Three-dimensional distribution of nonmethane hydrocarbons and halocarbons over the northwestern Pacific during the 1991 Pacific Exploratory Mission (PEM-West A)

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Abstract. A total of 1667 whole air samples were collected onboard the NASA DC-8 aircraft during the 6-week Pacific Exploratory Mission over the western Pacific (PEM-West A) in September and October 1991. The samples were assayed for 15 C2-C7 hydrocarbons and six halocarbons. Latitudinal (0.5øS to 59.5øN) and longitudinal (114øE to 122øW) profiles were obtained from samples collected between ground level and 12.7 km. Thirteen of the 18 missions exhibited at least one vertical profile where the hydrocarbon mixing ratios increased with altitude. Longitude-latitude color patch plots at three altitude levels and three-dimensional color latitude-altitude and longitude-altitude contour plots exhibit a significant number of middle-upper tropospheric pollution events. These and several lower tropospheric pollution plumes were characterized by comparison with urban data from Tokyo and Hong Kong, as well as with natural gas and the products from incomplete combustion. Elevated levels of nonmethane hydrocarbons (NMHC) and other trace gases in the upper-middle free troposphere were attributed to deep convection over the Asian continent and to typhoon-driven convection near the western Pacific coast of Asia. In addition, NMHCs and CH3CCl3 were found to be useful tracers with which to distinguish hydrocarbon and halocarbon augmented plumes emitted from coastal Asian cities into the northwestern Pacific.

Introduction

Nonmethane hydrocarbons (NMHCs) and halocarbons affect both tropospheric and stratospheric photochemistry. The sources of these atmospheric trace species are predominantly land based and the main mechanism for the removal of those hydrocarbons and halocarbons with abstractable hydrogen atoms is through oxidative reaction with hydroxyl radicals (OH) as in (1).

\[ \text{RH} + \text{HO} \rightarrow \text{R} \cdot + \text{H}_2\text{O} \]  

Nonmethane hydrocarbon emission patterns can be used to characterize anthropogenic sources such as fossil fuel leakage and incomplete combustion [Ehhalt and Rudolph, 1984; Blake et al., 1992, 1994, 1995; Smith, 1993]. Because all of the halocarbons reported here are anthropogenic and released predominantly in cities, their measurement can be used to estimate recent urban influence on an air mass. For example, an air parcel which has been augmented by biomass burning would be expected to contain elevated levels of ethane, ethene, and ethyne and many other hydrocarbons, while exhibiting no chlorofluorocarbon enhancement [Crutzen and Andreae, 1990; Blake et al., 1992, 1994; Smith, 1993]. Industrial activity would be indicated by elevated concentrations of chlorofluorocarbons, as well as CCl4 (carbon tetrachloride), CH3CCl3 (methyl chloroform), C2Cl4 ( perchloroethylene), and other halocarbons [Crutzen, 1980; Rasmussen et al., 1982; Blake et al., 1992, Smith; 1993]. Natural gas emissions are associated with elevated levels of methane, ethane, and other light alkanes with no accompanying halocarbons [Blake et al., 1994].

We report the general results of measurements of 15 saturated and unsaturated C2-C7 NMHCs and six halocarbons, namely, CCl2F2 (CFC-12), CCl3F (CFC-11), CCl2FCClF2 (CFC-113), CH3CCl3, CCl4, and C2Cl4, in air samples collected onboard the NASA DC-8 aircraft between September 7 and October 22, 1991, during NASA's Pacific Exploratory Mission over the western Pacific (PEM-West A). The mission flew from San Jose, California, around the North Pacific rim and back through the central Pacific, with many additional flights from Tokyo, Hong Kong, Guam, and Hawaii. Numerous vertical profiles in the altitude range from 0.3 km to 12.7 km were flown over the ocean, with additional vertical profiles near urban areas during landings. In addition, the meteorological consequences of several typhoon events were encountered during the project, including fast vertical transport associated with Typhoons Nat and Mireille. These flights provided an excellent opportunity to examine the large-scale transport and distribution of NMHCs and halocarbons in the northwestern Pacific region.
Experiment

