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#### Recommended Citation

de Gouw, J. A., et al. (2004), Chemical composition of air masses transported from Asia to the U.S. West Coast during ITCT 2K2: Fossil fuel combustion versus biomass-burning signatures, *J. Geophys. Res.*, 109, D23S20, doi:10.1029/2003JD004202.

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# Chemical composition of air masses transported from Asia to the U.S. West Coast during ITCT 2K2: Fossil fuel combustion versus biomass-burning signatures

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Received 1 October 2003; revised 5 December 2003; accepted 21 January 2004; published 17 July 2004.

[1] As part of the Intercontinental Transport and Chemical Transformation experiment in 2002 (ITCT 2K2), a National Oceanic and Atmospheric Administration (NOAA) WP-3D research aircraft was used to study the long-range transport of Asian air masses toward the west coast of North America. During research flights on 5 and 17 May, strong enhancements of carbon monoxide (CO) and other species were observed in air masses that had been transported from Asia. The hydrocarbon composition of the air masses indicated that the highest CO levels were related to fossil fuel use. During the flights on 5 and 17 May and other days, the levels of several biomass-burning indicators increased with altitude. This was true for acetonitrile (CH<sub>3</sub>CN), methyl chloride (CH<sub>3</sub>Cl), the ratio of acetylene (C<sub>2</sub>H<sub>2</sub>) to propane (C<sub>3</sub>H<sub>8</sub>), and, on May 5, the percentage of particles measured by the particle analysis by laser mass spectrometry (PALMS) instrument that were attributed to biomass burning based on their carbon and potassium content. An ensemble of back-trajectories, calculated from the U.S. west coast over a range of latitudes and altitudes for the entire ITCT 2K2 period, showed that air masses from Southeast Asia and China were generally observed at higher altitudes than air from Japan and Korea. Emission inventories estimate the contribution of biomass burning to the total emissions to be low for Japan and Korea, higher for China, and the highest for Southeast Asia. Combined with the origin of the air masses versus altitude, this qualitatively explains the increase with altitude, averaged over the whole ITCT 2K2 period, of the different biomass-burning indicators.

**INDEX TERMS:** 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; **KEYWORDS:** long-range transport, fossil-fuel combustion, biomass burning

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## 1. Introduction

[2] One goal of the Intercontinental Transport and Chemical Transformation experiment in 2002 (ITCT 2K2) was to study the long-range transport of trace gases and aerosol from Asia across the Pacific Ocean, and the implications for the background atmospheric composition at the surface in

North America. The occurrence of Asian dust in the atmosphere over the northern Pacific, Canada and the United States is a frequent phenomenon that has been described by several authors [*Van Curen and Cahill*, 2002, and references therein]. Since 1997, D. Jaffe and coworkers have studied the chemical and aerosol composition of Asian air transported to the northwestern United States [*Jaffe et al.*, 1999, 2001, 2003a; *Kotchenruther et al.*, 2001]. Rising emissions of pollutants in Asia have raised some concern that the background atmospheric composition in North America could be affected due to long-range transport [*Jacob et al.*, 1999; *Jaffe et al.*, 2003b]. The ITCT 2K2 experiment was conducted during April and May of 2002, and involved airborne measurements using the National Oceanic and Atmospheric Administration (NOAA) WP-3D aircraft, and ground-based measurements at Trinidad Head in northern California. Additional measurements were performed by D. Jaffe and coworkers, and involved

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**Table 1.** Emission Estimates of Carbon Monoxide (CO) From Asia in 2000 and the Relative Contribution From Different Source Categories<sup>a</sup>

	Region				
	China	Japan	Korea	SE Asia <sup>b</sup>	S Asia <sup>c</sup>
Total CO (Tg)	116	6.8	2.8	66	79
<i>Anthropogenic Sources, %</i>					
Total <sup>d</sup>	86	97	94	52	79
Industry	16	21	25	1	8
Domestic biofuel	31	4	3	31	48
Domestic fossil fuel	7	0	0	1	0
Transport	33	71	66	19	23
<i>Biomass-Burning Sources, %</i>					
Total <sup>d</sup>	14	3	6	48	21
Savanna fires	3	0	0	6	1
Forest fires	2	1	0	38	8
Crop residues	8	3	6	5	12

<sup>a</sup>From *Streets et al.* [2003].<sup>b</sup>Indonesia, Thailand, Vietnam, Myanmar, Malaysia, Philippines, Laos, Cambodia, Singapore and Brunei.<sup>c</sup>India, Pakistan, Bangladesh, Nepal, Sri Lanka and Bhutan.<sup>d</sup>The percentages have been rounded to the nearest integer number, which may cause the total to be different from the sum of the individual contributions.

ground-based measurements at the Cheeka Peak Observatory in Washington and airborne measurements off the coast of Washington. The NOAA WP-3D aircraft operated from Monterey in California, and intercepted and characterized air masses from Asia during several flights. *Nowak et al.* [2004] and *Brock et al.* [2004] have described the general gas-phase and aerosol observations, respectively, during these transport episodes. In this paper, the composition of volatile organic compounds (VOCs) of two Asian plumes is described in more detail and used to address the emission sources, in particular to distinguish between fossil fuel combustion and biomass burning.

[3] There is only a very limited amount of data available on trace gas emissions in Asia and particularly China, which is expected to be one of the main contributors to the pollution observed during ITCT 2K2. *Klimont et al.* [2002] presented an inventory of non-methane VOCs from China, but, due to a paucity of data, had to rely on the VOC speciation of North American and European sources for many source categories. The inventory was recently updated, extended to other trace gases and Asian countries, and compared with data from the NASA TRACE-P mission [*Streets et al.*, 2003]. It has been suggested that the inventory underestimates the emissions of carbon monoxide (CO) in China by 30% [*Palmer et al.*, 2003]. Table 1 gives a brief summary of the CO sources in 2000 in Asia. It is seen that there are large regional differences: transportation and industrial sources dominate the CO emissions from Japan and Korea, whereas the domestic use of biofuels and forest fires are significant sources of CO in China and Southeast Asia. Emissions from biofuel use and from the three biomass-burning categories in Table 1 (savanna and forest fires, and the burning of agricultural crop residues) are expected to be chemically similar, and are generally referred to as biomass burning in this work. Table 1 shows that this combined biomass-burning source is small in Japan (7%) and Korea (9%), but is very important in China (45%) and,

particularly, Southeast (79%) and South Asia (69%). For the VOCs the 2000 emission inventory of *Streets et al.* [2003] is less detailed and more uncertain, but the distribution of the sources across the region and over the different source categories are qualitatively comparable to CO.

[4] Recent progress on the characterization of the different source categories in Table 1 include work by *Tsai et al.* [2003], who measured the VOC emissions from various coal- and wood-fired stoves in China, and *Wang et al.* [2002a] who characterized the VOC emissions from transport in roadside measurements in China. Data on VOCs in urban atmospheres were reported for cities such as Hong Kong and Taipei [*Monod et al.*, 2001; *Ho et al.*, 2002], but are generally very limited. *Wang et al.* [2002b] made measurements at a rural site in eastern China and found the hydrocarbon composition to resemble that of the burning of biofuels and crop residues. Much of our understanding about Asian VOCs, however, has been derived from measurements made well outside the immediate source regions in the continental outflow over the Pacific Ocean. Ground-based measurements in Japan [*Kato et al.*, 2001], and airborne measurements during the NASA PEM-West B [*Blake et al.*, 1997] and TRACE-P missions [*Blake et al.*, 2003] have given the most detail.

[5] During ITCT 2K2, VOCs were measured onboard the NOAA WP-3D research aircraft by proton-transfer-reaction mass spectrometry (PTR-MS) [*Lindinger et al.*, 1998], and, in addition, whole air samples (WAS) were collected in-flight and analyzed post-flight by gas chromatography (GC) [*Schaufler et al.*, 1999, 2003]. In this work, the VOC data are used to distinguish between fossil fuel combustion and biomass-burning sources. Indicators used for biomass-burning emissions include acetonitrile (CH<sub>3</sub>CN) [*Holzinger et al.*, 1999; *de Gouw et al.*, 2003a; *Singh et al.*, 2003] and methyl chloride (CH<sub>3</sub>Cl) [*Lobert et al.*, 1999; *Blake et al.*, 1997, 2003]. In addition, the presence of both potassium and carbon in (non sea salt and non mineral dust) aerosols is used as a biomass-burning indicator [*Silva et al.* 1999; *Guazzotti et al.*, 2003; *Hudson et al.*, 2004]. The influence of fossil fuel combustion sources is inferred from the absence of the above indicators, and from elevated concentrations of short-chain (C<sub>3</sub>-C<sub>5</sub>) alkanes and tetrachloroethene (C<sub>2</sub>Cl<sub>4</sub>). The C<sub>3</sub>-C<sub>5</sub> alkanes are abundant in urban atmospheres [*Seila et al.*, 1989], but are less common from biomass burning [*Friedli et al.*, 2001; *Andreae and Merlet*, 2001]. C<sub>2</sub>Cl<sub>4</sub> is a commonly used halocarbon tracer for urban and industrial emissions [*McCulloch et al.*, 1999], and has been shown to be more abundant in air masses from Japan and Korea than it is in air from China and Southeast Asia [*Blake et al.*, 1997, 2003].

## 2. Airborne Measurements

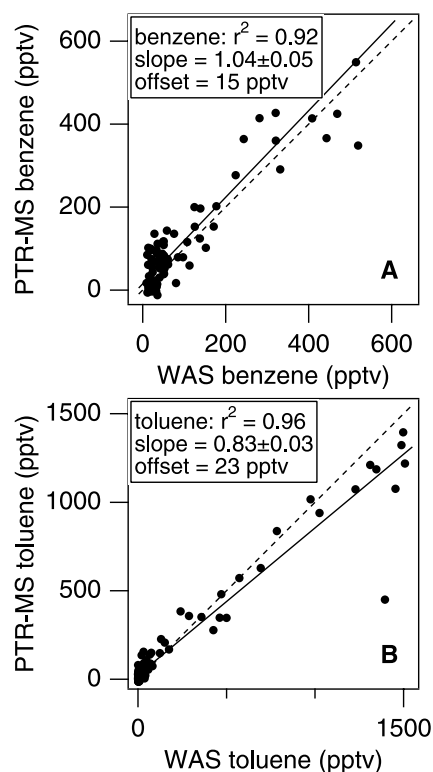
[6] Eleven research flights were made between 25 April and 17 May 2002, using a NOAA WP-3D research aircraft operated from Monterey, California. Flight objectives included the characterization of polluted air masses from Asia, a study of the emissions by ships in the Pacific Ocean, and measurements of regional air pollution in the San Francisco, Los Angeles and California Central Valley areas. Additional measurements were performed during the transfer flights from Tampa, Florida, to Monterey on 22 April,

and from Monterey to Broomfield, Colorado, on 19 May. The extensive instrumental payload of the NOAA WP-3D allowed a detailed characterization of the chemical and aerosol composition of the atmosphere [Nowak *et al.*, 2004; Brock *et al.*, 2004]. In addition to the measurements of organic compounds described below, we use in this work measurements of carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), the sum of odd nitrogen species (NO<sub>y</sub>), and information on the potassium and carbon content of individual particles from the PALMS (particle analysis by laser mass spectrometry) instrument. For a more detailed description of these measurements the reader is referred to Nowak *et al.* [2004], Brock *et al.* [2004] and Hudson *et al.* [2004].

