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Chemical characteristics of continental outflow from Asia to the troposphere over the western Pacific Ocean during September-October 1991: Results from PEM-West A

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Abstract. An important objective of the Pacific Exploratory Mission-West A (PEM-West A) was the chemical characterization of the outflow of tropospheric trace gases and aerosol particles from the Asian continent over the western Pacific Ocean. This paper summarizes the chemistry of this outflow during the period September - October 1991. The vertical distributions of CO, C_2H_6, and NO_x showed regions of outflow at altitudes below 2 km and from 8 to 12 km. Mixing ratios of CO were ≈ 130 parts per billion by volume (ppbv), ≈ 1000 parts per trillion by volume (pptv) for C_2H_6, and ≈ 100 pptv for NO_x in both of these regions. Direct outflow of Asian industrial materials was clearly evident at altitudes below 2 km, where halocarbon tracer compounds such as CH_3CCl_3 and C_2Cl_4 were enhanced about threefold compared to aged Pacific air. The source attribution of species outflowing from Asia to the Pacific at 8 -12 km altitude was not straightforward. Above 10 km altitude there were substantial enhancements of NO_y, O_3, CO, CH_4 SO_2, C_2H_6, C_3H_8, C_2H_2, and aerosol ^{210}Pb but not halocarbon industrial tracers. These air masses were rich in nitrogen relative to sulfur and contained ratios of C_2H_2/CO and C_3H_8/C_2H_6 (≈ 1.5 and 0.1 respectively) indicative of several-day-old combustion emissions. It is unclear if these emissions were of Asian origin, or if they were rapidly transported to this region from Europe by the high wind speeds in this tropospheric region (60 - 70 m s^{-1}). The significant cyclonic activity over Asia at this time could have transported to the upper troposphere emissions from biomass burning in Southeast Asia or emissions from the extensive use of various biomass materials for cooking and space heating. Apparently, the emissions in the upper troposphere were brought there by wet convective systems since water-soluble gases and aerosols were depleted in these air masses. Near 9 km altitude there was a distinct regional outflow that appeared to be heavily influenced by biogenic processes on the Asian continent, especially from the southeastern area. These air masses contained CH_4 in excess of 1800 ppbv, while CO_2 and OCS were significantly depleted (349 - 352 ppmv and 450 - 500 pptv, respectively). This signature seemingly reflected CH_4 emissions from wetlands and rice paddies with coincident biospheric uptake of tropospheric CO_2 and OCS.

1. Introduction

The mineralogy of sediments collected from the North Pacific Ocean between 30° and 40°N latitude is identical to that of aeolian mineral particles originating on the Asian continent [Blank et al., 1985]. The transport and deposition of Asian dust materials can,

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in fact, account for a substantial fraction of the nonbiogenic portion of Pacific sediments in this region. Atmospheric studies in the marine boundary layer at numerous island stations in the Pacific confirm the impact of long-range transport of aeolian materials from the Asian continent, that is particularly strong in the February through May time period [Duce et al., 1980]. This seasonal impact is most evident at higher latitudes, presumably resulting from the westerly wind regime there in the large-scale meteorological features [Merrill et al., 1985].

It is well documented that atmospheric nitrate (HNO_3 vapor + aerosol NO_3^-) mixing ratios in the boundary layer are consistently larger and more variable over the North Pacific compared to its equatorial and southern counterparts [Savoie et al., 1989; Prospero and Savoie, 1989]. Furthermore, the significant correlation of ^{210}Pb and nitrate over the North Pacific suggests a continental source for both species [Balkanski et al., 1993]. Indeed, the transport of ^{210}Pb over the Pacific Ocean appears to be closely tied to aeolian transport of mineral aerosols derived from the extensive arid regions of Asia [Turekian and Cochran, 1981; Uematsu et al., 1983; Prospero et al., 1985]. These atmospheric components show a pronounced annual seasonal cycle in their abundance in boundary layer air over the North Pacific that

appears to be linked to dust storm activity on the Asian continent [*Uematsu et al.*, 1983].

In contrast to nitrate, data for aerosol SO_4^{2-} do not necessarily imply a strong continental source [*Savoie and Prospero*, 1989]. The sulfur regime appears to be driven by a general predominance of natural emissions from the North Pacific, mainly of dimethylsulfide [*Savoie and Prospero*, 1989; *Arimoto et al.*, this issue]. Episodic impact of continental sources on aerosol SO_4^{2-} is evident at some North Pacific locations, particularly those at more northern latitudes (e.g., Midway and Shemya Islands) [*Prospero et al.*, 1985]. The absence of consistent correlation of atmospheric nitrate and ^{210}Pb with aerosol SO_4^{2-} suggests that these species have different sources and transport characteristics over the North Pacific [*Prospero et al.*, 1985].

At lower latitudes over the Pacific the influence of Asian continental sources is clearly evident during the January to May time frame. Numerous measurements made during the Sea-Air Exchange (SEAREX) program show this impact, including (1) a suite of natural organic materials, many typical of a vegetation origin [*Gagosian et al.*, 1981, 1982]; (2) high-molecular weight organic compounds of anthropogenic nature [*Atlas and Giam*, 1981]; and (3) lead with a distinct anthropogenic isotopic signature [*Settle and Patterson*, 1982]; and a broad spectrum of trace metals from natural and anthropogenic sources [*Duce et al.*, 1983].

At mid-Pacific equatorial locations the weak inputs of continental materials during the summer and fall months appear to be derived from continental areas to the east. The lead isotopic signature during these warmer months matches that of a western North American source region [*Settle and Patterson*, 1982]. The mineralogy of aeolian dust during this period is also distinctly different from that during springtime and indicative of North/South American-derived materials [*Buat-Menard et al.*, 1983].

The ground-based measurements summarized above have provided key information for establishing the basic regime for material transport over the western Pacific Ocean. The NASA Pacific Exploratory Mission over the western (PEM-West A) Pacific in fall 1991 expanded upon ground-based observations by providing information up to an altitude of about 12 km for a grid $0°$ - $40°N$ latitude and $110°$ - $180°E$ longitude. The airborne measurements during PEM-West A were conducted in September-October 1991 to study budgets of O_3 and its precursors, and sulfur, in the troposphere over the western Pacific during the summer/fall period of low aeolian dust outflow from the Asian continent. The objective of this paper is to provide a summary of the general chemical characteristics of continental outflow during PEM-West A. We compared fresh (<2 days from western Pacific rim landmasses) with more aged (2-5 days) continental outflow air masses to examine short-term aging effects on the chemical signatures. Companion papers discuss the details of the chemical gradients [*Smyth et al.*, this issue] in continental outflow relative to aged marine [*Gregory et al.*, this issue] air masses during PEM-West A.

2. Experiment

The airborne component of PEM-West A was conducted aboard the NASA Ames DC-8 research aircraft. Transit and intensive site science missions composed 18 flights, each averaging about 8 hours in duration and covering the altitude range of 0.3 to 12.5 km. The flights over the western Pacific Ocean from which the data for this paper are drawn were centered in the geographic grid bounded by approximately $15°$ - $40°N$ latitude and $115°$ - $145°E$ longitude. A geographic representation of the study region is shown in Figure 1. The base of operation for these missions progressed from (1) Yokota, Japan (four missions), to (2) Hong Kong (two missions) and on to (3) Guam (three missions). Data obtained on transit flights between these locations was also utilized in this paper.

The overall scientific rationale and description of the individual aircraft missions are described in the PEM-West A overview paper [*Hoell et al.*, this issue]. The salient features of the large-scale meteorological regime are provided by *Bachmeier et al.* [this issue]. Because we present here a broad description of the observed chemistry in continental outflow air masses during PEM-West A, it is impractical to provide the details here for the individual species measurements. Instead, the philosophy was adopted to present measurement-specific details in the PEM-West A overview paper [*Hoell et al.*, this issue]. Additional information for individual species is also summarized in *Gregory et al.* [this issue], with the details of species-specific measurements contained in numerous companion papers in this issue.

3. Formulation of Continental Outflow Data Set

3.1. Meteorological Basis

The detailed synoptic meteorological setting leading to outflow of Asian continental air masses over the western Pacific Ocean is described in companion papers [*Bachmeier et al.*, this issue; *Merrill*, this issue]. In later sections of this paper we present the general chemical characteristics of continental outflow from Asia and Japan that occurred at various altitudes. This section provides a brief description of the large-scale meteorological features.