Sampling

The whole air sampling apparatus was mounted onboard the NASA DC-8 jet aircraft. The stainless steel 1/4-inch OD inlet and outlet were installed on the port side of the aircraft, forward of the wing section. The gas-handling manifold and the two-stage metal bellows pump (Metal Bellows Company, MB-602), connected in series, were configured to allow the sample canisters to be routinely filled to 40 psig and the system to be operated at pressures up to 60 psig before activation of a pressure relief valve. The 2-L sample canisters were assembled in fixed sets of 24, connected to a single manifold and arranged in three parallel columns of eight canisters. Rack mountings were available on the aircraft for six of these 24-canister sets, allowing a maximum of 144 samples to be collected per flight. These 24-canister sets formed the basic unit for sampling operations onboard the DC-8 and for shipments between the various staging sites and the analytical laboratory, which was assembled in Japan at the Yokota US Air Force Base near Tokyo. Details of sample canister fabrication and filling procedures have been discussed earlier [Blake et al., 1992, 1994; Smith, 1993].

The operation of a field laboratory at Yokota Air Base, Japan, one of the main staging sites for this mission, reduced the time required for sample canister transportation between aircraft landing sites and the analytical laboratory. For staging sites other than Yokota the filled sample canister sets were shipped by air cargo on commercial flights to Tokyo and then transported to Yokota. On average, approximately 90 air samples were collected on each flight and analyzed within 7 days. The total number of sample canisters available for the mission was approximately 700, requiring multiple use of canisters to maintain this high sampling frequency. After the air samples from earlier flights had been satisfactorily assayed, the canisters were evacuated to a pressure of $10^{-2}$ torr and shipped back to the DC-8 for subsequent missions.

Chemical Analysis

Each sample was analyzed for NMHCs and halocarbons using two Hewlett-Packard 5890 series II gas chromatographs (GCs). One gas chromatograph (GC-1), was equipped with two flame ionization detectors (FIDs), while GC-2 was equipped with an electron capture detector (ECD). One of the FIDs monitored the output of a 30 m x 0.53 mm Al2O3/KCl PLOT column (J & W Scientific) with a hydrogen carrier flow of 9.5 mL/min and provided data on C2-C5 NMHC compounds. A 60 m x 0.25 mm, 0.25-μm film thickness DB-1 column (J & W Scientific) with a hydrogen carrier flow of 2.0 mL/min was installed in the second FID for the purpose of detecting C3-C10 NMHCs. Coupled to the ECD, GC-2 utilized a 50 m x 0.2 mm, 0.5-μm film thickness PONA column (Hewlett-Packard) with a hydrogen carrier flow of 1.2 mL/min for halocarbon separation and detection.

A precise volume of air (1309 mL STP) from each sample canister was trapped in a precollection loop (8 inch x 1/4-inch OD, stainless steel) filled with 1-mm-diameter glass beads and immersed in liquid nitrogen. The volatile contents of the sample were pumped off while the higher boiling gases remained on the glass beads. The contents of the loop were vaporized by heating with warm water and flushed with the hydrogen carrier gas through a splitter which divided the sample into three separate flow streams. Precisely reproducible percentages of the total flow were injected onto the various columns: 75% to the PLOT column, 15% to the DB-1, and 10% to the PONA. It was found that the sample split was very reproducible if the specific humidity of the sample was greater than 2.0 g H2O/kg air. Thus to raise the specific humidity of the driest samples, as much as 2.0 torr of purified water was added to the 2119 mL STP volume of the analytical vacuum line prior to sample introduction. Upon sample injection the initial temperature of GC-2 was held at -60°C for 30 s, and then ramped up to 240°C at 20°C/min, while the initial temperature of -20°C for GC-1 was ramped up to 200°C at 20°C/min. A complete analysis cycle, including return to the cooled initial conditions, required 20 min. The gas chromatographs were interfaced to three Spectra Physics 4400 computing integrators and a computer, using LABNET software (Spectra Physics) for data capture and storage. To monitor the consistency and reproducibility of the analytical system, a secondary standard (dry ambient air collected at Niwot Ridge, Colorado, NOAA CMDL by Paul Steele) was analyzed after every eight ambient samples. Throughout the project a second cylinder of whole air was assayed every other day. These mixing ratios were compared to those obtained from the working standard to ascertain that the working standard mixing ratios did not change over the period of the experiment. Approximately 60 air samples could be analyzed during a 24-hour period. The chromatographic apparatus was run continuously (24 hours/4, 7 days/week) from September 17 to November 2, 1991. Detailed descriptions of the analytical setup, standards and calibrations have been given previously [Blake et al., 1992, 1994]. While data from the integrators provided preliminary concentration values for the reported compounds, after returning to our home laboratory, the chromatograms were examined to confirm that the baselines were correctly drawn and that the peaks showed no unusual characteristics.