[7] During every flight, a total of 80 whole air samples (WAS) were collected in electro-polished stainless steel gas canisters. The canisters were transported to the NCAR laboratory in Boulder, where they were analyzed within a few days for hydrocarbons and halocarbons using several gas chromatography (GC) techniques. Schauffler *et al.* [1999, 2003], and references therein, described the methods of sampling and analysis. Hydrocarbons used in this work are alkanes (C<sub>2</sub>-C<sub>5</sub>), alkenes (C<sub>2</sub>-C<sub>3</sub>), alkynes (acetylene; C<sub>2</sub>H<sub>2</sub>) and aromatic VOCs (benzene and toluene), and were determined with a 10% uncertainty [Ryerson *et al.*, 2003]. In addition, data are presented for the halocarbons methyl chloride (CH<sub>3</sub>Cl) and tetrachloroethene (C<sub>2</sub>Cl<sub>4</sub>), which had measurement uncertainties of 3.3% and 11.5%, respectively [Schauffler *et al.*, 2003].

[8] Airborne measurements of methanol (CH<sub>3</sub>OH), acetonitrile (CH<sub>3</sub>CN), acetone (CH<sub>3</sub>COCH<sub>3</sub>) and other VOCs (acetaldehyde, dimethyl sulfide, isoprene, benzene, toluene and higher aromatics) were made with a proton-transfer-reaction mass spectrometer (PTR-MS; Ionicon Analytik) [Lindinger *et al.*, 1998]. PTR-MS has been used since 1999 for fast-response VOC measurements from a number of airborne platforms [e.g., Crutzen *et al.*, 2000]. Over the last few years we have made a significant effort to characterize the sensitivity and selectivity of PTR-MS with regard to many VOCs. The selectivity was studied by combining PTR-MS with a gas chromatographic pre-separation method [de Gouw *et al.*, 2003a, 2003b; Warneke *et al.*, 2003]. PTR-MS and gas chromatography/mass spectrometry (GC-MS) measurements of numerous VOCs were compared during a ship-based experiment, and were generally found to agree within ±15% at levels well above the detection limits of the two instruments [de Gouw *et al.*, 2003c].

[9] Only PTR-MS measurements of acetonitrile (CH<sub>3</sub>CN), benzene and toluene are used in this paper; the benzene and toluene data are used only for comparison with the WAS results in the next paragraph. Acetonitrile is measured at 42 amu in PTR-MS, i.e., its molecular mass +1 amu. The measurement precision of PTR-MS is limited by the background signals due to impurities in the system, and by the Poissonian counting statistics of the ion signals [de Gouw *et al.*, 2003c]. During ITCT 2K2, the 1σ noise in the acetonitrile data was less than 20 pptv. The response of the PTR-MS with respect to acetonitrile was calibrated using a standard mixture of acetonitrile and six other VOCs (methanol, acetaldehyde, dimethyl sulfide, acetone, benzene and toluene) in nitrogen. The calibration accuracy is estimated to be 15%. The only other species that are known to be detectable in PTR-MS at 42 amu are the C<sub>3</sub>-C<sub>5</sub> alkanes



**Figure 1.** Comparison between the PTR-MS and WAS results for (a) benzene and (b) toluene from the 13 May flight over the Los Angeles basin. The solid lines show the results of an orthogonal distance regression analysis. The dashed lines are the 1:1 relationship.

[de Gouw *et al.*, 2003a]. However, the sensitivity for these species is very low [de Gouw *et al.*, 2003c], and their interfering contribution to the acetonitrile measurements is negligible for the data reported here.

[10] Of the VOCs used in this paper, only benzene and toluene were quantified both by PTR-MS and the WAS. The PTR-MS results for benzene and toluene were mostly at or below detection limits in the free troposphere (140 pptv for benzene and 80 pptv for toluene for a 1s integration time [de Gouw *et al.*, 2003c]). The PTR-MS and WAS results for the May 13th flight over the Los Angeles basin are compared in Figure 1. The figure shows the correlation between the WAS results and the PTR-MS data, which were linearly interpolated onto the midpoints of the WAS sampling periods for the purpose of this plot. The correlation between the PTR-MS and WAS data was good: the linear correlation coefficient,  $r^2$ , was 0.92 for benzene and 0.96 for toluene. The solid lines in Figure 1 show the results of a two-sided, or orthogonal distance regression (ODR) analysis, which minimizes the orthogonal distance between the data points and the fitted line [Bakwin *et al.*, 1997]. The slopes of the ODR fits in Figure 1 ( $1.04 \pm 0.05$  for benzene,  $0.83 \pm 0.03$  for toluene) are both equal to one within the combined ±18% calibration uncertainties of the WAS (±10%) and PTR-MS (±15%) measurements. It should be noted that the standards used to calibrate the WAS and PTR-MS measurements were not compared for this experiment. The scatter of ±50 pptv (1σ) in the data points in

Figure 1 is caused mostly by the limited ion counting statistics of the PTR-MS instrument [de Gouw et al., 2003c]. We conclude that the PTR-MS and WAS data for benzene and toluene agreed within the combined uncertainties, which confirms earlier work [Warneke et al., 2001].

### 3. Results and Discussion

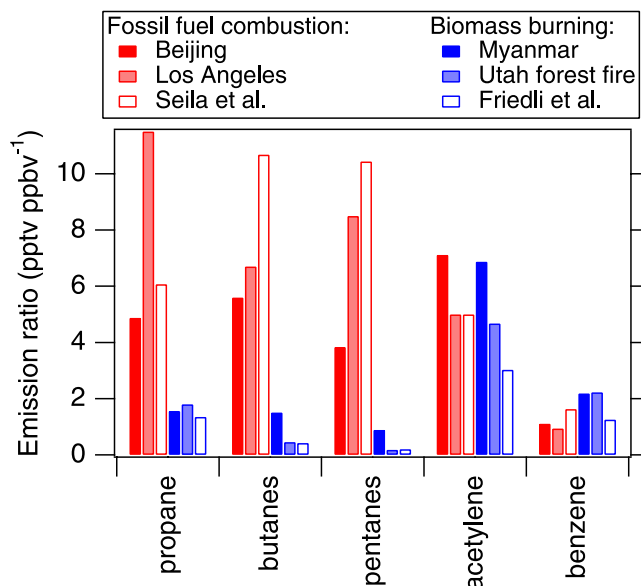
#### 3.1. Distinction Between Biomass Burning and Fossil Fuel Combustion Sources

[11] Gas-phase species that are used here as biomass-burning indicators include acetonitrile ( $\text{CH}_3\text{CN}$ ) and methyl chloride ( $\text{CH}_3\text{Cl}$ ), two relatively inert trace gases whose atmospheric lifetimes of several months are long enough to be transported in the free troposphere across the Pacific without significant chemical loss. Acetonitrile has been shown to be a good indicator of biomass-burning emissions: it is strongly emitted from forest fires but is not observed in elevated concentrations in urban air [Holzinger et al., 1999; de Gouw et al., 2003a; Singh et al., 2003]. Methyl chloride has been used as a biomass-burning indicator by many authors [Blake et al., 1997, 2003]. It is more commonly emitted from tropical biomass burning than it is from wildfires in temperate forests [Lobert et al., 1999; Friedli et al., 2001]. The emissions in Asia are the highest in Southeast Asia, India and China, but are relatively small in Japan [Lobert et al., 1999]. Tetrachloroethene ( $\text{C}_2\text{Cl}_4$ ) is used as an indicator of urban and industrial pollution. It has a lifetime of several weeks and is not significantly removed during the transport across the Pacific.  $\text{C}_2\text{Cl}_4$  is released from a wide variety of industrial, commercial and consumer applications, and its emissions in Asia are far higher in Japan ( $39 \text{ Gg year}^{-1}$  in 1990) than they are in China ( $4 \text{ Gg year}^{-1}$ ) [McCulloch et al., 1999].

[12] A third biomass-burning indicator used in this work is the percentage of particles that are attributed to biomass burning ( $\text{BB}_{\text{aerosol}}$ ), based on the carbon and potassium content measured by the PALMS instrument. In PALMS single particles are detected and ionized by a pulsed laser, and a time-of-flight mass spectrometer is used to determine the mass spectrum of the ionic fragments. Several authors have shown that potassium is commonly present in particles from biomass-burning sources [Silva et al., 1999; Andreae and Merlet, 2001; Guazzotti et al., 2003]. From PALMS measurements in several different biomass-burning plumes, the presence of both carbon and potassium in a particle was found to be a good indicator of biomass burning [Hudson et al., 2004]. In this work  $\text{BB}_{\text{aerosol}}$  is defined as:

$$\text{BB}_{\text{aerosol}} = \frac{\sum \text{particles for which } \left( \frac{C^{1/3} \times K^{2/3}}{0.529} > 0.05 \right)}{\sum \text{all particles}} \times 100\%, \quad (1)$$

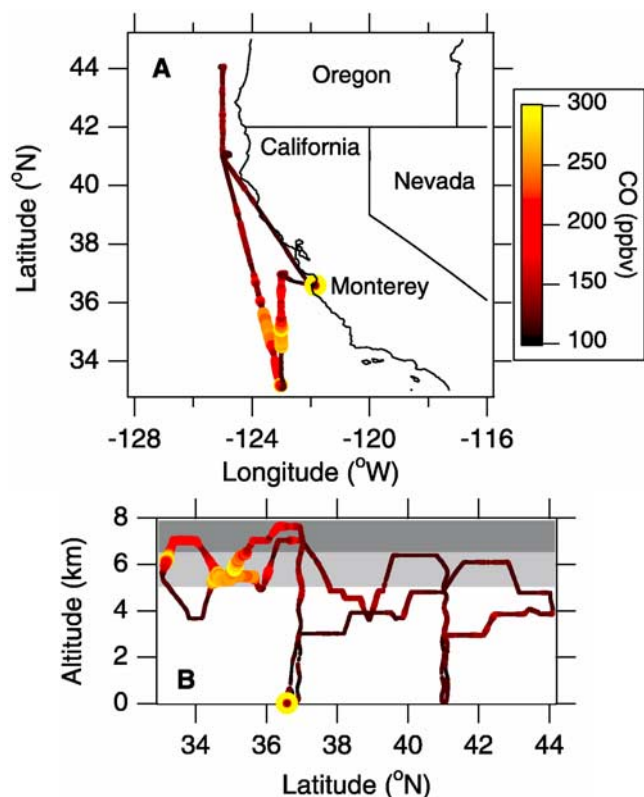
where  $C$  is the fraction of the signal at 12 amu (carbon), and  $K$  the fraction at 39 amu (potassium) in the mass spectrum of individual particles. The expression  $C^{1/3} \times K^{2/3}/0.529$  has a maximum value of 1, if the spectrum consists of approximately 33% carbon and 67% potassium. However, the mass spectra for individual particles always show more



**Figure 2.** VOC emission ratios relative to CO for different fossil fuel combustion and biomass-burning sources. The data for Beijing and Myanmar are from the 2000 emissions inventory [Streets et al., 2003], the data for Los Angeles and the Utah fire are from the ITCT 2K2 experiment. The data from Seila et al. [1989] are from a compilation of hydrocarbons in 39 U.S. cities, and Friedli et al. [2001] from a study of 7 wildfires in North America.

complexity, and a particle is considered to be of biomass-burning origin, if  $(C^{1/3} \times K^{2/3})/0.529$  is larger than 0.05. Potassium is also present in sea-salt and mineral dust particles, and the value of  $K$  in equation (1) has been corrected for these contributions (for more details see Hudson et al. [2004]). The summation in equation (1) is either made over 200 consecutive particles, when  $\text{BB}_{\text{aerosol}}$  is shown as a function of time, or over all particles in a 250 m altitude bin, when  $\text{BB}_{\text{aerosol}}$  is shown as a function of altitude. We note that the parameter  $\text{BB}_{\text{aerosol}}$  only refers to the fraction of particles attributed to biomass-burning sources, but does not hold information about the concentrations. In air masses where other sources of particles dominate, e.g., sea salt aerosol in the marine boundary layer, the parameter  $\text{BB}_{\text{aerosol}}$  is thus small, even though the biomass-burning influence may not be negligible.