An extensive subtropical ridge of high pressure was centered over the central western Pacific area near $30°$-$35°N$ and $160°$-$170°E$. This high often caused low-altitude easterly flow of aged marine air to persist at Guam and off the eastern coast of Japan. The air masses associated with this flow essentially constitute the chemical classification termed "aged marine" discussed by *Gregory et al.* [this issue]. Here we contrast the chemistry of "fresh" (<5 days old) outflowing air with that of aged marine (≥ 10 days).

A second large anticyclone located over central and eastern China counteracted the marine flow by providing steady north to northwesterly flow of continental air across the Sea of Japan and the East and South China Seas. We sampled this low altitude flow several times during PEM-West A, as it was responsible for bringing "fresh continental emissions" out over the coastal western Pacific Ocean.

In the middle to upper troposphere the flow was predominately westerly off the Asian continent, especially north of $30°$ latitude. Rapid westerly flow occurred in the 7- to 12.5-km altitude region due to the Japan (polar) jet [*Merrill et al.*, 1985; *Kritz et al.*, 1990]. Convective activity over China could potentially inject ground level emissions into this jet region where they would be subjected to rapid transport eastward over Japan and the North Pacific Ocean. A large majority of the constant altitude flight legs in the 2 - 7 and 7 - 12.5 km regions were influenced by such Asian continental outflow during missions conducted from Japan and Hong Kong.

3.2. Measurement Database

Extensive processing of final archived data was required to obtain the data products utilized in our analysis here. Archived data for each species measured in PEM-West A is maintained by
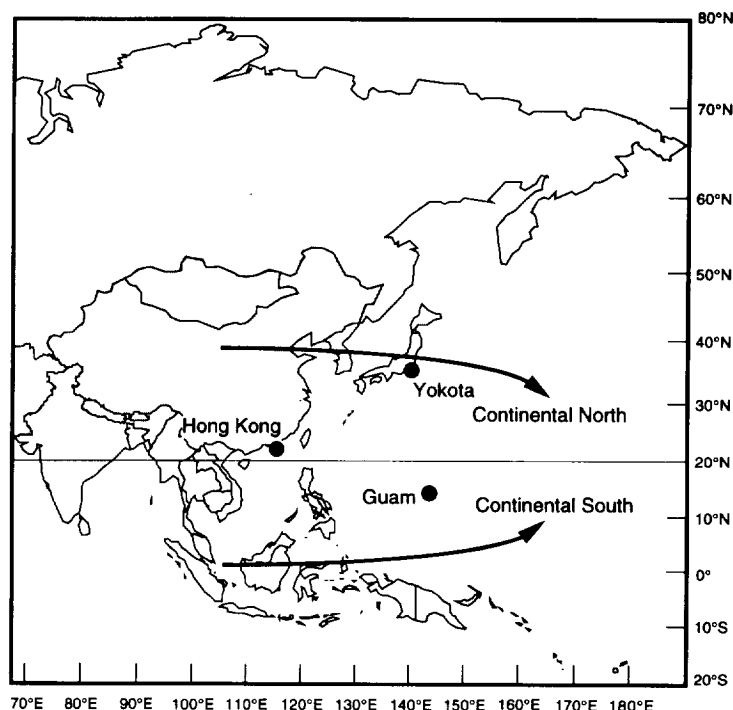
Figure 1. Geographical representation of the PEM-West A study region showing the continental north (CN) and continental south (CS) source areas. The line at 20°N denotes the geographic division between the CN and the CS source regions.

the NASA Global Tropospheric Chemistry project office at Langley Research Center in Hampton, Virginia. Because of extreme diversity in measurement time resolutions for the various species of interest, merged data products were produced for several desired intervals. These data products were generated at the Georgia Institute of Technology (GIT) under the supervision of S. Sandholm and J. Bradshaw. Here we utilized 90-s-averaged data that correspond to the highest-resolution GIT NO_x (NO + NO_2) and NO_y (total reactive odd nitrogen) measurements. For consistency, the GIT NO and NO_y measurements are used in this paper, with the NO data filtered to correspond only to a solar zenith angle of 0° - 60°. It should be noted that the chemiluminescence NO measurements reported by *Kondo et al.*, [this issue] were indistinguishable from the GIT two-photon laser-induced fluorescence values utilized here. The measurements of faster response instruments (e.g., meteorological parameters and chemical species including O_3, CO, CO_2, CH_4, and N_2O) were averaged to correspond to the 90-s-based time intervals.

Merged data products on various other time resolutions were utilized for species with longer time resolutions (e.g., sulfur gases, acidic gases, peroxides, peroxyacetylnitrate (PAN), hydrocarbons, and aerosol species). The hydrocarbon data used here are from measurements reported by *Blake et al.*, [this issue].

For all species their limit of detection values were utilized for measurement intervals reported as such. For the analysis of continental outflow presented in this paper the mixing ratios of most species were generally well above their stated limits of detection, except for cases where the short-lived hydrocarbons and soluble species were depleted in air masses classified as aged 2 - 5 days.

3.3. Classification of Database

Isentropic back trajectories were utilized to identify time intervals that corresponded to constant altitude flight legs where

the sampled air masses had recently passed over continental areas [*Merrill*, this issue]. Spiral data were not utilized in our analysis due to heterogeneity in air masses and practical limitations imposed by the vertical density of trajectories. The eastern edge of the continental area considered was defined geographically as the Pacific rim arc landmasses composed of Japan, the Peoples's Republic of China, Taiwan, and Indonesia. Examination of the times since the air masses last passed over continental areas revealed that a natural break in groupings occurred around 2 days. Back trajectories indicated that it was unlikely that air masses were sampled with emissions less than 1 - 1.5 days old. Thus we compare here the chemical composition of "fresh" (<2 days) with "short-term" aged (>2 but <5 days) air masses of continental origin over coastal waters of the western Pacific Ocean.

Data for tropospheric species measured in PEM-West A were classified according to the above scheme and then broken into three altitude regions of <2, 2 - 7, and 7 - 12.5 km. The vertical groupings were purposely kept simple due to the constraint of only using constant altitude data. The <2-km group essentially represents the marine boundary layer, clearly defined by the vertical distribution of sea-salt aerosol particles [*Browell et al.*, this issue]. The next altitude group of 2-7 km was selected to provide information on the middle tropospheric region. The final altitude grouping reflects outflow in the upper troposphere.

We further divided the vertical air mass classifications into two groups referred to here as "continental north" (CN) and "continental south" (CS). The back trajectories showed that two basic flow regimes dominated: (1) >20°N latitude the flow originated over central or northern China and (2) <20°N latitude, the flow had various origins, with some over southeastern Asia and others near Indonesia. The line in Figure 1 indicates the 20°N division between the CN and CS source regions. It is likely that the latitudinal differences in these air mass histories exposed them to various amounts and types of continental emissions which

should be reflected in their chemical compositions. We therefore compared the chemical characteristics of the CN and CS groupings for the altitude regions of <2, 2 - 7, and 7 - 12.5 km. Excellent examples of typical air mass trajectories for the CN and CS source regions are presented by *Merrill* [this issue], *Gregory et al.* [this issue], and *Smyth et al.* [this issue].

4. Characterization of Continental Outflow

4.1. Chemical Characteristics of <2-Day Transport Cases

The largest mixing ratios of many chemical species in CN outflow were observed at <2 km altitude (Table 1). It appears that anthropogenic activities in Asia and Japan contributed significantly to the chemical composition of the low-altitude outflow. Mixing ratios of halocarbon compounds such as CH_3CCl_3 and C_2Cl_4 were significantly enhanced at <2 km compared to their values at higher altitudes and in aged marine air [*Gregory et al.*, this issue]. Asian hydrocarbon signatures show that CH_3CCl_3 is a particularly good tracer for industrial activities in this region

[*Blake et al.*, this issue]. The concentrated industrial activity along the eastern coast of the People's Republic of China is a likely source of some of the outflow emissions that we sampled [*Kato and Akimoto*, 1992].

The relatively small mixing ratios of NO_x ($NO_x = NO + NO_2$, median = 132 pptv) in the air masses sampled at low altitude are indicative of photochemical aging of a few days. Many of the air mass trajectories indicated about 1 day of transit time from over source regions in Asia and Japan to where we sampled them [*Merrill*, this issue]. In addition, the SO_2/non-sea-salt (nss)-SO_4^{2-} ratios (not shown) were less than 1.0 on the average, also suggesting several days of aging since emission inputs to the sampled air masses.