The precision of the air sample measurements, based on 10 air samples collected during a constant altitude leg of mission 15, was 3% or 3 pptv (whichever was larger) for the alkanes and ethyne and 5% or 5 pptv (whichever is larger) for the olefins. Measurement precision for CCF-12, CFC-11, CFC-113, CH3CCl3, CCl4, and C2Cl4 was 0.7%, 0.8%, 1.4%, 3.8%, 1.7%, and 4.2%, respectively. The precision estimates represent upper limit values because these successive samples may not have had identical mixing ratios. The limit of detection for benzene and toluene was 5 pptv, while that for the remaining NMHCs was 3 pptv. The reported halocarbons were always present at concentrations well above their detection limits.

Results

The flight paths and locations of the 1667 whole air samples collected onboard the DC-8 during missions 4 to 21 (missions 1 to 3 were test flights) are displayed in Figure 1. Figure 2 shows the grab-sampling distribution as a function of altitude and latitude. The figures reflect the good altitudinal, latitudinal, and longitudinal sampling coverage by the DC-8 but also show that in accord with the major goal of the Pacific Exploratory Mission-West the most densely sampled region was concentrated in the western Pacific between 12° and 32°N latitude and between 120° and 150° E longitude.

While attempts were made to sample many different types of air masses, the atmosphere was not randomly sampled so may bias the air mass descriptions discussed below. In addition, the very complex and diverse meteorological conditions encountered during the 6-week sampling period mean that the averaged data should not be construed to represent a particular outflow scenario. Rather, they are intended to present an averaged trace gas.
Plate 1. Ethane color patch plot for three altitude ranges.
Plate 2. CH₃CCl₃ color patch plot for three altitude ranges.
distribution for the sampled areas of the northern Pacific region during September and October 1991. By contrast, the week-long intensive missions flown out of Japan, Hong Kong, and Guam allow the regional data to be considered more as a "snapshot."

The meteorological aspects of the project are described in an overview by Bachmeier et al. [this issue], but some general features are summarized here. The mean flows averaged for the PEM-West A time frame include a high-pressure system over the western North Pacific which, at lower tropospheric altitudes, brought marine air from the east across the Guam region and toward Japan from the south to southwest. High pressure at lower altitudes over central and eastern China tended to bring continental air across the Sea of Japan and over the East China and South China Seas. The middle and upper troposphere north of 25°-30°N was dominated by westerly flow off the Asian continent. Long-range transport was also affected by the several tropical cyclones that occurred during the mission which tended to track northeastward close to the east coast of Asia.

**Fingerprint Characterization**

Samples collected near large accessible NMHC and halocarbon sources such as Tokyo, Hong Kong, and San Jose and in more remote regions exhibiting enhanced mixing ratios were characterized or "fingerprinted," as was incomplete combustion from vehicle exhaust [Blake and Rowland, 1995]. This fingerprinting was achieved by subtracting appropriate "background" mixing ratios from each hydrocarbon and halocarbon measurement. Ideally, air of the same composition as that which originally diluted the source material would provide the background mixing ratio values. Thus, the average mixing ratios of several samples collected in close proximity immediately prior to or after encountering a "plume" exhibiting relatively enhanced trace gas mixing ratios were usually employed. After background subtraction, these residual or "excess" concentrations were added together according to their classification as NMHC or halocarbon, then the percentage contribution made to the category...
Plate 3. Ethane mixing ratios in pptv as latitude-altitude and longitude-altitude 3-D contours.