[13] As indicators of fossil fuel combustion emissions, we use the concentrations of short-chain,  $\text{C}_{3-5}$ , alkanes, which are abundant in urban atmospheres [Seila et al., 1989], but are less common from biomass-burning sources [Friedli et al., 2001; Andreae and Merlet, 2001]. Emission ratios of various VOCs versus CO are shown in Figure 2 for six different cases. The emission ratios for Beijing and Myanmar are taken from the Streets et al. [2003] emission inventory, and represent two qualitatively different source regions in Asia that are compared, further below, with the hydrocarbon observations during the Asian transport events. Emissions from Beijing are dominated by fossil fuel combustion sources: 63% of the total CO emission is from transport, 20% from industry and 11% from the domestic use of fossil fuels. In contrast, the emissions from the Southeast Asian country of Myanmar are dominated by



**Figure 3.** Flight track of the NOAA WP-3D on 5 May, color- and size-coded by the measured CO mixing ratio.

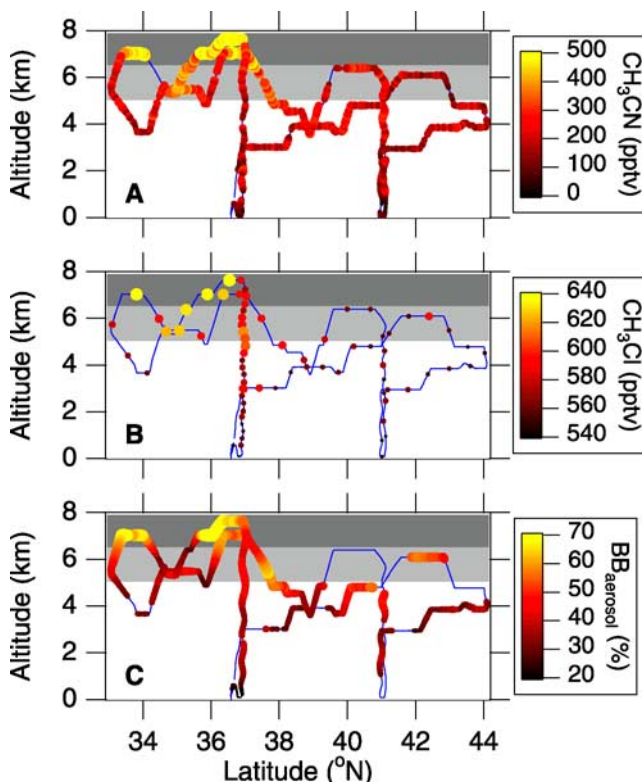
biomass burning: 74% of the total CO comes from biomass burning, mostly forest fires, and an additional 20% is from the domestic use of biofuels [Streets *et al.*, 2003]. For comparison, we have added to Figure 2 the VOC emission ratios for Los Angeles and a wildfire in Utah, observed during the ITCT 2K2 experiment, and data from Seila *et al.* [1989] for 39 U.S. cities and Friedli *et al.* [2001] for 7 wildfires in North America (no CO data were available for the work by Seila *et al.* [1989], and the numbers have been placed on the same scale by setting the emission ratio for acetylene arbitrarily to 5 pptv ppbv<sup>-1</sup>). Other hydrocarbons that were measured in the canister samples are not shown in Figure 2, but were either not used here to distinguish between biomass burning and fossil fuel sources (ethane), or were mostly reacted away by the time the air masses were intercepted by the NOAA WP-3D (ethylene, propylene, toluene). Figure 2 shows that acetylene and benzene cannot be used as indicators of either fossil fuel or biomass-burning emissions: the range of values observed for fossil fuel and biomass-burning sources overlap too much. On the other hand, Figure 2 shows that the emission ratios for the C<sub>3-5</sub> alkanes are significantly higher for fossil fuel combustion than for biomass-burning sources: the difference is well outside the variability observed within each category.

### 3.2. Flight on 5 May 2002

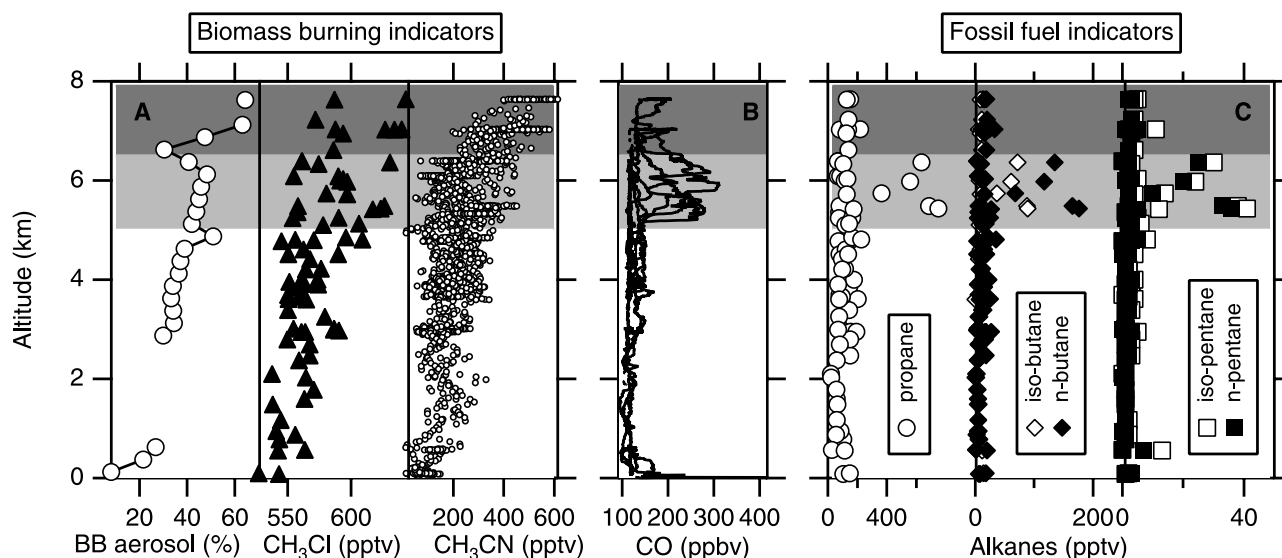
[14] On 5 May 2002, the NOAA WP-3D extensively sampled an Asian transport event that had been forecasted [Forster *et al.*, 2004] and has been described in detail by several authors [Cooper *et al.*, 2004; Nowak *et al.*, 2004; Brock *et al.*, 2004]. Figure 3 shows the flight track on that

day, color- and size-coded by the measured CO mixing ratios. It can be seen that high CO levels of up to 300 ppbv were observed in a layer between 5 and 6.5 km altitude (light gray area in Figure 3b), and between 34 and 36°N latitude. Cooper *et al.* [2004] have shown using back-trajectory calculations that the sampled air masses likely had come from a broad region in eastern Asia centered on central China. The transport across the Pacific took place in about 8 days, at altitudes between 6 and 8 km and latitudes from 40°N to 60°N. The transport mechanism involved a combination of two warm conveyor belts (WCB). One WCB lofted the pollutants above eastern Asia, and as it decayed, a portion was entrained into the upper regions of a second WCB forming east of Japan, which subsequently transported the pollution to North America [Cooper *et al.*, 2004].

[15] Figure 4 shows the results for acetonitrile, methyl chloride and BB<sub>aerosol</sub>, measured during the flight on May 5. The figure shows elevated levels of all three biomass-burning indicators in a layer above 6.5 km altitude (dark gray area in Figures 3b and 4a–4c), and between 33 and 37°N latitude. This layer was at a higher altitude than the 5–6.5 km layer with the highest CO mixing ratios in Figure 3b. It is seen that at the highest flight levels, about 70% of the particles measured by the PALMS instrument are attributed to a biomass-burning origin. The uncertainty in this percentage is large, however: the PALMS instrument sampled particles with a high efficiency only in the size range 0.3–3.0 μm, and the percentage is of course highly



**Figure 4.** Measurement results from the flight on 5 May for (a) acetonitrile (CH<sub>3</sub>CN), (b) methyl chloride (CH<sub>3</sub>Cl) and (c) the percentage of particles attributed to biomass burning (BB<sub>aerosol</sub>; see text).



**Figure 5.** Altitude profiles for several species measured during the flight on 5 May. Those measured between 5 and 6.5 km altitude (light gray area) are attributed to predominantly fossil fuel combustion, and above 6.5 km (dark gray area) to biomass-burning sources.

sensitive to the somewhat arbitrary definition of biomass-burning particles of equation (1). The different biomass-burning indicators in Figure 4 agree fairly well with each other, but there are also differences. In the case of  $BB_{aerosol}$  this is not unexpected, because the particles can be removed in clouds, which certainly must have occurred to a certain extent during the transport in the warm conveyor belt [Cooper *et al.*, 2004]. In contrast, acetonitrile and methyl chloride are relatively insoluble and would be largely unaffected by cloud processing.

[16] Figure 5 shows the altitude profiles for the different biomass burning and fossil fuel combustion indicators measured during the flight on 5 May. The mixing ratio of CO (Figure 5b) shows background values of slightly more than 100 ppbv below 5 km altitude, strong enhancements of up to 300 ppbv in the layer between 5 and 6.5 km, and smaller but significant enhancements in the layer above 6.5 km. The three biomass-burning indicators all increase with altitude (Figure 5a), whereas the  $C_{3-5}$  alkanes have higher mixing ratios in the layer between 5 and 6.5 km (Figure 5c). These results suggest that the compounds observed between 5 and 6.5 km are predominantly related to fossil fuel combustion emissions, whereas the layer observed above 6.5 km is more strongly influenced by biomass-burning emissions. The biomass-burning indicators are less abundant but not completely absent in the layer between 5 and 6.5 km, indicating that there may be a minor component of biomass burning in that layer as well. Below 5 km altitude, the air composition resembles that of the background troposphere. Despite clear chemical differences between the two polluted layers described above, the meteorological analysis of Cooper *et al.* [2004] did not show a clear difference in source region. The accuracy of 8-day back-trajectory calculations and the  $1^\circ \times 1^\circ$  resolution of the trajectory model may be insufficient to resolve these details.