Ratios of C_2H_2/CO and C_3H_8/C_2H_6 can provide useful information on the relative age of air masses [*Singh and Zimmerman*, 1992]. Air masses over the western Pacific that had undergone significant atmospheric processing from photochemical aging and mixing exhibited C_2H_2/CO values of <1.0 (pptv/ppbv) and < 0.10 (pptv/pptv) for C_3H_8/C_2H_6 [*Smyth*, this issue]. For air

Table 1. Mixing Ratios of Principal Species Measured in Fresh (< 2 days) Asian Continental-North Outflow for Isentropic Back-Trajectories Originating > 20°N Latitude

Species	< 2 km					2 – 7 km					7 – 12 km				
	Mean	s.d.	Median	Range	N	Mean	s.d.	Median	Range	N	Mean	s.d.	Median	Range	N
NO	17	14	17	2.2 - 59	67	18	6.2	17	7.5 - 34	70	58	43	54	1.7 - 203	137
NO_x	121	74	132	14 - 290	67	59	15	59	27 - 91	70	101	37	93	41 - 249	73
HNO_3	216	148	186	23 - 501	14	64	40	65	20 - 128	9	50	32	45	20 - 133	10
PAN	143	108	156	2.5 - 378	26	155	85	161	31 - 347	17	76	48	75	18 - 169	35
NO_y	897	420	805	341 - 1660	67	485	124	467	249 - 751	70	585	118	574	356 - 884	81
O_3	54	10	57	34 - 66	78	51	10	52	30 - 77	86	46	19	36	24 - 99	166
CO	130	12	129	106 - 159	69	106	22	98	82 - 167	78	118	23	127	70 - 151	156
CH_4	1783	20	1785	1748 - 1819	75	1760	27	1755	1719 - 1837	78	1757	18	1756	1722 - 1818	156
CO_2	354	2.3	355	349 - 357	58	352	0.69	352	350 - 354	54	352	1.1	352	349 - 354	107
N_2O	309.7	0.51	309.8	308.2 - 310.7	59	309.3	0.41	309.2	308.5 - 310.5	77	309.4	0.43	309.4	307.4 - 310.4	131
SO_2	366	341	222	52 - 954	21	76	19	70	54 - 121	16	118	23	121	67 - 153	35
DMS	23	14	27	2.2 - 45	18	4.5	1.7	4.0	3.0 - 7.0	4	7.3	3.5	8	2.2 - 14	12
CS_2	12	7.3	11	5.7 - 34	21	2.5	1.6	2.9	0.40 - 5.0	15	3.3	2.6	1.9	0.80 - 10	34
OCS	498	14	499	473 - 523	20	516	39	514	460 - 597	17	514	11	515	475 - 527	27
HCOOH	645	211	704	332 - 1015	14	405	217	376	153 - 717	11	188	151	148	77 - 626	11
CH_3COOH	680	229	708	289 - 1158	14	623	252	612	333 - 996	11	436	184	387	281 - 956	11
H_2O_2	1269	436	1353	618 - 2367	44	1426	714	1162	378 - 2537	37	387	320	298	46 - 1069	40
CH_3OOH	599	204	519	312 - 950	44	609	273	476	260 - 1255	37	165	59	146	87 - 312	36
Ethane	1257	316	1167	815 - 1850	40	946	274	976	543 - 1472	21	941	156	958	639 - 1250	60
Ethene	64	45	48	15 - 192	40	27	20	20	8.0 - 76	21	29	11	27	9.5 - 73	60
Propane	398	258	322	156 - 1362	40	131	81	130	38 - 314	21	117	37	123	37 - 180	60
i-Butane	86	56	74	27 - 297	40	27	22	22	9.0 - 79	15	13	4.7	12	3.6 - 20	51
n-Butane	146	122	124	48 - 663	40	37	48	26	4.0 - 175	20	22	8.9	22	5.7 - 37	59
Ethyne	399	193	373	195 - 868	40	238	206	176	69 - 725	21	217	76	228	47 - 467	60
1-Butene	7.4	2.5	7	4.1 - 16	25	6.7	4.8	4.5	3.0 - 20	12	6.4	4.5	4.5	3.1 - 21	30
i-Pentane	58	41	47	15 - 187	40	14	9.8	15	3.0 - 34	13	8.2	3.0	8.5	3.3 - 15	36
n-Pentane	43	37	30	12 - 189	40	11	10	8.5	3.0 - 34	14	6.5	2.1	7.1	3.2 - 11	33
n-Hexane	14	9.7	9	4.3 - 43	34	4.3	1.4	4.0	3.0 - 6.0	6	NA	NA	NA	N A	NA
Benzene	114	55	100	41 - 268	40	60	49	39	15 - 192	19	43	22	44	11 - 82	56
^{11}F	265	6.6	267	246 - 275	37	264	3.5	264	260 - 274	21	266	3.8	266	253 - 280	60
^{12}F	506	9.4	508	482 - 532	38	502	6.5	500	494 - 523	18	502	2.2	501	498 - 506	51
^{113}F	84	7.5	82	75 - 116	39	77	2.3	77	75 - 84	21	76	3.2	77	63 - 79	60
CH_3CCl_3	160	40	146	130 - 330	38	132	9.7	129	116 - 149	21	119	6.7	120	102 - 131	60
CCl_4	113	4.8	113	99 - 122	39	111	2.9	110	107 - 118	21	107	5.3	109	93 - 113	60
C_2Cl_4	13	5.7	12	4.4 - 32	39	6.9	3.4	6.5	2.7 - 16	21	2.9	0.70	2.8	1.8 - 4.7	60
C_3H_8/C_2H_6	0.30	0.12	0.27	0.15 - 0.74	40	0.13	0.06	0.13	0.06 - 0.29	21	0.12	0.02	0.13	0.06 - 0.17	60
C_2H_2/CO	3.1	1.3	2.7	1.7 - 6.2	35	2.1	1.3	1.8	0.81 - 5.0	20	1.8	0.43	1.7	0.93 - 3.2	51
NO_3^-	122	112	72	8.6 - 275	5	4.3	3.7	2.3	2.1 - 8.6	3	5.3	NA	5.3	5.3 - 5.3	1
nss-SO_4^{2-}	32	681	274	19 - 1517	5	107	72	94	34 - 206	4	33	18	33	20 - 45	2
NH_4^+	1037	913	944	35 - 2253	5	381	494	174	61 - 1113	4	86	NA	86	86 - 86	1
^{210}Pb	15	7.3	13	6.2 - 23	5	13.3	0.96	13.5	12.0 - 14	4	4.1	4.7	1.8	0.56 - 12	5
^{7}Be	146	74	149	58 - 226	4	269	121	242	153 - 438	4	352	235	435	86 - 534	3

Mixing ratios are stated in parts per trillion by volume; except for CO, CH_4, N_2O and O_3 that are in parts per billion by volume; CO_2 in parts per million by volume, and radioisotopes in femto curies per standard cubic meter. Ratio of C_2H_2/CO is stated in pptv/ppbv. NA means not available.

masses originating over the CN and CS source regions the ratios were much higher, indicative of relatively fresh emissions to the atmosphere (Tables 1 and 2). Both ratios had their largest values in boundary layer air outflowing from the CN region (medians of 2.7 for C_2H_2/CO and 0.27 for C_3H_8/C_2H_6). Thus these ratios and associated general chemical composition showed that the CN boundary layer outflow from Asia and Japan contained the freshest emission signatures over the western Pacific. Note that we did not encounter (<2 day) boundary layer outflow from the CS region (Table 2).

On the average, values of C_2H_2/CO and C_3H_8/C_2H_6 in air masses in the 2- to 12-km altitude range were reasonably constant and about 50% less than in the CN boundary layer outflow. The ratios were, however, still significantly elevated compared to aged

marine air over the western Pacific Ocean [*Gregory et al.*, this issue; *Smyth*, this issue].

