Bq ^{222}Rn m^{-3} ultimately yielding 470 μBq ^{210}Pb m^{-3} within the aging plume (with 72% of this produced in 7 days and 92% by the end of the second week).

It should be noted that the model is also quite sensitive to the prescribed activity of ^{210}Pb in background air. The median-estimated plume age decreases from 16.6 to 4.5 days when background ^{210}Pb is increased from 0 to 93 μBq m^{-3} (assuming 3.7 Bq ^{222}Rn m^{-3} and no ^{210}Pb in the fresh plume). However, measured ^{210}Pb activities over the South Pacific outside of the plumes constrain the background to values less than 35 μBq m^{-3}, which yields median-estimated ages in the range of 13.7-16.6 days for the same initial conditions.

4.3. Implications of the Simple Model Results

The complete lack of observational constraints on the initial composition of the plumes that were advected to the South Pacific (from Africa or possibly even South America) during the PEM-Tropics campaign precludes quantitative assessment of the utility of such a simple modeling exercise. It is clear that the HC and CO mixing ratios are likely to vary considerably as a function of fuel and fire type, and the local meteorological conditions [e.g., *Lobert et al.*, 1991; *McKenzie et al.*, 1997].

Nevertheless, the model estimates of plume ages are in reasonable agreement with transport times from south Africa derived from back trajectory calculations. R. Lusher et al. (unpublished manuscript, 1999) report a mean transit time of roughly 8 days from South Africa to interception during PEM-Tropics for plumes that came in from the west. This is half the median age estimated for an initial ^{222}Rn activity of 3.7 Bq m^{-3} (Figure 6), but essentially the same as our estimate if initial ^{222}Rn is 7.4 Bq m^{-3} (Figures 4 and 6). Both analyses suggest that a significant fraction of the intercepted plumes were in the 5-14 day old range.

The model clearly demonstrates that all of the plumes entrained significant amounts of background air during transport. This finding is in agreement with more elaborate advective/photochemical models that cannot create air masses resembling the PEM-Tropics plumes out of any of the air masses sampled during GTE/TRACE- A without entraining large fractions of South Pacific background air (B. Heikes and F. Flocke, personal communication, April 1998). However, our estimates of dilution must be regarded as upper limits in most cases because of the mixture of "in plume" and "out of plume" time reflected in many of our sample collection intervals. In theory, it would be possible to account for this "sampling artifact" dilution and calculate better estimates of "transport" dilution, but the large uncertainties in our knowledge of the initial conditions imposed on the model suggest that such an exercise would have little merit.

5. Conclusions

Observed enhancements of ^{210}Pb in biomass burning impacted air masses over the South Pacific lend support to a conceptual model linking these plumes to fires in Africa. Wet convective uplift over or near Africa appears to have lofted boundary layer air with elevated ^{222}Rn activities, primary combustion products, and precursors of O_3, PAN, HNO_3, HCOOH, and CH_3COOH well into the free troposphere. Precipitation scavenging in the wet convective systems depleted the mixing ratios of aerosol-associated soluble ions and their soluble gaseous precursors in the lifted boundary layer air. The prevailing westerlies then advected these air masses to the PEM-Tropics study region where they were intercepted by the DC-8.

A simple aging and dilution model, initialized with plausible, but very poorly constrained, estimates of the composition of such lifted boundary layer air, reproduced ^{210}Pb activities over the South Pacific very well. The ratios of four HC tracers of biomass burning over CO were also reasonably captured by the model (generally to better than 20%).

Model-calculated ages of the plumes are one of the principal results. These were highly dependent on the prescribed activity of ^{222}Rn in the fresh plumes (which is not known), but using values which should bound typical boundary layer activities produced ages that agreed with independent ages based on back trajectories to within better than a factor of 2. This exercise demonstrates the potential power of ^{222}Rn and ^{210}Pb as transport tracers, but also points out the need for a greatly expanded observational data base on their distribution in the free troposphere.

Acknowledgments. We would like to thank M. Schultz for sharing the results of his calculations with the Harvard photochemical model, and B. Heikes and F Flocke for sharing preliminary output from their attempts to model the evolution of PEM-Tropics plumes. The efforts of the Ames DC-8 flight and ground crews that made PEM-Tropics a success are greatly appreciated This research was supported by the NASA Global Tropospheric Chemistry Program.

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(Received August 3, 1998; revised January 20, 1999;
accepted February 3, 1999.)