Plate 4. Ethyne mixing ratios in pptv as latitude-altitude and longitude-altitude 3-D contours.

general features

Tables 3a and 3b give the median, average, standard deviation, maximum, and minimum concentrations of the measured total by each trace gas was calculated. The fingerprint for a particular source was then established by averaging the percentage contributions of all samples collected near that source. Tables 1a and 1b show the background values used for each set of source samples, the excess concentrations in parts per trillion by volume (pptv), and the average percentage contributions for each source type. As an example of the fingerprint calculation, samples collected over Tokyo at the end of mission 5 contained a total halocarbon excess of 648 pptv. The excess of CH$_3$CCl$_3$ over background was 366 pptv. Thus CH$_3$CCl$_3$ represented 57% of total excess halocarbons measured in Tokyo air. Methyl chloroform was also found to be the dominant halocarbon emission from both Hong Kong and San Jose, accounting for 34% and 43% of the halocarbon total over background, respectively. This suggests that CH$_3$CCl$_3$ is likely to be an excellent tracer for polluted air parcels originating from industrial cities around the Pacific region. However, these results should be interpreted with caution as each city fingerprint was calculated employing samples collected on single aircraft approaches, and as such should serve as a guide rather than as being representative of the typical average. For example, on the approach to San Jose (October 22, 1991) a very large brush/suburban fire was taking place in the Oakland area. In addition, no samples were available from cities deep in the continent of Asia.

Table 1b shows that incomplete combustion, mainly from vehicle exhaust, is characterized by high alkene and ethyne, and low ethane and propane contributions. Table 2 shows that the alkynes are relatively short-lived in the atmosphere ($t < 2$ days) and so are expected to persist only long enough to be observed close to their source regions or as indicators of rapid air mass transport. However, ethyne has a relatively long lifetime of approximately 23 days (Table 2), allowing it to persist long enough in the atmosphere to act as a tracer for air masses that have been transported over long distances. Table 1b shows that Tokyo, Hong Kong, and San Jose also exhibit significant ethane and propane components, revealing the presence of additional hydrocarbon sources in cities, namely natural gas and propane gas used for cooking and heating [Blake and Rowland, 1995]. City emissions therefore represent the complex mix of incomplete combustion and natural gas and propane leakage, typical of an urban environment.

Tables 3a and 3b give the median, average, standard deviation, maximum, and minimum concentrations of the measured...
Table 1a. Halocarbon Fingerprint Signatures From Various Urban and Individual Sources, and Selected Enhanced Plumes

| Source Fingerprints | Samples | Avg Long (E) | Avg Lat (N) | Avg Alt (m) | CFC-12 | CFC-11 | CFC-113 | CH$_3$CCl$_3$ | CCl$_4$ | C$_2$Cl$_4$ |
|---------------------|---------|--------------|-------------|-------------|--------|--------|--------|-------------|--------|----------|
| Tokyo, mission 5    | 4       | 139          | 36          | 530         | 500    | 252    | 78     | 158         | 107    | 8        |
| representative background, pptv |         |              |             |             |        |        |        |             |        |          |
| excess mixing ratio, pptv |     |              |             |             | 75     | 30     | 82     | 366         | 19     | 76       |
| fingerprint, % halocarbon contribution | |              |             |             | 12     | 5      | 13     | 57          | 3      | 12       |
| Hong Kong, mission 13 | 1       | 114          | 22          | 1370        | 492    | 258    | 76     | 137         | 111    | 5        |
| representative background, pptv |         |              |             |             |        |        |        |             |        |          |
| excess mixing ratio, pptv |     |              |             |             | 36     | 28     | 12     | 58          | 5      | 30       |
| fingerprint, % halocarbon contribution | |              |             |             | 22     | 17     | 7      | 34          | 3      | 18       |
| San Jose, mission 21 | 7       | 238          | 37          | 800         | 513    | 267    | 80     | 162         | 112    | 13       |
| representative background, pptv |         |              |             |             |        |        |        |             |        |          |
| excess mixing ratio, pptv |     |              |             |             | 59     | 18     | 28     | 143         | 13     | 71       |
| fingerprint, % halocarbon contribution | |              |             |             | 18     | 5      | 8      | 43          | 4      | 21       |
| Incomplete combustion |         |              |             |             |        |        |        |             |        |          |
| vehicle exhaust, [Blake et al., 1994] |         |              |             |             |        |        |        |             |        |          |