4.2. Chemical Characteristics of 2- to 5-Day Transport Cases

Air masses with transport times of 2 - 5 days since their last landfall were sampled only at 7 - 12 km for the CN cases and in the 2- to 7 and 7- to 12-km altitude ranges for the CS region (Tables 3 and 4). Mixing ratios of most species were very similar in air masses classified as <2- and 2- to 5-day transport cases. This was true even for some of the more reactive hydrocarbon compounds (e.g., ethene). In addition, values of the ratios C_2H_2/CO and C_3H_8/H_2H_6 were not significantly different for the two transport cases. These results emphasize the point that the <2-day outflow cases were already aged, perhaps several days, before

Table 2. Mixing Ratios of Principal Species Measured in Fresh (< 2 days) Asian Continental-South Outflow for Isentropic Back-Trajectories Originating < 20°N Latitude

Species	2 – 7 km					7 – 12 km				
	Mean	s.d.	Median	Range	N	Mean	s.d.	Median	Range	N
NO	17	31	9.4	1.7 - 163	27	90	51	77	19 - 205	74
NO_x	44	49	33	17 - 276	27	149	59	141	63 - 318	74
HNO_3	68	27	74	32 - 99	5	15	9.5	14	< 5 - 16	13
PAN	19	30	8.0	2.2 - 99	10	117	43	111	38 - 232	22
NO_y	406	133	409	227 - 838	27	633	129	609	380 - 939	74
O_3	24	6	24	15 - 44	33	56	9	54	26 - 85	129
CO	97	28	93	71 - 216	31	104	8.9	104	80 - 127	125
CH_4	1723	19	1718	1710 - 1797	31	1794	32	1802	1715 - 1849	125
CO_2	353	1.1	352	352 - 356	24	351	1.2	350	349 - 353	112
N_2O	309.3	0.24	309.3	308.7 - 309.8	31	309.6	0.37	309.6	308.2 - 310.2	124
SO_2	267	572	46	34 - 1676	8	157	45	143	104 - 271	26
DMS	7.0	5.7	7.0	3.0 - 11.2	2	2.5	0.58	2.5	2.1 - 3.6	4
CS_2	5.8	13	0.87	0.54 - 38	8	1.6	0.93	1.2	0.57 - 4.6	27
OCS	494	11	491	484 - 516	8	475	23	474	397 - 517	27
HCOOH	339	143	302	188 - 608	6	319	241	280	90 - 1001	13
CH_3COOH	511	175	481	280 - 796	6	704	423	631	247 - 1601	13
H_2O_2	1813	89	1824	1667 - 1982	11	279	122	275	103 - 608	33
CH_3OOH	818	205	718	670 - 1245	11	110	52	97	52 - 209	29
Ethane	514	55	536	437 - 579	7	765	103	760	508 - 957	28
Ethene	37	36	19	13 - 100	7	19	11	16	7.7 - 61	28
Propane	38	10	38	25 - 53	7	75	27	69	31 - 172	28
i-Butane	18	14	12	7.3 - 34	3	8.7	6.8	6.8	4.3 - 33	20
n-Butane	11	4.4	10	6.5 - 18	7	15	14	10	4.3 - 73	24
Ethyne	84	22	81	57 - 124	7	181	64	187	63 - 299	28
1-Butene	8.4	8.7	4.4	3.1 - 25	7	5.2	3.3	4.8	3.3 - 13	9
i-Pentane	8.5	1.7	9.3	6.1 - 9.8	3	8.9	7.9	4.8	3.6 - 27	10
n-Pentane	4.5	2.3	4.2	3.3 - 9.7	6	6.4	4.5	4.7	3.3 - 16	9
n-Hexane	9.5	NA	9.5	9.5 - 9.5	1	3.5	0	3.5	3.5 - 3.5	2
Benzene	24	7.2	21	15 - 37	7	31	17	31	6.8 - 69	27
[11]F	262	2.1	263	259 - 264	7	265	3.5	264	258 - 274	27
[12]F	499	7.0	500	489 - 507	7	501	4.2	502	490 - 511	27
[113]F	77	1.2	77	76 - 79	7	77	1.9	77	72 - 82	27
CH_3CCl_3	132	11	130	117 - 151	7	122	9	126	103 - 141	27
CCl_4	108	2.4	109	103 - 110	7	109	4.0	110	99 - 118	27
C_2Cl_4	3.6	0.86	3.3	2.7 - 5.1	6	3.0	0.80	3.1	1.3 - 4.3	27
C_3H_8/C_2H_6	0.08	0.02	0.08	0.05 - 0.10	7	0.15	0.22	0.09	0.03 - 0.98	28
C_2H_2/CO	1.0	0.38	0.90	0.68 - 1.7	7	1.7	0.47	1.7	0.77 - 2.5	28
NO_3^-	< 5	NA	NA	N A	31	28	13	28	< 5 - 37	6
nss-SO_4^{2-}	< 9	NA	NA	N A	1	34	22	28	13 - 72	6
NH_4^+	< 25	NA	NA	N A	1	34	13	34	< 25 - 52	6
[210]Pb	0.99	NA	0.99	0.99 - 0.99	1	6.8	2.2	7.1	4.1 - 11	7
[7]Be	194	NA	194	194 - 194	1	255	190	234	< 10 - 467	7

Table 3. Mixing Ratios of Principal Species Measured in Aged (2-5 days) Asian Continental-North Outflow for Isentropic Back-Trajectories Originating >20°N Latitude

Species	7 - 12 km				
	Mean	s.d.	Median	Range	N
NO	44	60	35	1.5 - 358	81
NO_x	83	19	79	55 - 162	53
HNO_3	36	5.7	36	27 - 42	5
PAN	42	34	30	6.9 - 96	26
NO_y	406	127	364	212 - 640	43
O_3	39	12	34	25 - 61	99
CO	103	16	110	72 - 122	84
CH_4	1736	15	1730	1719 - 1782	84
CO_2	352	1.1	352	350 - 353	63
N_2O	309.3	0.25	309.3	308.9 - 309.9	70
SO_2	120	49	98	67 - 216	18
DMS	37	18	37	7.4 - 80	16
CS_2	6.3	3.1	4.7	3.1 - 12	19
OCS	509	22	514	438 - 526	14
HCOOH	157	52	152	82 - 213	5
CH_3COOH	308	128	325	115 - 469	5
H_2O_2	682	433	636	91 - 1460	16
CH_3OOH	231	74	213	119 - 359	11
Ethane	757	64	783	563 - 828	46
Ethene	29	12	26	5.3 - 68	46
Propane	83	20	85	27 - 124	46
i-Butane	13	5.0	13	3.2 - 23	43
n-Butane	24	8.1	22	5.6 - 40	44
Ethyne	165	26	171	67 - 200	46
1-Butene	4.7	2.2	4.6	3.4 - 12	20
i-Pentane	11	4.4	12	3.3 - 19	41
n-Pentane	9.8	3.9	10	3.5 - 17	42
n-Hexane	4.4	1.8	4.9	3.1 - 9.6	10
Benzene	46	17	45	10 - 105	44
[11]F	259	7.4	258	248 - 277	46
[12]F	492	2.9	494	488 - 494	4
[113]F	75	3.4	75	70 - 83	46
CH_3CCl_3	126	5.2	125	113 - 136	46
CCl_4	108	3.2	108	104 - 116	46
C_2Cl_4	3.2	0.62	3.1	2.6 - 4.9	46
C_3H_8/C_2H_6	0.11	0.02	0.11	0.04 - 0.15	46
C_2H_2/CO	1.5	0.15	1.5	0.84 - 1.7	37
NO_3^-	40	34	37	6.4 - 81	4
nss-SO_4^{2-}	40	23	39	15 - 66	4
NH_4^+	43	11	41	33 - 55	3
[210]Pb	4.5	3.6	4.4	0.51 - 8.7	4
[7]Be	91	42	74	63 - 152	4

we sampled them. It appears that much of the outflowing air had already undergone significant atmospheric processing before we intercepted it over the coastal western Pacific Ocean.

4.3. Vertical Distribution

Plots of species vertical distribution shown in this section are organized into three categories: (1) principal species emitted from combustion processes, (2) water-soluble species, and (3) biogenic or air mass tracer species. The vertical distribution of selected species in CN air masses with transport times of <2 days is shown in Figures 2a,2b, and 2c. These plots illustrate some interesting characteristics of the continental outflow. The CO data, for example, indicate a probable combustion influence on the chemistry below 4 km and above 10 km altitudes (Figure 2a). The

median CO mixing ratio in the upper troposphere and in the boundary layer were essentially equal at 130 parts per billion by volume (ppbv) (Table 1). There also appeared to be an altitude region between 4 and 8 km containing cleaner air masses with mixing ratios of CO ≈ 100 ppbv.