[17] Figure 6 shows scatterplots of the  $C_{3-5}$  alkanes and benzene versus acetylene for the flight on 5 May. In all cases there are two different groups of points, most notably

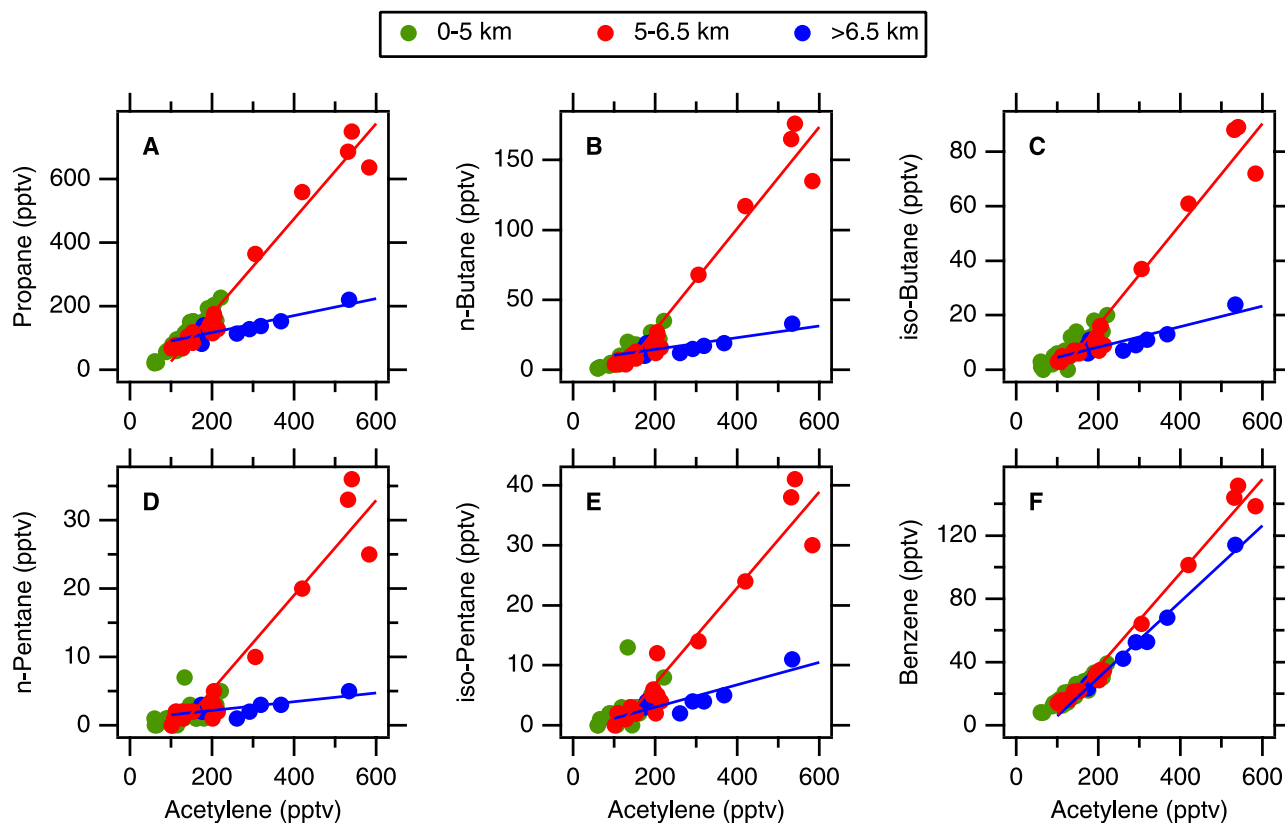
for the  $C_{3-5}$  alkanes and to a lesser extent for benzene. Enhancement ratios for all the VOCs versus acetylene,  $\Delta VOC/\Delta C_2H_2$  (where the  $\Delta$  signifies the enhancement over background values), were determined from the slopes of the lines fit to the data in Figure 6, and are given in Table 2. Acetylene is used rather than CO for two reasons: (1) CO can be formed during the transport by photo-oxidation of hydrocarbons and (2) acetylene emission ratios versus CO are similar for biomass burning and fossil fuel combustion emissions (see Figure 2). From Figure 6 and Table 2 it can be seen that for the  $C_{3-5}$  alkanes the enhancement ratios in the 5–6.5 km layer were much higher than in the layer above 6.5 km, whereas the benzene enhancements were more similar.

[18] The 4th column of Table 2 contains the emission ratios for the  $C_{3-5}$  alkanes and benzene versus acetylene. As the 5–6.5 km layer is attributed to fossil fuel combustion emissions, the observed enhancement ratios are compared with the emission ratios for Beijing. The layer above 6.5 km, on the other hand, is attributed to biomass-burning emissions, and the observed enhancement ratios are compared with the emission ratios for Myanmar. In many cases the observed enhancement ratios are significantly smaller than the assumed emission ratios, and part of the difference is due to chemical removal during the transport that is more efficient, particularly, for the butanes and pentanes than it is for acetylene. The effect of chemical removal on the enhancement ratios can be estimated by:

$$\Delta VOC/\Delta C_2H_2 = ER \times \exp\{-(k_{VOC+OH} - k_{C_2H_2+OH})[OH]\Delta t\}, \quad (2)$$

where ER is the emission ratio, and  $k_{VOC+OH}$  and  $k_{C_2H_2+OH}$  are the rate coefficients for the reactions of OH with the different VOCs and  $C_2H_2$ , respectively. The concentration of hydroxyl radicals, [OH], is assumed to be  $7.7 \times 10^5$  molecules  $cm^{-3}$  using the climatological distribution of Spivakovsky *et al.* [2000] for April at  $44^\circ N$  latitude and a





**Figure 6.** Correlation between acetylene and (a) propane, (b) n-butane, (c) iso-butane, (d) n-pentane, (e) iso-pentane, and (f) benzene observed in three altitude bins during the flight on May 5.

pressure of 500 hPa, i.e., the latitude and altitude where most of the transport took place according to the analysis by Cooper *et al.* [2004]. The time elapsed since the emission of the pollution,  $\Delta t$ , was assumed to be 8 days [Cooper *et al.*, 2004]. The  $\Delta\text{VOC}/\Delta\text{C}_2\text{H}_2$  enhancement ratios, corrected for chemical removal according to equation (2), are given in the last column of Table 2. In particular for the layer above 6.5 km, the agreement between the observed enhancement ratios and the values calculated from equation (2) is within the respective uncertainties. In the 5–6.5 km layer, the agreement is reasonable for the butanes and pentanes, but less good for propane and benzene. The differences may point to problems with the assumed emissions. Propane emission ratios are highly variable (see Figure 2), and the  $\Delta\text{C}_3\text{H}_8/\Delta\text{C}_2\text{H}_2$  ratio between 5 and 6.5 km ( $1.50 \pm 0.07$ ) is, in fact, between the values in Figure 2 for Beijing (0.69) and Los Angeles (2.3). Benzene emissions from traffic have been effectively reduced in the United States because of their potential impact on human health. This may not be true for emissions in Asia, where direct measurements of hydrocarbons from traffic have been scarce. Streets *et al.* [2003] compared the boundary-layer outflow from China on two TRACE-P flights with the results from a model calculation and found lower values in the model particularly for aromatics. On the basis of the high  $\Delta\text{alkane}/\Delta\text{C}_2\text{H}_2$  ratios in the layer between 5 and 6.5 km and the low ratios in the layer above 6.5 km, we conclude that the hydrocarbon composition of the two layers is largely consistent with our assumption that the air masses sampled between 5 and

6.5 km were most strongly influenced by fossil fuel combustion, and above 6.5 km by biomass burning.

[19] Several authors have used tetrachloroethene ( $\text{C}_2\text{Cl}_4$ ) as an indicator of urban and industrial emissions [Blake *et al.*, 1997, 2003]. Figure 7 shows the correlation between  $\text{C}_2\text{Cl}_4$  and CO in the three altitude ranges used above. Enhancement ratios of  $\text{C}_2\text{Cl}_4$  versus CO,  $\Delta\text{C}_2\text{Cl}_4/\Delta\text{CO}$ , were determined from the slopes of the lines fit to the

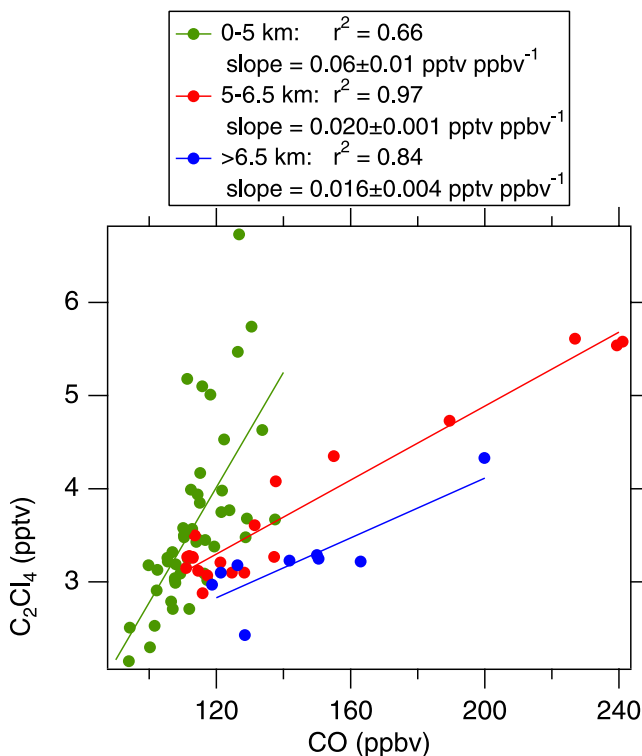
**Table 2.** Enhancement Ratios of VOCs Versus Acetylene in the 5–6.5 km and >6.5 km Layers Observed on 5 May and Calculated Using Assumed Emission Ratios and a Correction for Chemical Removal (See Text)

VOC	$r^2$	$\Delta\text{VOC}/\Delta\text{C}_2\text{H}_2$		
		Observed	Source	Corrected
<i>5–6.5 km: Urban/Industrial Sources</i>				
Propane	0.98	$1.50 \pm 0.07$	0.69 <sup>a</sup>	$0.57 \pm 0.04^c$
Butanes	0.98	$0.55 \pm 0.03$	0.79 <sup>a</sup>	$0.33 \pm 0.12$
Pentanes	0.96	$0.149 \pm 0.010$	0.54 <sup>a</sup>	$0.10 \pm 0.07$
Benzene	0.99	$0.297 \pm 0.009$	0.16 <sup>a</sup>	$0.12 \pm 0.01$
<i>&gt;6.5 km: Biomass-Burning Sources</i>				
Propane	0.83	$0.26 \pm 0.07$	0.23 <sup>b</sup>	$0.19 \pm 0.01$
Butanes	0.80	$0.08 \pm 0.02$	0.22 <sup>b</sup>	$0.09 \pm 0.03$
Pentanes	0.83	$0.025 \pm 0.006$	0.13 <sup>b</sup>	$0.02 \pm 0.02$
Benzene	0.99	$0.241 \pm 0.010$	0.32 <sup>b</sup>	$0.24 \pm 0.03$

<sup>a</sup>Emission ratios for Beijing from the Streets *et al.* [2003] inventory.