| Plume Fingerprints | Samples | Avg Long (E) | Avg Lat (N) | Avg Alt (m) | CFC-12 | CFC-11 | CFC-113 | CH$_3$CCl$_3$ | CCl$_4$ | C$_2$Cl$_4$ |
|---------------------|---------|--------------|-------------|-------------|--------|--------|--------|-------------|--------|----------|
| Mission 10, S Taiwan | 10      | 124          | 22          | 12080       | 502    | 269    | 78     | 121         | 111    | 3        |
| average plume, pptv |         |              |             |             |        |        |        |             |        |          |
| representative background, pptv |         |              |             |             | 502    | 269    | 78     | 121         | 111    | 3        |
| excess mixing ratio, pptv |     |              |             |             | 0      | 0      | 0      | 0           | 0      | 0        |
| fingerprint, % halocarbon contribution | |              |             |             |        |        |        |             |        |          |
| Mission 13, S Korea | 6       | 127          | 30          | 390         | 509    | 271    | 84     | 159         | 115    | 16       |
| average plume, pptv |         |              |             |             |        |        |        |             |        |          |
| representative background, pptv |         |              |             |             | 504    | 263    | 76     | 117         | 105    | 5        |
| excess mixing ratio, pptv |     |              |             |             | 5      | 8      | 8      | 42          | 10     | 11       |
| fingerprint, % halocarbon contribution | |              |             |             | 6      | 9      | 9      | 50          | 12     | 13       |
| Mission 13, E China | 13      | 119          | 23          | 650         | 508    | 268    | 79     | 139         | 115    | 11       |
| average plume, pptv |         |              |             |             |        |        |        |             |        |          |
| representative background, pptv |         |              |             |             | 497    | 262    | 75     | 123         | 107    | 3        |
| excess mixing ratio, pptv |     |              |             |             | 11     | 5      | 4      | 15          | 8      | 8        |
| fingerprint, % halocarbon contribution | |              |             |             | 21     | 10     | 8      | 30          | 15     | 16       |
| Mission 14, S Japan | 17      | 129          | 17          | 920         | 509    | 268    | 82     | 146         | 114    | 11       |
| average plume, pptv |         |              |             |             |        |        |        |             |        |          |
| representative background, pptv |         |              |             |             | 503    | 267    | 78     | 122         | 109    | 4        |
| excess mixing ratio, pptv |     |              |             |             | 5      | 2      | 4      | 24          | 5      | 7        |
| fingerprint, % halocarbon contribution | |              |             |             | 11     | 4      | 10     | 51          | 10     | 15       |
Table 1b. Nonmethane Hydrocarbon Fingerprint Signatures From Various Urban and Individual Sources, and Selected Enhanced Plumes