These values of CO are very similar to the ones determined in November 1981 by a gas filter radiometer operating in the experiment "Measurement of Air Pollution from Satellites" (MAPS) flown on the NASA space shuttle [*Newell et al.*, 1988]. Over China the MAPS instrument recorded CO mixing ratios as large as 115 ppbv with an average of 102 ppbv. Since the MAPS instrument responds to CO in the middle to upper troposphere, it was concluded by *Newell et al.* [1988] that this CO was derived from surface sources and brought to higher altitudes by active convection or large-scale rising motions. Vertical transport of CO from the boundary layer to 9 km altitude by convective systems has also been reported over North America [*Kleinman and Daum*, 1991]. The PEM-West A experiment was conducted in the fall time period, when the meteorological regime over China was dominated by cyclonic activity [*Bachmeier et al.*, this issue]. Thus it is likely that vertical transport was quite active over Asian continental source regions.

In the CN air masses the NO_x vertical distribution was very similar to that of CO, but in this case the enhanced mixing ratios above 10 km could either be due to combustion emissions or other source inputs such as from the stratosphere [*Liu et al.*, this issue]. Interestingly, there was no significant enhancement of NO_y above 10 km and, in fact, PAN exhibited its smallest mixing ratio values there (<50 parts per trillion by volume (pptv)). The O_3 and aerosol distributions also showed low concentrations in this altitude region [*Browell et al.*, this issue]. These decreased vertical trends in PAN and O_3 suggest a limited photochemical influence on the chemistry at high altitude.

The middle tropospheric data appear to show chemical characteristics that indicate a ground level source over Asia. Near 9 km altitude, there appears to be significant outflow of ^{210}Pb, PAN, and O_3 that are likely to be of Asian continental origin [*Dibb et al.*, this issue]. The relatively small mixing ratios of water-soluble species (i.e., HCOOH, CH_3COOH, HNO_3, H_2O_2, CH_3OOH, and SO_2) at 9 km altitude suggests that the outflowing materials were transported to this height by wet convective activity over Asia (Figure 2b). The strong correlation with ^{210}Pb but not [7]Be indicates that the elevated mixing ratios of O_3 at 9 km altitude may have originated from a photochemical rather than a stratospheric source [*Dibb et al.*, this issue]. However, significant photochemical production of other species such as the carboxylic acids in the upper troposphere would seem unlikely, based on the O_3 and PAN vertical distributions. The ratio HCOOH/CH_3COOH exhibited decreased values with increased altitude (Table 1), indicative of a combustion influence in the upper troposphere [*Talbot et al.*, 1988].

Outflow below 5 km altitude contained clear signals of industrial contamination, as evidenced by enhanced mixing ratios of the tracer species C_2Cl_4 (Figure 2c). In the middle to upper troposphere, mixing ratios of C_2Cl_4 were near values typical of aged marine air [*Gregory et al.*, this issue]. This observation suggests that the air masses sampled in the boundary layer and at high altitude might have different source regions.

Examination of the vertical distribution of biogenic tracer species can facilitate the interpretation of air mass sources. In Figure 2c we show plots of CO_2, CH_4, and OCS. Although these species are ambiguous biogenic tracers, their vertical distributions indicate some possible scenarios. Carbon dioxide mixing ratios

Table 4. Mixing Ratios of Principal Species Measured in Aged (2-5 days) Asian Continental-South Outflow for Isentropic Back-Trajectories Originating < 20°N Latitude

| Species	2 – 7 km					7 – 12 km				
	Mean	s.d.	Median	Range	N	Mean	s.d.	Median	Range	N
NO	5.8	4.3	5.2	1.5 - 23	57	4.4	2.5	3.1	2.1 - 8.5	17
NO_x	34	13	32	18 - 71	49	49	4.8	48	42 - 60	17
HNO_3	60	34	67	< 5.0 - 95	9	5	NA	5	5 - 5	1
PAN	16	7.3	18	2.5 - 24	14	NA	NA	NA	N A	NA
NO_y	193	55	180	123 - 363	39	NA	NA	NA	N A	NA
O_3	29	9.1	26	20 - 72	94	30	1.3	30	28 - 32	19
CO	95	13	101	67 - 108	90	109	0.98	109	107 - 111	18
CH_4	1717	9.5	1716	1702 - 1749	90	1709	4.4	1707	1704 - 1721	18
CO_2	353	0.38	353	352 - 353	71	353	0.05	353	353 - 353	18
N_2O	309.1	0.13	309.1	308.9 - 309.5	61	309.0	0.14	309.0	308.7 - 309.2	17
SO_2	50	12	49	34 - 105	30	81	2.1	81	77 - 83	6
DMS	4.1	1.3	4.3	2.6 - 6.7	11	< 1	NA	< 1	< 1 - < 1	5
CS_2	1.8	1.4	1.1	0.65 - 4.8	30	0.84	0.05	0.84	0.81 - 0.95	5
OCS	503	5.5	502	496 - 516	27	505	2.8	504	502 - 508	5
HCOOH	149	50	147	78 - 244	9	90	NA	90	90 - 90	1
CH_3COOH	226	99	203	120 - 413	9	248	NA	248	248 - 248	1
H_2O_2	1116	424	973	783 - 2498	20	NA	NA	NA	N A	NA
CH_3OOH	722	316	548	384 - 1261	20	NA	NA	NA	N A	NA
Ethane	568	114	625	350 - 668	16	664	23	652	650 - 690	3
Euhene	11	6.6	8.5	5.3 - 27	16	9.5	4.4	7.7	6.2 - 14	3
Propane	29	11	34	9.3 - 43	16	38	0.58	38	37 - 38	3
i-Butane	< 2	NA	< 2	< 2 - 4.5	16	< 2	NA	< 2	< 2 - < 2	3
n-Butane	< 2	NA	< 2	< 2 - 5.3	16	< 2	NA	< 2	< 2 - < 2	3
Ethyne	78	28	92	29 - 101	16	101	2.1	100	99 - 103	3
1-Butene	< 2	NA	< 2	< 2 - 7.5	16	< 2	NA	< 2	< 2 - < 2	3
i-Pentane	< 2	NA	< 2	< 2 - < 2	16	< 2	NA	< 2	< 2 - < 2	3
n-Pentane	< 2	NA	< 2	< 2 - < 2	16	< 2	NA	< 2	< 2 - < 2	3
n-Hexane	< 2	NA	< 2	< 2 - < 2	16	< 2	NA	< 2	< 2 - < 2	3
Benzene	26	13	26	7.5 - 65	16	31	5.9	29	27 - 38	3
^{11}F	263	4.2	265	250 - 268	16	261	0	261	261 - 261	3
^{12}F	503	6.3	502	494 - 518	16	494	0.57	495	494 - 495	3
^{113}F	76	1.7	77	70 - 77	16	76	0.35	76	76 - 77	3
CH_3CCl_3	122	6.1	124	110 - 131	16	128	4.5	128	123 - 132	3
CCl_4	108	2.7	108	100 - 112	16	110	0.52	110	109 - 110	3
C_2Cl_4	2.5	0.34	2.6	2.1 - 3.2	16	2.6	0.21	2.6	2.4 - 2.7	3
C_3H_8/C_2H_6	0.05	0.01	0.05	0.02 - 0.07	16	0.06	0.002	0.06	0.06 - 0.06	3
C_2H_2/CO	0.81	0.22	0.90	0.43 - 0.98	15	0.93	0.03	0.92	0.91 - 0.96	3
NO_3^-	7.5	5.5	7.5	< 5.0 - 13	3	34	NA	34	34 - 34	1
$nss-SO_4^{2-}$	30	16	38	12 - 40	3	15	NA	15	15 - 15	1
NH_4^+	49	28	49	< 25 - 69	3	27	NA	27	27 - 27	1
^{210}Pb	3.1	2.9	1.6	1.3 - 6.4	3	1.6	NA	1.6	1.6 - 1.6	1
^7Be	193	72	190	123 - 267	3	< 10	NA	< 10	< 10 - < 10	7

were centered around 352 parts per million by volume (ppmv), with a likely anthropogenic enhancement in the boundary layer. From 2 to 9 km altitude, decreased values of CO_2 probably reflect its uptake by the biosphere and suggest that these air masses had recent inputs of near-surface air. The relatively large values of C_2H_2/CO and C_3H_8/C_2H_6 at all altitudes lend further support to the idea that these air masses had recently acquired inputs from surface sources.

One could argue that the values of OCS below about 520 pptv are indicative of biogenic or soil uptake of this species [Chin and Davis, 1993]. The situation is a bit more complicated for CH_4, where various ecosystems can either be a source or a sink of it. In addition, CH_4 has clear anthropogenic signals from various combustion and waste treatment processes [Harriss et al., 1994].

Undoubtedly, a combination of source/sink relationships have produced the complex CH_4 distribution shown in Figure 2c [Matsueda et al., 1993].