<sup>b</sup>Emission ratios for Myanmar from the Streets *et al.* [2003] inventory.

<sup>c</sup>Uncertainties are estimated assuming uncertainties of  $\pm 25\%$  for  $\Delta t$  and  $\pm 33\%$  in [OH].



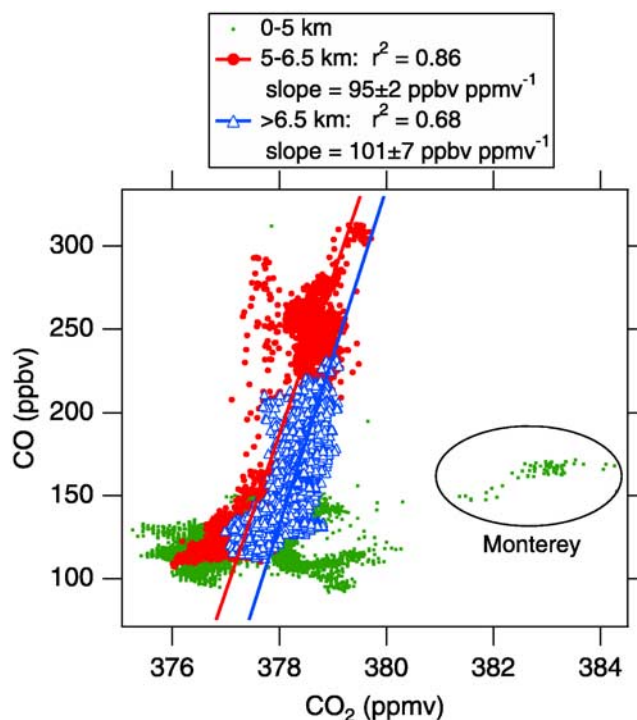
**Figure 7.** Correlation between  $C_2Cl_4$  and CO observed in three altitude bins during the flight on 5 May.

data in Figure 7. In the 5–6.5 km layer the  $\Delta C_2Cl_4/\Delta CO$  ratio was approximately  $0.020 \text{ pptv ppbv}^{-1}$ , which is at the low end of the range of values observed by *Blake et al.* [1997, 2003]. From the emissions inventories of CO [*Streets et al.*, 2003] and  $C_2Cl_4$  [*McCulloch et al.*, 1999] we estimate the  $\Delta C_2Cl_4/\Delta CO$  ratio to be  $0.98 \text{ pptv ppbv}^{-1}$  in air masses from Japan and  $0.006 \text{ pptv ppbv}^{-1}$  in air masses from China. The observed ratios are much more consistent with a Chinese origin of these air masses than with a Japanese origin in agreement with *Cooper et al.* [2004]. The  $\Delta C_2Cl_4/\Delta CO$  ratio in the layer above 6.5 km was slightly lower than in the 5–6.5 km layer, but there was only one sample in which  $C_2Cl_4$  was significantly enhanced. The highest mixing ratios of  $C_2Cl_4$  were observed below 5 km, where the  $\Delta C_2Cl_4/\Delta CO$  ratio was also higher, which suggests that these air masses may have been impacted by emissions from a more industrialized region. However, this result is obtained by comparing samples across a 5 km altitude range, which air masses may have originated in very different regions of the atmosphere.

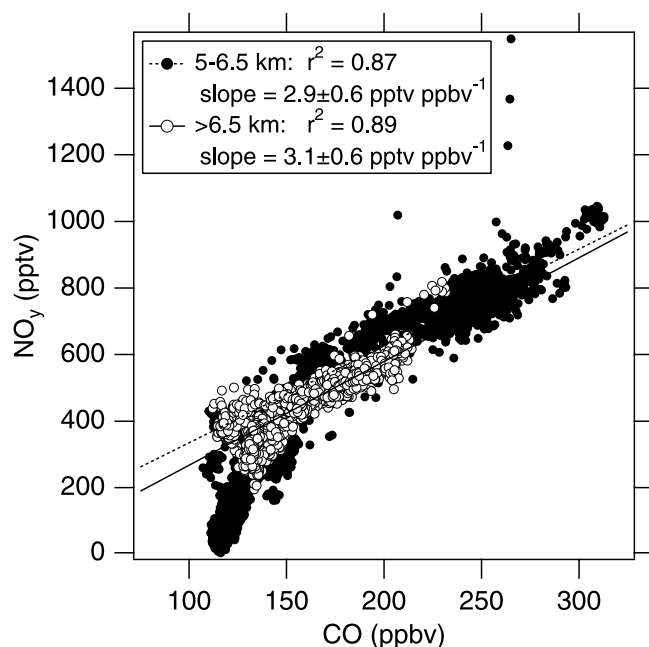
[20] Figure 8 shows a scatterplot of CO versus  $CO_2$  measured during the flight on 5 May. The data have been divided in the three altitude ranges used above. Below 5 km the correlation between CO and  $CO_2$  is poor. Only in the vicinity of Monterey did the sampled air masses contain enhanced CO and  $CO_2$ . Above 5 km the degree of correlation between CO and  $CO_2$  is higher, and the  $\Delta CO/\Delta CO_2$  ratios are relatively high in comparison with western sources. *Koike et al.* [2003] have studied the  $\Delta CO/\Delta CO_2$  ratio versus air mass origin during TRACE-P, and found consistently higher ratios for China versus Japan. This agrees with the emission inventory of *Streets et al.*

[2003], according to which the  $\Delta CO/\Delta CO_2$  emission ratio is  $8.9 \text{ ppbv ppmv}^{-1}$  for Japan,  $48 \text{ ppbv ppmv}^{-1}$  for China and  $61 \text{ ppbv ppmv}^{-1}$  for Southeast Asia. The  $\Delta CO/\Delta CO_2$  ratios found on 5 May for both the 5–6.5 km and >6.5 km layers (Figure 8) were high compared with these numbers. The differences in  $\Delta CO/\Delta CO_2$  ratios between the different parts of Asia are caused by cleaner combustion technologies in Japan, and the larger contribution from biomass burning to the total emissions in China and Southeast Asia. High  $\Delta CO/\Delta CO_2$  ratios are found from forest fires and biofuel use [*Friedli et al.*, 2001; *Andreae and Merlet*, 2001]. For domestic biofuel combustion in Africa, *Ludwig et al.* [2003] reported  $\Delta CO/\Delta CO_2$  ratios in the range of  $60\text{--}140 \text{ ppbv ppmv}^{-1}$ . High  $\Delta CO/\Delta CO_2$  ratios do not just occur in biomass burning, however: *Zhang et al.* [1995] measured  $\Delta CO/\Delta CO_2$  ratios in the exhaust from vehicles in various cities worldwide. In this study, the median  $\Delta CO/\Delta CO_2$  ratio ranged from  $12 \text{ ppbv ppmv}^{-1}$  in Hong Kong and  $17 \text{ ppbv ppmv}^{-1}$  in Seoul, to  $61 \text{ ppbv ppmv}^{-1}$  in Taipei,  $190 \text{ ppbv ppmv}^{-1}$  in Bangkok and  $300 \text{ ppbv ppmv}^{-1}$  in Kathmandu. The high  $\Delta CO/\Delta CO_2$  ratios found here for the 5–6.5 km layer on 5 May suggest that the origin of this air mass was in China and/or Southeast Asia but not in Japan. This finding is corroborated by the observation above of a relatively low  $\Delta C_2Cl_4/\Delta CO$  enhancement ratio in the 5–6.5 km layer and by the trajectory analysis of *Cooper et al.* [2004].

[21] For biomass-burning sources the  $NO_x$  to CO ratio is smaller than in emissions from fossil fuel combustion. The emission inventory of *Streets et al.* [2003] gives a  $\Delta NO_x/\Delta CO$  ratio of  $16 \text{ pptv ppbv}^{-1}$  for Myanmar,  $51 \text{ pptv ppbv}^{-1}$  for Beijing and  $200 \text{ pptv ppbv}^{-1}$  for Japan.



**Figure 8.** Correlation between CO and  $CO_2$  observed during the flight on 5 May. The red and blue lines show the results of an orthogonal distance regression analysis.



**Figure 9.** Correlation between  $\text{NO}_y$  and CO observed during the flight on 5 May.

For comparison, Ludwig *et al.* [2003] derive a global mean  $\text{NO}_x$  to CO ratio of 29 pptv ppbv<sup>-1</sup> for biofuel use, somewhere in between the values for Myanmar and Beijing. Figure 9 shows the correlation between  $\text{NO}_y$  and CO for the two layers observed on 5 May. As shown by Nowak *et al.* [2004] the  $\Delta\text{NO}_y/\Delta\text{CO}$  ratio was surprisingly similar for all the transport episodes during ITCT 2K2, and the same holds for the two layers on 5 May: the  $\Delta\text{NO}_y/\Delta\text{CO}$  ratio, determined from the slopes of the lines fit to the data in Figure 9, is  $2.9 \pm 0.6$  pptv ppbv<sup>-1</sup> for the layer between 5–6.5 km and  $3.1 \pm 0.6$  pptv ppbv<sup>-1</sup> above 6.5 km. Both ratios are considerably smaller than the expected  $\Delta\text{NO}_x/\Delta\text{CO}$  ratio at the source: after conversion of  $\text{NO}_x$  into  $\text{NO}_y$ , a significant fraction of the  $\text{NO}_y$  is removed from the atmosphere, most likely by surface deposition and uptake of nitric acid ( $\text{HNO}_3$ ) on cloud droplets and aerosol [Koike *et al.*, 2003]. The similar  $\Delta\text{NO}_y/\Delta\text{CO}$  ratios observed in the two layers on 5 May and the different assumed  $\Delta\text{NO}_x/\Delta\text{CO}$  ratios at the source may imply that  $\text{NO}_y$  was more efficiently lost in the air masses that were observed between 5 and 6.5 km. A different degree of cloud processing could be the explanation, but no evidence for this was obtained from the meteorological analyses of Cooper *et al.* [2004].