| Source Fingerprints | Ethane | Ethene | Ethyne | Propane | Propene | i-Butane | n-Butane | i-BuTene | n-BuTene | i-Pentane | n-Pentane | i-Pentene | n-Hexane | Benzene | Toluene |
|---------------------|--------|--------|--------|---------|---------|----------|----------|----------|----------|----------|----------|----------|----------|---------|---------|
| Tokyo, mission 5    |        |        |        |         |         |          |          |          |          |          |          |          |          |         |         |
| representative background, pptv | 676    | 38     | 112    | 92      | 0       | 35       | 53       | 0        | 25       | 19       | 0        | 9        | 45       | 32      |
| excess mixing ratio, pptv | 815    | 1153   | 605    | 892     | 272     | 517      | 943      | 71       | 473      | 298      | 19       | 211      | 152      | 1063    |
| fingerprint, % NMHC contribution | 11     | 15     | 8      | 12      | 4       | 7        | 13       | 1        | 6        | 4        | 0        | 3        | 2        |         |
| Hong Kong, mission 13 |        |        |        |         |         |          |          |          |          |          |          |          |          |         |         |
| representative background, pptv | 1038   | 23     | 311    | 102     | 8       | 8        | 18       | 5        | 6        | 4        | 0        | 0        | 65       | 10      |
| excess mixing ratio, pptv | 1271   | 667    | 1480   | 723     | 38      | 313      | 521      | 13       | 287      | 177      | 5        | 119      | 499      | 870     |
| fingerprint, % NMHC contribution | 18     | 10     | 21     | 10      | 1       | 4        | 7        | 0        | 4        | 3        | 0        | 2        | 7        | 12      |
| San Jose, mission 21 |        |        |        |         |         |          |          |          |          |          |          |          |          |         |         |
| representative background, pptv | 844    | 12     | 153    | 224     | 8       | 26       | 45       | 4        | 19       | 10       | 0        | 0        | 61       | 0       |
| excess mixing ratio, pptv | 2075   | 467    | 759    | 1399    | 151     | 387      | 756      | 38       | 550      | 220      | 44       | 60       | 146      | 245     |
| fingerprint, % NMHC contribution | 28     | 6      | 10     | 19      | 2       | 5        | 10       | 1        | 7        | 3        | 1        | 1        | 2        | 3       |
|Incomplete combustion|        |        |        |         |         |          |          |          |          |          |          |          |          |         |         |
| vehicle exhaust, [Blake et al., 1995] |        |        |        |         |         |          |          |          |          |          |          |          |          |         |         |
| fingerprint, % NMHC contribution | 3      | 24     | 19     | 1       | 9       | 1        | 7        | 1        | 3        | 8        | 2        | 2        | 11       | 8       |

| Plume Fingerprints | Ethane | Ethene | Ethyne | Propane | Propene | i-Butane | n-Butane | i-BuTene | n-BuTene | i-Pentane | n-Pentane | i-Pentene | n-Hexane | Benzene | Toluene |
|--------------------|--------|--------|--------|---------|---------|----------|----------|----------|----------|----------|----------|----------|----------|---------|---------|
| Mission 10, S Taiwan|        |        |        |         |         |          |          |          |          |          |          |          |          |         |         |
| average plume mixing ratio, pptv | 1015   | 30     | 213    | 129     | 11      | 13       | 26       | 2        | 7        | 0        | 0        | 0        | 60       | 0       |
| representative background, pptv | 418    | 7      | 35     | 11      | 0       | 0        | 0        | 0        | 0        | 0        | 0        | 0        | 6        | 0       |
| excess mixing ratio, pptv | 664    | 20     | 211    | 125     | 11      | 13       | 26       | 2        | 7        | 7        | 0        | 0        | 56       | 0       |
| fingerprint, % NMHC contribution | 58     | 2      | 18     | 11      | 1       | 1        | 2        | 0        | 1        | 1        | 0        | 0        | 5        | 0       |
| Mission 13, E China|        |        |        |         |         |          |          |          |          |          |          |          |          |         |         |
| average plume mixing ratio, pptv | 1641   | 67     | 436    | 932     | 15      | 193      | 391      | 9        | 125      | 122      | 0        | 30       | 112      | 93      |
| representative background, pptv | 1029   | 33     | 360    | 191     | 10      | 35       | 51       | 4        | 20       | 13       | 0        | 3        | 95       | 13      |
| excess mixing ratio, pptv | 622    | 41     | 74     | 695     | 2       | 145      | 293      | 5        | 94       | 98       | 0        | 27       | 29       | 80      |
| fingerprint, % NMHC contribution | 28     | 2      | 3      | 32      | 0       | 7        | 13       | 0        | 4        | 4        | 0        | 1        | 1        | 4       |
|Mission 13, S Japan|        |        |        |         |         |          |          |          |          |          |          |          |          |         |         |
| average plume mixing ratio, pptv | 1656   | 110    | 664    | 514     | 10      | 103      | 160      | 7        | 63       | 42       | 1        | 12       | 177      | 42      |
| representative background, pptv | 508    | 19     | 60     | 47      | 15      | 2        | 12       | 7        | 2        | 3        | 1        | 0        | 16       | 5       |
| excess mixing ratio, pptv | 1148   | 91     | 603    | 467     | -6      | 102      | 148      | 0        | 61       | 39       | 0        | 12       | 162      | 37      |
| fingerprint, % NMHC contribution | 40     | 3      | 21     | 16      | 0       | 4        | 5        | 0        | 2        | 1        | 0        | 0        | 6        | 1       |
|Mission 14, S Japan|        |        |        |         |         |          |          |          |          |          |          |          |          |         |         |
| average plume mixing ratio, pptv | 953    | 41     | 258    | 228     | 22      | 48       | 70        | 9        | 26       | 19       | 1        | 5        | 88       | 24      |
| representative background, pptv | 558    | 48     | 96     | 43      | 29      | 6        | 11       | 15       | 4        | 3        | 0        | 3        | 27       | 18      |
| excess mixing ratio, pptv | 395    | -7     | 162    | 185     | -7      | 43       | 59       | -5       | 22       | 16       | 1        | 3        | 61       | 6       |
| fingerprint, % NMHC contribution | 42     | -1     | 17     | 20      | -1      | 5        | 6        | -1       | 2        | 2        | 0        | 0        | 7        | 1       |
Table 2. Estimated Atmospheric Lifetimes of Selected Nonmethane Hydrocarbons (NMHCs) and Halocarbons