For comparison to the CN data, the vertical distribution of the same ensemble of species in CS air masses with transit times of <2 days is depicted in Figures 3a, 3b, and 3c. Here we find a picture not significantly different from the CN case. Mixing ratios of CO were moderately elevated in the upper troposphere (100 - 120 ppbv) but not so much as in the CN air masses (120 - 160 ppbv). Very similar mixing ratios of NO_x, PAN, NO_y, and O_3 were observed in the middle and upper troposphere in both air mass classifications.

Although the data for the CS case were sparse, the vertical distribution of water-soluble species (Figure 3b) was similar to

2a

2b

2c
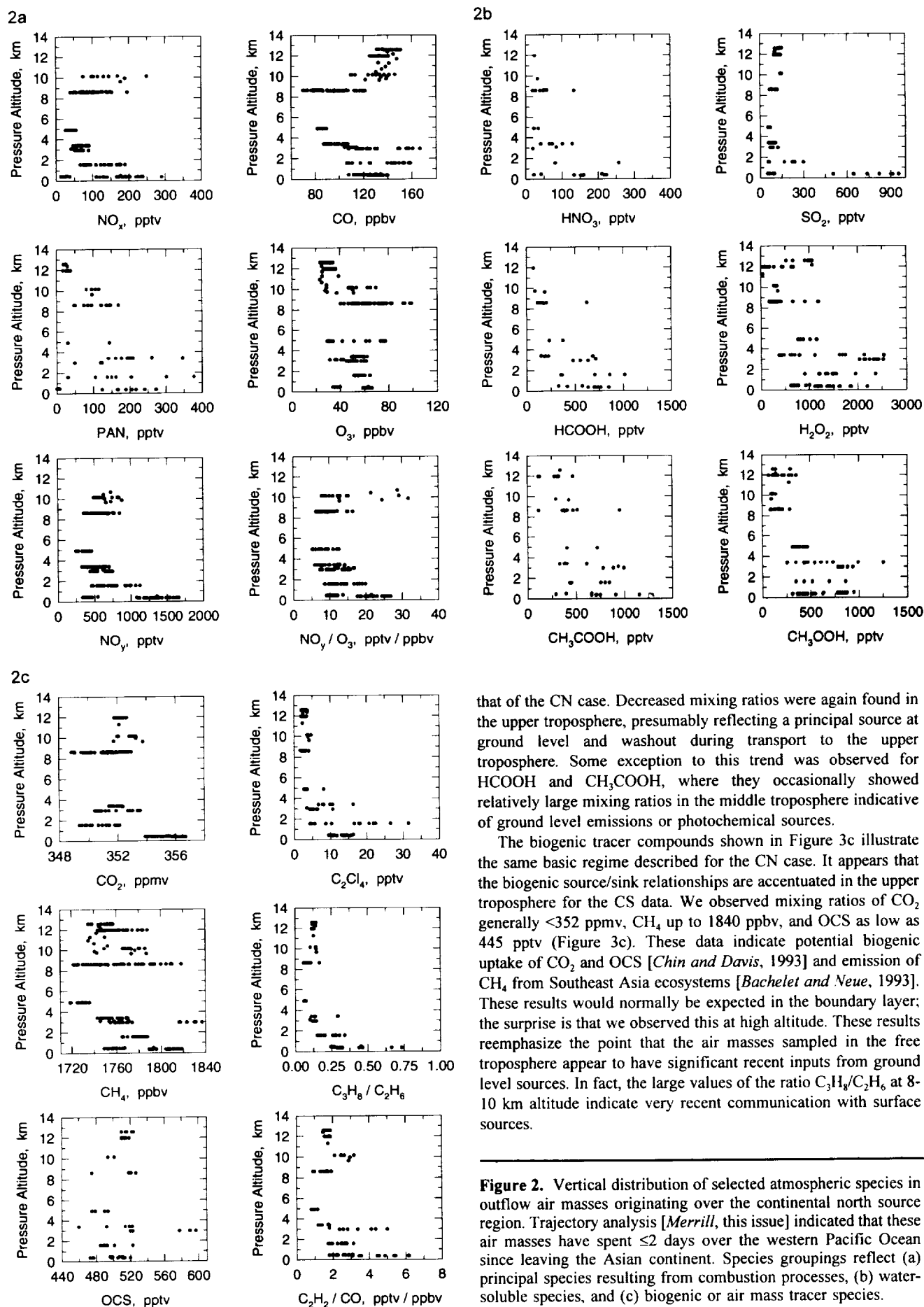
that of the CN case. Decreased mixing ratios were again found in the upper troposphere, presumably reflecting a principal source at ground level and washout during transport to the upper troposphere. Some exception to this trend was observed for HCOOH and CH_3COOH, where they occasionally showed relatively large mixing ratios in the middle troposphere indicative of ground level emissions or photochemical sources.

The biogenic tracer compounds shown in Figure 3c illustrate the same basic regime described for the CN case. It appears that the biogenic source/sink relationships are accentuated in the upper troposphere for the CS data. We observed mixing ratios of CO_2 generally <352 ppmv, CH_4 up to 1840 ppbv, and OCS as low as 445 pptv (Figure 3c). These data indicate potential biogenic uptake of CO_2 and OCS [Chin and Davis, 1993] and emission of CH_4 from Southeast Asia ecosystems [Bachelet and Neue, 1993]. These results would normally be expected in the boundary layer; the surprise is that we observed this at high altitude. These results reemphasize the point that the air masses sampled in the free troposphere appear to have significant recent inputs from ground level sources. In fact, the large values of the ratio C_3H_8/C_2H_6 at 8-10 km altitude indicate very recent communication with surface sources.

Figure 2. Vertical distribution of selected atmospheric species in outflow air masses originating over the continental north source region. Trajectory analysis [Merrill, this issue] indicated that these air masses have spent ≤2 days over the western Pacific Ocean since leaving the Asian continent. Species groupings reflect (a) principal species resulting from combustion processes, (b) water-soluble species, and (c) biogenic or air mass tracer species.

3a

3b

3c
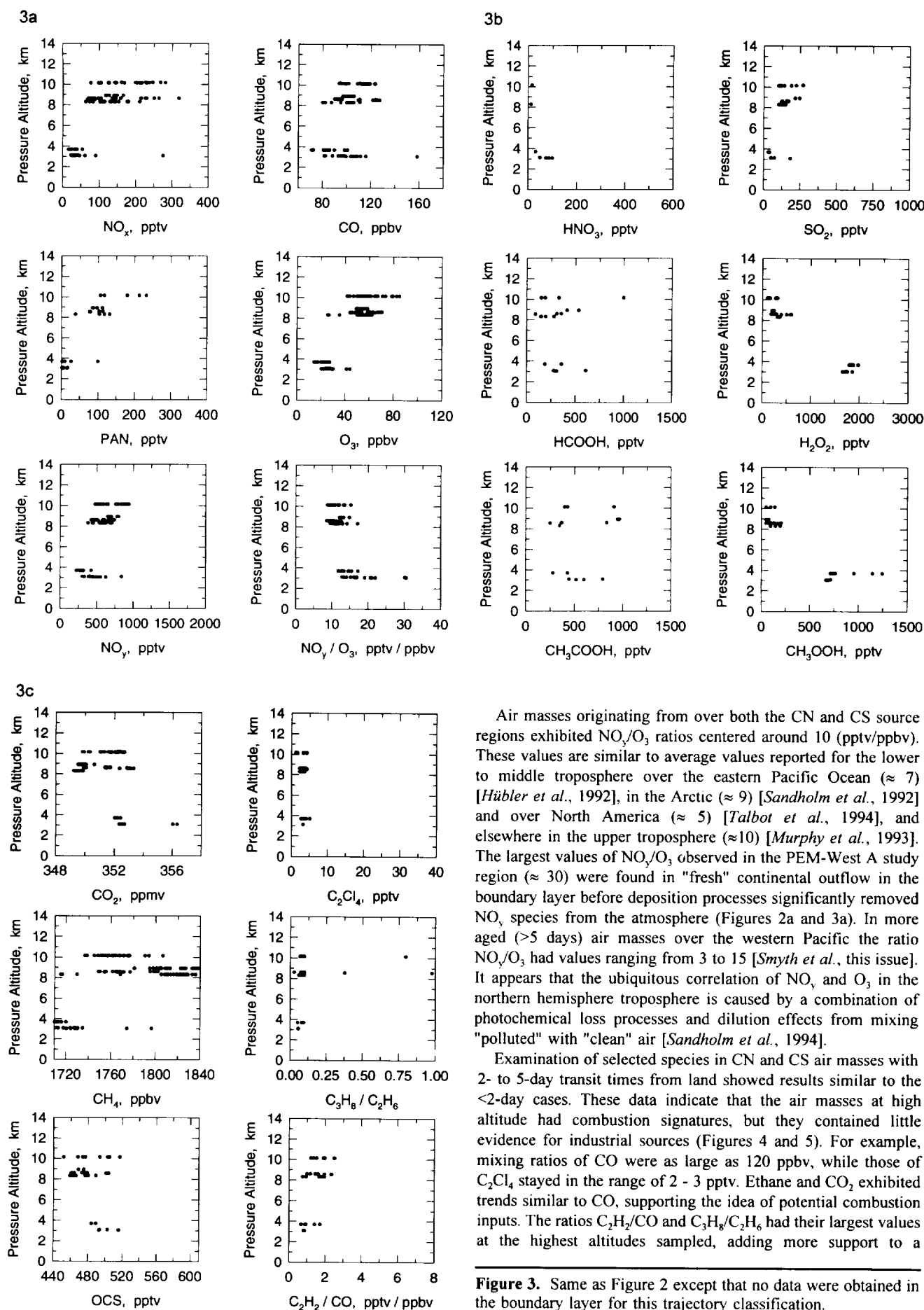
Air masses originating from over both the CN and CS source regions exhibited NO_y/O_3 ratios centered around 10 (pptv/ppbv). These values are similar to average values reported for the lower to middle troposphere over the eastern Pacific Ocean ($\approx$ 7) [Hübler et al., 1992], in the Arctic ($\approx$ 9) [Sandholm et al., 1992] and over North America ($\approx$ 5) [Talbot et al., 1994], and elsewhere in the upper troposphere ($\approx$10) [Murphy et al., 1993]. The largest values of NO_y/O_3 observed in the PEM-West A study region ($\approx$ 30) were found in "fresh" continental outflow in the boundary layer before deposition processes significantly removed NO_y species from the atmosphere (Figures 2a and 3a). In more aged (>5 days) air masses over the western Pacific the ratio NO_y/O_3 had values ranging from 3 to 15 [Smyth et al., this issue]. It appears that the ubiquitous correlation of NO_y and O_3 in the northern hemisphere troposphere is caused by a combination of photochemical loss processes and dilution effects from mixing "polluted" with "clean" air [Sandholm et al., 1994].