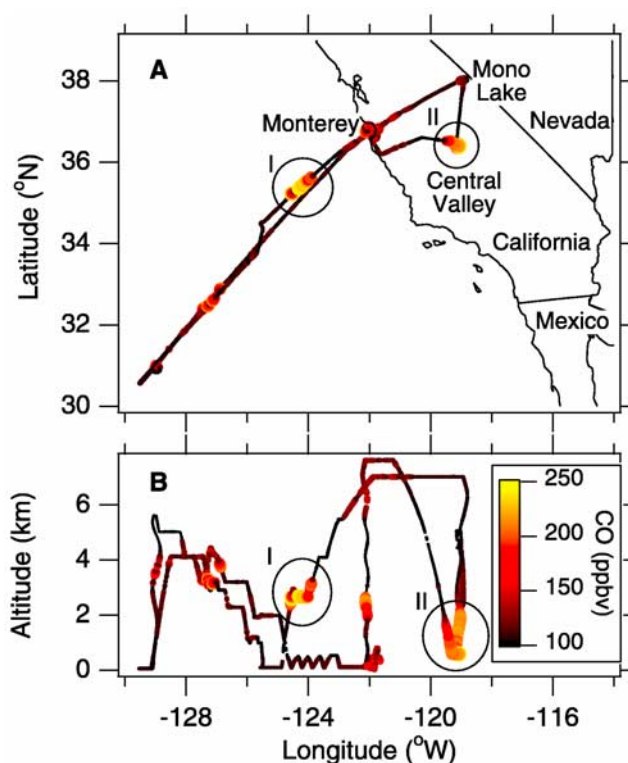
### 3.3. Flight on 17 May 2002

[22] The second most intense event of Asian transport was observed on 17 May 2002. Figure 10 shows the flight track of the NOAA WP-3D and the CO mixing ratios that were measured during the flight. Enhanced CO levels of up to 250 ppbv were observed in four different locations over the Pacific Ocean. The highest CO was observed in location I in Figure 10. Brock *et al.* [2004] have shown that this air mass likely had come from southeastern China after a transport time of approximately 14 days. These authors suggested that after being advected from southeastern China, this air mass was lifted to an altitude of 6–7 km

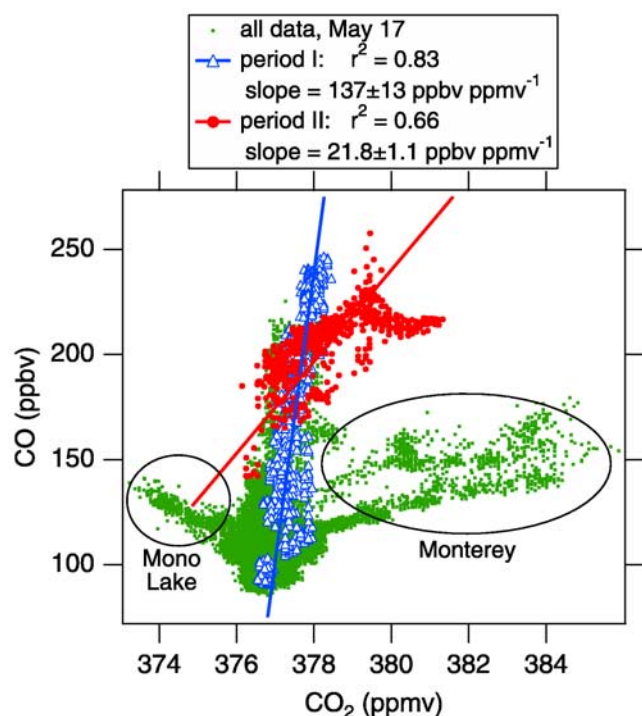
in a mid-Pacific cyclone, followed by a slow descent to 2–4 km altitude toward the U.S. west coast. Most particles were removed by cloud processing approximately 8 days prior to 17 May, and subsequently new particles were formed and grew from the  $\text{SO}_2$  and  $\text{H}_2\text{SO}_4$  precursors that were still present at measurable amounts in location I [Brock *et al.*, 2004]. The last part of the flight on 17 May took place over California and included vertical profiles over Mono Lake and Central Valley. High CO mixing ratios of up to 250 ppbv were encountered at low altitudes over the California Central Valley (location II in Figure 10), and are attributed to continental emissions.

[23] Figure 11 shows a scatterplot of CO versus  $\text{CO}_2$  from the flight on 17 May. Blue triangles indicate the data sampled in location I, and red circles the data from location II. The rest of the data is shown by the green dots. The  $\Delta\text{CO}/\Delta\text{CO}_2$  ratio in location I was clearly higher than in location II, which demonstrates the difference between the air from Asia (high  $\Delta\text{CO}/\Delta\text{CO}_2$ ; see Figure 8) and air with a local emission signature (low  $\Delta\text{CO}/\Delta\text{CO}_2$ ). At altitudes below 1 km close to Monterey, the NOAA WP-3D also encountered air with enhanced CO and  $\text{CO}_2$ . The  $\Delta\text{CO}/\Delta\text{CO}_2$  ratio was similar to that found in location II, again indicating the influence of local North American sources. Over Mono Lake, the  $\Delta\text{CO}/\Delta\text{CO}_2$  ratio was found to be negative: CO was moderately enhanced in the planetary boundary layer (PBL), but the  $\text{CO}_2$  was reduced in comparison with the free troposphere, most likely, because of uptake in the forested mountains immediately upwind of this area.

[24] Figure 12 shows the altitude profiles of several species measured on 17 May. For this plot a subset of the



**Figure 10.** Flight track of the NOAA WP-3D on 17 May, color- and size-coded by the measured CO mixing ratio.

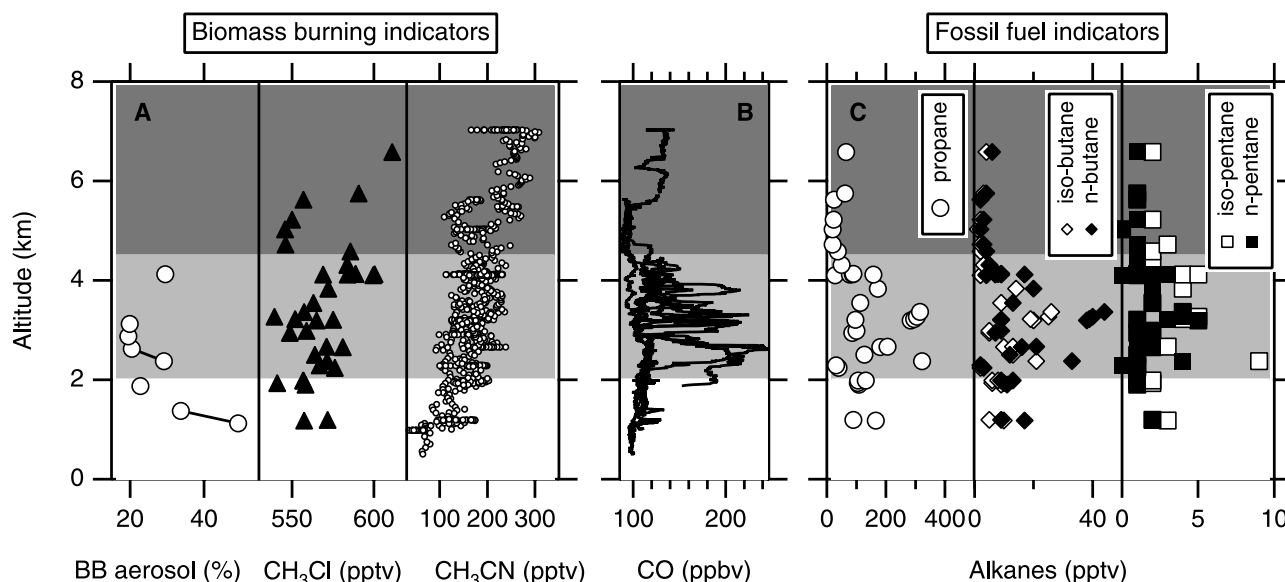


**Figure 11.** Correlation between CO and CO<sub>2</sub> observed during the flight on 17 May. The red and blue lines show the results of an orthogonal distance regression analysis. The periods I and II refer to the time intervals indicated in Figure 10.

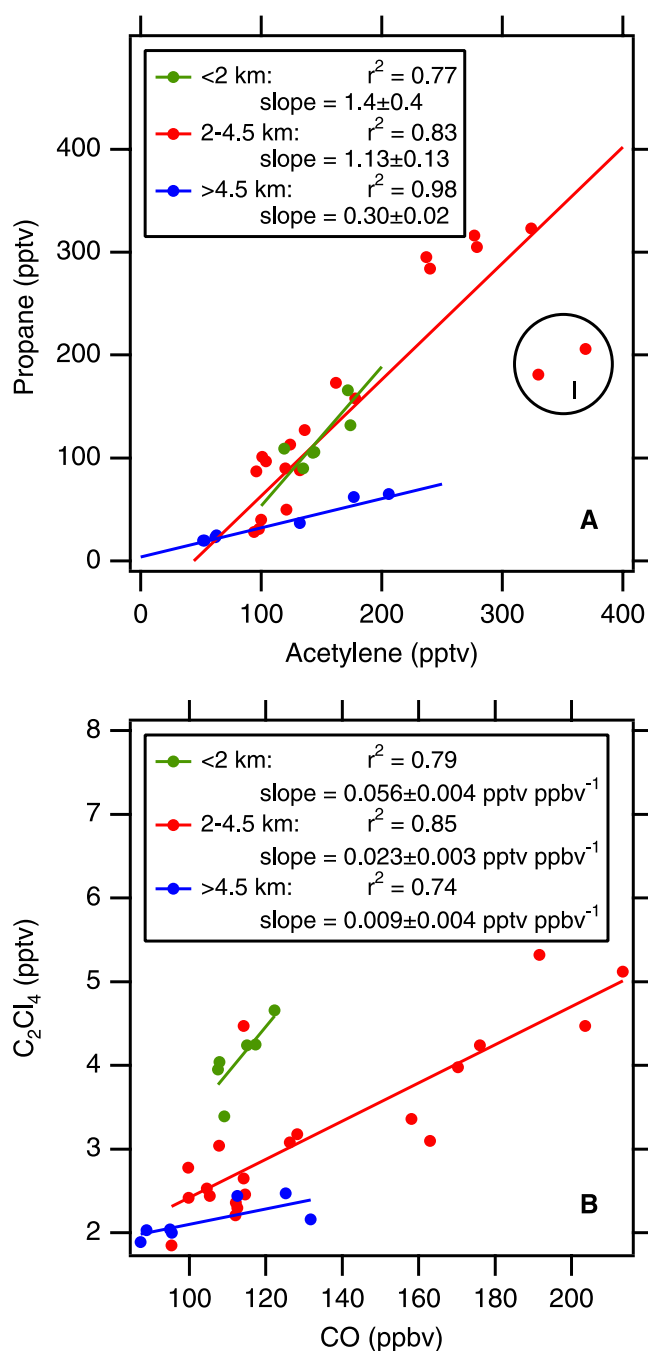
ITCT 2K2 data was used of measurements that were not influenced by North American emissions as described by Brock *et al.* [2004]. Figure 12b shows the altitude profile of CO. Strong enhancements of CO of up to 250 ppbv were observed between 2 and 4.5 km. At 5 km the CO levels are

at their background levels of just over 100 ppbv. Above 5 km CO is enhanced, but not as much as between 2 and 4.5 km. Figure 12a shows the altitude profiles of the different biomass-burning indicators used in this work. The mixing ratios of acetonitrile and methyl chloride were not significantly enhanced in the layer between 2 and 4.5 km, which suggests a minor influence from biomass-burning sources. There are only limited data available for the parameter  $BB_{\text{aerosol}}$  from this flight, and they also show no enhancement in the 2–4.5 km layer. Two biomass-burning indicators (acetonitrile and methyl chloride) increased with altitude, as seen before on 5 May (Figure 5). There was a reasonable correlation between acetonitrile and CO above 4.5 km ( $r^2 = 0.77$ ), and the  $\Delta\text{CH}_3\text{CN}/\Delta\text{CO}$  enhancement ratio derived from the data was  $1.95 \pm 0.11$  pptv ppbv<sup>-1</sup>. This number is in the range of values reported for fires in the literature (1–5 pptv ppbv<sup>-1</sup>) [Holzinger *et al.*, 1999; Christian *et al.*, 2003], and is much higher than the ratio of 0.1 pptv ppbv<sup>-1</sup> that was observed over Los Angeles during ITCT 2K2 [de Gouw *et al.*, 2003a]. Figure 12c shows the altitude profiles of propane, butanes and pentanes, which were elevated in the layer between 2 and 4.5 km. All of the enhancements, particularly for the pentanes are much smaller than on 5 May, most likely because of the longer transport time of the air mass on May 17 (14 days in comparison with 8 days for 5 May). We conclude that the pollution from Asia observed between 2 and 4.5 km is primarily from fossil fuel combustion sources, consistent with the observation of enhanced SO<sub>2</sub> in the air mass observed in location I. An influence of biomass-burning emissions is detected above 4.5 km. These observations are fairly similar to the findings from 5 May, with the difference that the layer with the highest CO mixing ratios is observed at lower altitudes on 17 May.