Examination of selected species in CN and CS air masses with 2- to 5-day transit times from land showed results similar to the <2-day cases. These data indicate that the air masses at high altitude had combustion signatures, but they contained little evidence for industrial sources (Figures 4 and 5). For example, mixing ratios of CO were as large as 120 ppbv, while those of C_2Cl_4 stayed in the range of 2 - 3 pptv. Ethane and CO_2 exhibited trends similar to CO, supporting the idea of potential combustion inputs. The ratios C_2H_2/CO and C_3H_8/C_2H_6 had their largest values at the highest altitudes sampled, adding more support to a

Figure 3. Same as Figure 2 except that no data were obtained in the boundary layer for this trajectory classification.
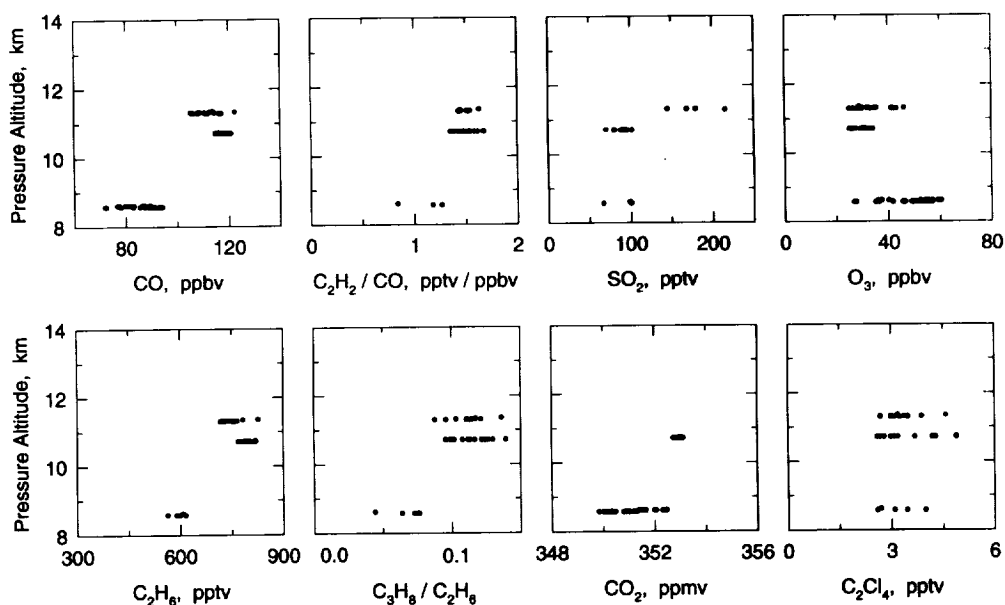
Figure 4. Distribution of selected atmospheric species in the middle to upper troposphere in outflow air masses originating over the continental north source region. Trajectory analysis [Merrill, this issue] indicated that these air masses have spent 2 - 5 days over the western Pacific Ocean since passing over the Asian continent.

scenario of ground level emissions recently influencing this region. Sulfur dioxide also tended to have its largest mixing ratios coincident with those in CO, but here we cannot rule out the possibility of stratospheric inputs of Mount Pinatubo sulfur [Liu et al., this issue]. The mixing ratios of O_3 and activities of ^7Be, however, were rather low at high altitude ($\approx$ 40 ppbv and a few hundred fCi scm^{-1}, respectively), indicating a weak stratospheric influence on the chemistry there [Dibb et al., this issue].

4.4. Chemical Source Signature of Pacific Rim Region

It is desirable to derive a qualitative description of the atmospheric chemical signature derived from the Pacific rim region. We did this for various species by subtracting their

median mixing ratio in the free tropospheric CN and CS cases (2 - 12 km altitude) from their median value in aged (>10 days since landfall) marine air [Gregory et al., this issue]. The results of these calculations (delta CN and CS) are presented in Table 5. Obviously, these calculations do not accurately portray the potential sources of short-lived species over the Pacific rim region.

This comparison showed significant enrichment of the trace gases NO_y, O_3, CO, CH_4, SO_2, HCOOH, H_2O_2, C_2H_6, C_3H_8, C_2H_2, F-12, plus aerosol NH_4^+ and ^{210}Pb in the Asian continental outflow (Table 5). Modest enhancements are also apparent for several other species, particularly in air masses derived from the CN source region. Clearly, combustion and related photochemical
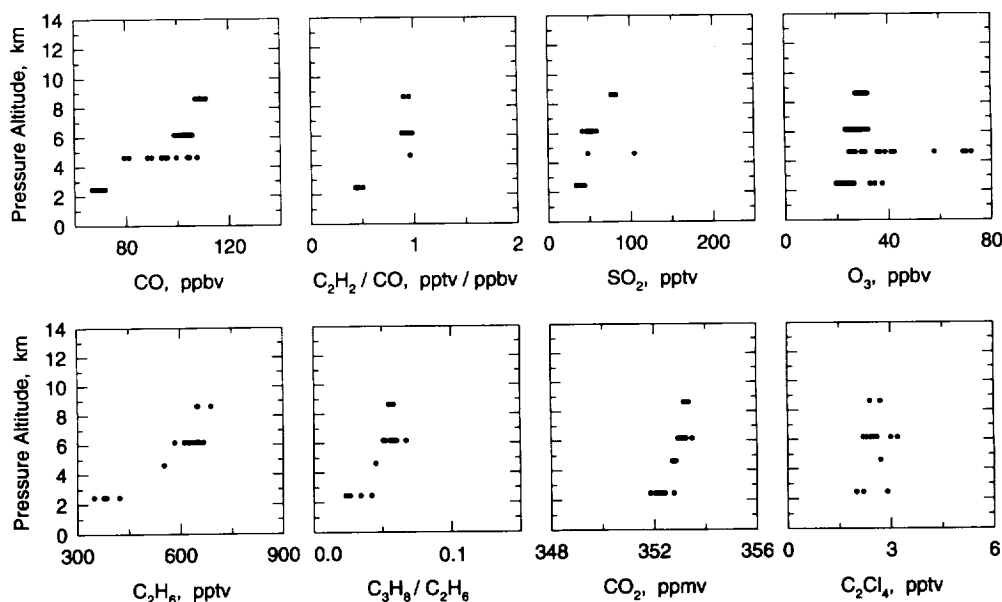

Figure 5. Same as Figure 4.