[25] The correlation between propane and acetylene for the flight on 17 May is shown in Figure 13a. Samples that



**Figure 12.** Altitude profiles for several species measured during the flight on 17 May. Measurements that had been influenced by North American emissions have been omitted from the plot. The pollutants measured between 2 and 4.5 km altitude (light gray area) are attributed to fossil fuel combustion sources, and above 4.5 km (dark gray area) to biomass-burning sources.



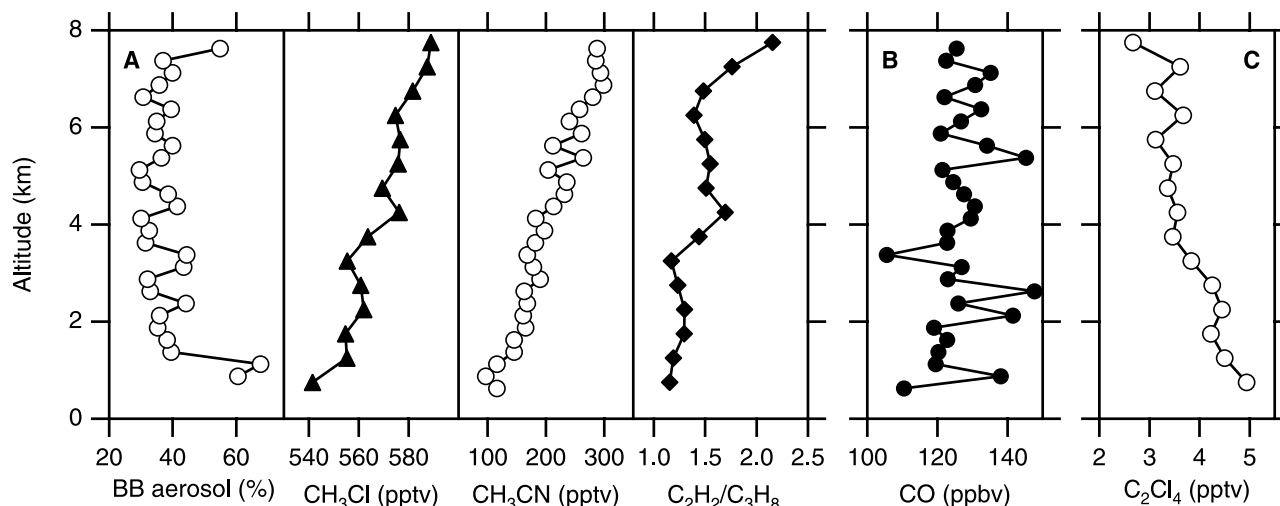
**Figure 13.** Trace gas correlations observed during the flight on 17 May. Figure 13a shows the correlation between propane and acetylene in three altitude bins; Figure 13b shows the correlation between C<sub>2</sub>Cl<sub>4</sub> and CO in the same altitude bins. Samples that were influenced by North American emissions have been omitted from this analysis. The data points indicated by I were obtained in location I in Figure 10.

had been influenced by North American emissions, in the California Central Valley and around Mono Lake, have been omitted from this plot. Similarly to the observations in Figure 6, there are two groups of points: the  $\Delta C_3H_8/\Delta C_2H_2$  ratio was high ( $1.13 \pm 0.13$ ) between 2 and 4.5 km, where the Asian outflow was observed, and low

( $0.30 \pm 0.02$ ) above 4.5 km. These numbers are similar to the  $\Delta C_3H_8/\Delta C_2H_2$  ratios reported above for the two different layers on 5 May ( $1.50 \pm 0.07$  for 5–6.5 km;  $0.26 \pm 0.07$  for >6.5 km). The samples in location I, indicated by the circle in Figure 13a, had intermediate  $\Delta C_3H_8/\Delta C_2H_2$  ratios. Figure 13b shows the correlation between C<sub>2</sub>Cl<sub>4</sub> and CO for the flight on 17 May. The transport layer between 2 and 4.5 km shows a reasonable correlation between C<sub>2</sub>Cl<sub>4</sub> and CO. The  $\Delta C_2Cl_4/\Delta CO$  enhancement ratio, determined from the slopes of the lines fit to the data, is low at  $0.023$  pptv ppbv<sup>-1</sup> and comparable to the enhancement ratio observed on 5 May in the main transport layer between 5 and 6.5 km (Figure 7). Above 4.5 km the  $\Delta C_2Cl_4/\Delta CO$  ratio is even lower, consistent with the assumption that this layer was mostly influenced by biomass-burning emissions. Similarly to 5 May the highest  $\Delta C_2Cl_4/\Delta CO$  ratio is observed below the transport layer. We conclude from the high  $\Delta CO/\Delta CO_2$  and the low  $\Delta C_2Cl_4/\Delta CO$  enhancement ratios in the transport layer between 2 and 4.5 km that this air mass may have originated in China, consistent with the trajectory analysis of Brock *et al.* [2004].

### 3.4. Average Altitude Profiles

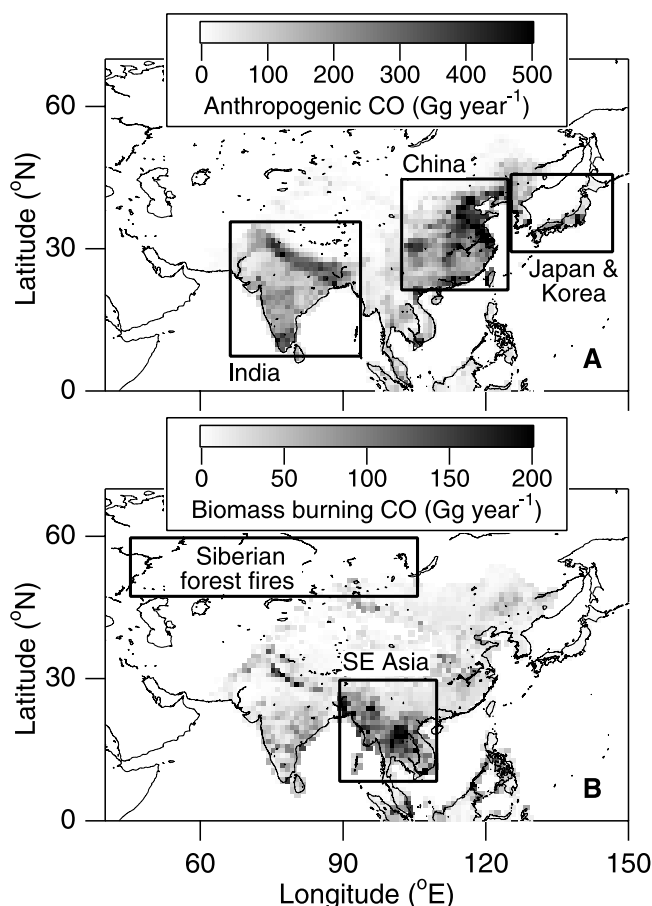
[26] The results from both 5 May and 17 May suggest an influence of biomass-burning emissions at the highest flight levels of the NOAA WP-3D, and above the layers that showed strong indications of fossil fuel combustion sources. The presence of biomass-burning indicators at high altitudes was observed on more flights, and is addressed in this section. Figure 14 shows the average altitude profiles of the biomass-burning indicators, CO and tetrachloroethene. Data from all flights were used, except the transfer flights to and from Monterey (22 April and 19 May). In addition, only measurements were used that were not influenced by North American emissions using the data selection described by Brock *et al.* [2004]. It is seen in Figure 14a that three biomass-burning indicators, methyl chloride, acetonitrile and the acetylene to propane ratio, increased on average with altitude. One limitation of using the C<sub>2</sub>H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> ratio as a biomass-burning indicator is that the ratio increases with air mass age due to the slightly longer atmospheric lifetime of acetylene in comparison with propane. This would likely increase the ratio at low altitudes, where radical concentrations are higher and the sampled air masses typically spent longer during the transport across the Pacific, i.e., it does not explain the vertical gradient observed in Figure 14. The fraction of biomass-burning aerosols (BB<sub>aerosol</sub>) was fairly constant as a function of altitude with higher values around 1 km and at the highest flight altitude of the NOAA WP-3D. The high values around 1 km altitude are attributed to a local, North-American influence. As mentioned above, the data had been filtered for local influences, but the filter was entirely based on measurements of gas-phase species [Brock *et al.*, 2004], and evidently is not a perfect filter for the PALMS data set. Figures 14b and 14c show the averaged altitude profile of CO and C<sub>2</sub>Cl<sub>4</sub>, respectively. CO was nearly independent of altitude, whereas C<sub>2</sub>Cl<sub>4</sub> decreased with altitude. These trends are markedly different from the altitude profiles of acetonitrile, methyl chloride and the C<sub>2</sub>H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> ratio in Figure 14a. A possible explanation for these findings will be discussed in the remainder of this section.



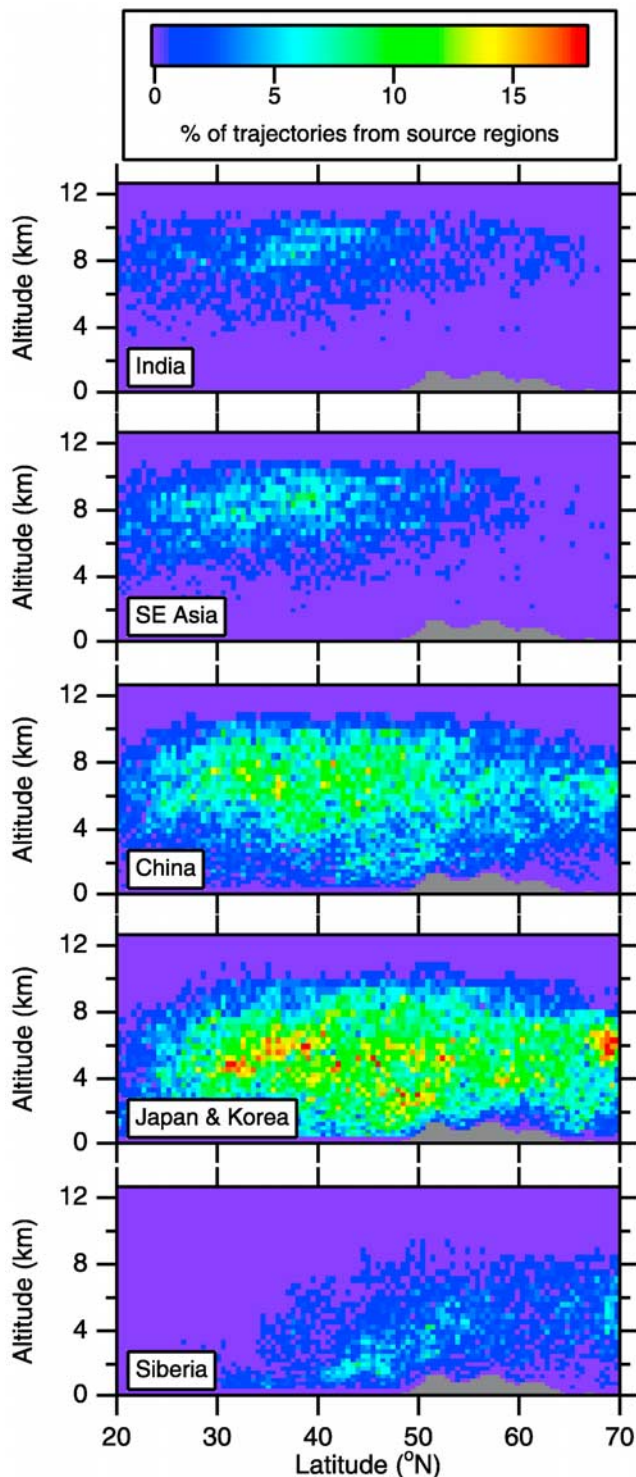
**Figure 14.** Average altitude profiles for several trace gases measured during ITCT 2K2. The data are from all flights except the two transit flights (22 April and 19 May), and have been filtered for North American influences.

[27] Figure 15 shows the distribution of anthropogenic and biomass-burning CO emissions in Asia, according to the emission inventory of *Streets et al.* [2003]. It is apparent that the anthropogenic emissions are the highest in eastern China, whereas Southeast Asia shows the highest biomass-burning emissions. We note that the domestic use of biofuels, a significant source of CO in Southeast Asia and rural China, is categorized as anthropogenic in the *Streets et al.* [2003] emission inventory, whereas the emissions of biofuel combustion can be expected to be qualitatively similar to those from biomass burning. The boxes in Figure 15 indicate the most important source regions, and a back-trajectory analysis was performed to determine at which altitudes and latitudes, on average, the outflow from these source regions was observed during ITCT 2K2. In addition to the Asian source regions, a part of Siberia was added to the analysis: data from the MODIS satellite indicated the presence of extensive forest fires in this region.

[28] An ensemble of 10-day back-trajectories was calculated using the method outlined in *Cooper et al.* [2004] for end points at  $-125^{\circ}\text{W}$  longitude and a range of pressures (1000–125 hPa in steps of 25 hPa), latitudes ( $20\text{--}70^{\circ}\text{N}$  at  $1^{\circ}$  intervals) and start times (20 April to 19 May; every 6 hours). The total number of trajectories was thus over  $2.2 \times 10^5$ , which allows us to discuss their average behavior with more confidence than we have in the individual 10-day back-trajectories. The percentage of trajectories that passed within the lowest 3 km over the different source regions in Figure 15 is shown in Figure 16 as a function of latitude and altitude. Some trajectories were influenced by more than one source region and contribute to the total for each corresponding region in Figure 16. The figure shows that up to 20% of the back-trajectories came from Japan and Korea. A similar percentage of back-trajectories came from China, but the influence was detected at somewhat higher altitudes and further south. A smaller percentage of back-trajectories came from Southeast Asia and India, and their influence was at even higher altitudes. The major process that transports emissions from central Asia to the western Pacific in the



**Figure 15.** Inventory of (a) anthropogenic and (b) biomass-burning CO emissions in 2000 [*Streets et al.*, 2003]. The source regions indicated are used in the trajectory analysis.

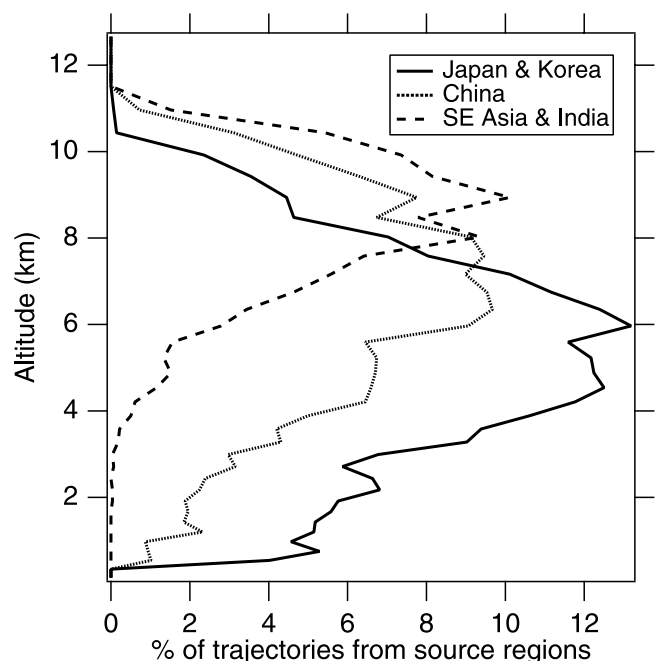


**Figure 16.** Fraction of back-trajectories from the different source regions in Figure 16, calculated at a longitude of  $-125^{\circ}\text{W}$  and for the period 20 April to 19 May.

spring is frontal lifting ahead of southeastward-moving cold fronts, and transport in the boundary layer behind the cold front [Liu *et al.*, 2003; Cooper *et al.*, 2004]. The outflow from Southeast Asia, on the other hand, primarily proceeds by deep convection [Liu *et al.*, 2003; Kondo *et al.*, 2004], which may explain why the trajectories from Southeast Asia were

generally observed at higher altitude than those from Japan and Korea. It should be mentioned that the trajectory model used here does not account specifically for sub-grid scale convective transport, but does capture the general ascending motion of air masses in the tropics. Only a small percentage of back-trajectories came from the region where Siberian forest fires were detected, and their influence was generally further north and at low altitudes during ITCT 2K2 (see Figure 16). The use of trajectory calculations to predict the outflow from forest fires, Siberian and Southeast Asian, is complicated by the fact that wildfire emissions can be injected into the free troposphere at altitudes much higher than 3 km [Lavoué *et al.*, 2000]. Nevertheless, it seems unlikely that the positive altitude gradient of biomass-burning indicators in Figure 14 is fully attributable to wildfires in Siberia. Instead, this gradient is more likely due to the increasing influence of China and Southeast Asia at higher altitudes, combined with the high biomass-burning emissions in these regions.

[29] The percentages in Figure 16 were averaged over the latitude range ( $31\text{--}42^{\circ}\text{N}$ ) that was most extensively sampled by the NOAA WP-3D during ITCT 2K2, and the result is shown in Figure 17 as a function of altitude. The influence from Japan and Korea was the highest, on average, between 4 and 6 km altitude. The influence from China was observed at higher altitudes and was the highest between 6 and 8 km. The combined percentage of back-trajectories from Southeast Asia and India peaked between 8 and 10 km. Below 7.5 km the highest percentage of back-trajectories came from Japan and Korea. However, as the total emissions from China for many species are much larger than those from Japan and Korea [Streets *et al.*, 2003], the influence of China is expected to dominate at altitudes well below 7.5 km.



**Figure 17.** Fraction of back-trajectories from different source regions as a function of altitude between  $31$  and  $42^{\circ}\text{N}$  latitude.

[30] The increasing trend of three biomass-burning indicators with altitude (Figure 14a) is consistent with the origin of the air masses observed at the different altitudes, and the fact that the contribution of biomass burning to the total emissions is low in Japan and Korea, higher in China and the highest in Southeast Asia (Table 1). The decreasing trend of  $C_2Cl_4$  with altitude is explained by considering that the source of this trace gas is much larger in Japan than it is in China and Southeast Asia [McCulloch *et al.*, 1999]. However, the average mixing ratio of  $C_2Cl_4$  was the highest at low altitudes (Figure 14c), whereas the fraction of back-trajectories from Japan was only small (Figure 17). This may be explained by the fact that the calculated trajectories only run back for 10 days, which is short compared with the atmospheric lifetime of  $C_2Cl_4$  and the average transport time of air masses across the ocean at low altitudes. CO is released from fossil fuel combustion and from biomass burning. The finding that CO was relatively independent of altitude (Figure 14b) may be explained by the combined effects of an increasing trend with altitude of CO from biomass burning, similar to acetonitrile and methyl chloride (Figure 14a), and a decreasing trend with altitude of CO from fossil fuel combustion, similar to  $C_2Cl_4$  (Figure 14c). The parameter  $BB_{aerosol}$  does not increase with altitude like the other biomass-burning indicators. On some flights there was a good correlation between  $BB_{aerosol}$  and acetonitrile, e.g., May 5 (Figure 4), whereas on other flights there was none. As mentioned before, an important difference between aerosols and gas-phase species is that aerosols can be removed in clouds, whereas insoluble trace gases such as acetonitrile and methyl chloride are not. Cloud processing may thus be a factor in the different behaviors with altitude of  $BB_{aerosol}$  and the gas-phase biomass-burning indicators.

#### 4. Conclusion

[31] During two research flights, on 5 and 17 May 2002, the NOAA WP-3D aircraft sampled air masses off the U.S. west coast that were influenced by Asian emissions. The layers with the highest enhancements of CO were attributed, in both cases, to fossil fuel combustion emissions because of enhanced levels of short-chain alkanes, and the absence of several biomass-burning indicators. Relatively low  $\Delta C_2Cl_4/\Delta CO$  and high  $\Delta CO/\Delta CO_2$  enhancement ratios were consistent with a Chinese origin of these air masses, in agreement with a meteorological analysis. On both days, a layer with elevated levels of species indicative of biomass burning (acetonitrile, methyl chloride, and particles attributed to biomass burning based on their carbon and potassium content) was observed at higher altitudes, concurrent with low alkane levels. An increased influence of biomass burning at the highest flight altitudes of the WP-3D was observed throughout the ITCT 2K2 mission, which was explained by combining an emissions inventory with a back-trajectory analysis. It was shown that air masses from Southeast Asia and China, where biomass-burning emissions are relatively high, were typically transported across the Pacific Ocean at higher altitudes than the air masses from Japan and Korea, which contain a higher fraction of pollutants from fossil fuel combustion.

[32] It has been shown that polluted air masses from Asia are regularly observed at higher altitudes above the U.S.

west coast during the spring. An influence on the surface air quality in the United States was not directly observed in this study and remains uncertain. Our understanding of the long-range transport of pollutants from Asia, and the analysis of the data presented here, is limited by a paucity of data on the emission sources. Detailed measurements are required in the major metropolitan areas in eastern China, as well as in the biomass-burning regions in Southeast Asia.

[33] **Acknowledgments.** We thank the crew and support team of the NOAA WP-3D aircraft, and our ITCT collaborators. In particular, we acknowledge useful discussions with Dan Murphy and Chuck Brock of the NOAA Aeronomy Laboratory, Caroline Forster of the Technical University in Munich, and Rynda Hudman, Qinbin Li and Daniel Jacob of Harvard University. This work was financially supported by the NOAA Office of Global Programs. NCAR is operated by the University Corporation for Atmospheric Research under the sponsorship of the NSF.

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