Table 5. Comparison of Principal Species in Asian Continental-North (CN) and Continental-South (CS) Outflow in the Altitude Range of 2-12 km

Species	CN		CS		ΔCN	ΔCS
	Median	±95% C.I.	Median	±95% C.I.		
NO	44	5.5	71	11	32*	59*
NO$_x$	80	5.8	121	15	40*	81*
HNO$_3$	56	17	53	32	39*	36*
PAN	102	20	86	22	88*	72*
NO$_y$	539	21	572	33	428*	461*
O$_3$	48	2.0	50	2.4	25*	27*
CO	114	3.0	102	2.4	37*	25*
CH$_4$	1758	2.8	1780	6.5	67*	89*
CO$_2$	352	0.15	351	0.24	-1.0*	-2.0*
N$_2$O	309.3	0.06	309.5	0.06	0.2	0.4
SO$_2$	105	8.3	183	94	47*	125*
DMS	6.6	1.8	4.7	3.6	1.2	-0.70
CS$_2$	3.1	0.68	2.5	2.1	2.2	1.6
OCS	515	7.7	479	7.6	18*	-18*
HCOOH	297	95	325	102	241*	269*
CH$_3$COOH	529	104	632	190	139	242
H$_2$O$_2$	886	171	663	207	524*	301*
CH$_3$OOH	390	70	305	109	9	-76
Ethane	943	42	714	48	483*	254*
Ethene	28	3.0	23	6.6	16*	11*
Propane	120	12	67	9.9	101*	48*
i-Butane	16	3.1	9.8	3.6	≥ 16	≥ 10
n-Butane	26	5.8	14	4.7	≥ 26	≥ 14
Ethyne	223	27	162	24	260*	123*
1-Butene	6.5	1.4	6.6	3.3	1.8	2.0
i-Pentane	9.7	1.7	8.6	4.2	≥ 10	≥ 9
n-Pentane	7.9	1.8	5.7	2.1	≥ 8	≥ 6
n-Hexane	4.3	1.4	5.1	8.6	≥ 4	≥ 5
Benzene	48	7.3	30	5.5	40*	20*
[11]F	266	0.85	264	1.2	4.0*	2.0*
[12]F	502	0.92	501	1.7	6.0*	5.0*
[113]F	77	0.69	77	0.63	1.0	1.0
CH$_3$CCl$_3$	122	2.1	125	3.6	3.0	4.0
CCl$_4$	108	1.1	109	1.3	-1.0	0
C$_2$Cl$_4$	3.9	0.56	3.1	0.29	1.7*	0.90*
C$_3$H$_8$/C$_2$H$_6$	0.12	0.008	0.14	0.07	≈ 0.08*	≈ 0.10*
C$_2$H$_2$/CO	1.9	0.18	1.5	0.18	1.5*	1.1*
NO$_3^-$	42	68	28	9.5	29*	15
nss-SO$_4^{2-}$	82	71	34	23	58*	10
NH$_4^+$	121	83	43	9.0	≈ 300	≈ 20
[210]Pb	8.2	4.5	6.1	2.4	7.7*	5.6*
[7]Be	304	154	243	207	NA	NA

Significant enrichment or depletion of species in outflow relative to aged (south) marine air illustrates the asian emission signature. C.I., Confidence Interval.

*Indicates species significantly (p = 0.05) enriched or depleted in continental outflow compared to aged (south) marine air.

activity are probably sources for many of these species [*Kato and Akimoto*, 1992].

Biogenic activities on the Asian continent may exert important influence on the atmospheric distribution of several trace gases over the western Pacific Ocean [*Matsueda et al.*, 1993]. For example, the CO$_2$ data indicate uptake of it over the continents, with the strongest sink over the heavily vegetated CS region. This also appears to be the case for OCS, where it appears to have a net atmospheric sink over the CS region but be released from the CN area. Asia is also implicated to be a net source of CH$_4$, with

the strongest sources over the Southeastern continent. At least part of the CH$_4$ enhancement is undoubtedly due to its release from wetland ecosystems in southeast Asia [*Bachelet and Neue*, 1993; *Khalil et al.*, 1990]. However, anthropogenic activities are also likely sources of CH$_4$ in Asia [*Khalil et al.*, 1990].

Recent estimates of Asian atmospheric emissions of SO$_2$ and NO$_x$ reveal that Chinese sources are rich in sulfur (10 Tg S yr^{-1}) and lower in nitrogen (2.24 Tg N yr^{-1}) content (H. Akimoto et al., Atmospheric chemistry of the East-Asian northwest Pacific region, submitted to Proceedings of the 37th Conference in the OHOLO

Conference series, 1994]. The other Pacific rim countries, including Japan, together release annually 1.62 Tg S and 1.02 Tg N to the atmosphere. The resultant nss-SO_4/NO_3 emission ratio should range from 3.01 over China to 0.57 near Japan [*Arimoto et al.*, this issue]. Values within this range were observed at the PEM-West A ground level sampling stations and in aerosol samples collected from the DC-8 at 0.3 km altitude near Taiwan [*Arimoto et al.*, this issue].

Examination of the NO_y signals from air masses originating over the CN and CS source regions shows the potential for similar emission strengths from each. In fact, the PEM-West A aircraft data indicate a somewhat different picture than that observed at the ground level stations. The aircraft data set indicates a Pacific rim region that is regionally rich in atmospheric emissions of nitrogen relative to sulfur. Ground level studies, however, clearly show a strong influence of anthropogenic sulfur emissions relative to nitrogen in this area [*Zhao and Xiong*, 1988; *Galloway*, 1989; *Arimoto et al.*, this issue]. Since we do not know the initial composition of the air masses feeding eastward into the CN and CS source regions, it is not possible to determine with our present data set how much of the NO_y (or any other species) originated from Asia compared to what was already in the "background" air.

Particularly in the middle to upper tropospheric region, it is possible that other source regions contributed substantially to the chemistry. The wind speeds are very large in the upper troposphere (60 - 70 m s^{-1}), and this could bring several-day-old emissions from Europe into our study region [*Newell et al.*, this issue]. The so-called "Japan jet" is coupled to this rapid upper tropospheric transport and it is known to carry Asian continental emissions across the North Pacific to California on a timescale of 3 days or less [*Kritz et al.*, 1990].

The PEM-West A upper tropospheric data are not inconsistent with a biomass-burning source signature. Species such as CO, C_2H_6, and NO_y should be enhanced in such emissions with little likelihood of inputs of industrial tracer compounds. Biomass burning in southeastern Asia and on the various islands chains to the south may have been active during our study period. We did, in fact, encounter over the Celebes Sea what appeared to be a biomass fire plume emerging from the Borneo region [*Blake et al.*, this issue]. In addition, there is extensive use of biomass materials for household cooking and space heating in Asia [*Galloway*, 1989]. Convective activity could transport these combustion emissions to high altitude where they would have a good opportunity to be rapidly swept into our study region [*Newell et al.*, this issue].

European emissions could also contribute to the chemistry at high altitude, but they should contain significant amounts of industrial tracer compounds. The fact that the mixing ratios of industrial tracers (e.g., C_2Cl_4 and CH_3CCl_3) at high altitude were near those of aged marine air over the Pacific argues against a European influence.

The PEM-West A data indicate that Asian sources are significant contributors of chemical species to the atmosphere over the western Pacific. The direct outflow at low altitude was clearly of Asian origin. It is a complicated issue, however, to confidently identify a unique Asian signature from other potential long-range sources to the free troposphere over the western Pacific.

5. Conclusions

We have presented the chemical characteristics of Asian continental outflow over the western Pacific Ocean. Mixing ratios of most species and the ratios C_2H_2/CO and C_3H_8/C_2H_6 were very

similar in air masses classified as <2 and 2 - 5 days of transport from over the Pacific rim landmasses. It appears that much of the outflowing air had already undergone significant photochemical processing before being advected over the western Pacific Ocean.

At low altitude the chemistry was clearly dominated by Asian source emissions under outflow conditions. In the free troposphere the situation was much more complex, with the possibility of a mixture of Asian and long-range transport influencing the distribution of trace gases and aerosol species. In addition, biogenic metabolism processes on the Asian continent appear to be important for influencing the distribution of CO_2, CH_4, and OCS over the western Pacific.

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