| Compound    | OH Rate a | Lifetime (Days) b |
|-------------|-----------|-------------------|
| CFC-11      | 42-66 yr  |                   |
| CH₃CCl₃    | 0.01      | 5.7 yr            |
| C₂Cl₄       | 0.17      | 122               |
| Ethane      | 0.27      | 78                |
| Ethyne      | 0.90      | 23                |
| Propane     | 1.15      | 18                |
| Benzene     | 1.23      | 17                |
| i-Butane    | 2.34      | 9                 |
| n-Butane    | 2.54      | 8                 |
| i-Pentane   | 3.90      | 5                 |
| n-Pentane   | 3.94      | 5                 |
| n-Hexane    | 5.61      | 4                 |
| Toluene     | 5.96      | 3                 |
| Ethene      | 8.52      | 2                 |
| Propene     | 26.3      | 0.8               |
| 1-Butene    | 31.4      | 0.7               |
| 1-Pentene   | 31.4      | 0.7               |
| Isoprene    | 101       | 0.2               |

Rate constants for CH₃CCl₃ and C₂Cl₄ taken from DeMore et al. [1992].
Rate constants for NMHCs taken from Atkinson [1990].

a Units: 10⁻¹² x k(298).
b Lifetimes of hydrocarbons are calculated by comparison with the CH₃CCl₃ lifetime of 5.7 years, Prinn [1992].
c WMO, [1992].

hydrocarbons and halocarbons after the data have been separated into three altitude sections, 7 to 12.7 km, 2 to 7 km, and below 2 km, which were chosen to represent the middle-upper free troposphere, lower free troposphere, and planetary boundary layer (PBL), respectively. There are 533, 713, and 421 air samples in each section, which constitute approximately 21%, 38%, and 22% of the total air column, respectively [U.S. Standard Atmosphere, 1976]. All compounds exhibit higher mixing ratios in the PBL due to the proximity of surface sources. However, the NMHCs (Table 3b) typically show higher median concentrations in the middle-upper and PBL altitude sections than in the lower free troposphere. This was a general feature of the NMHCs and will be discussed in more detail below. Several of the very short lived hydrocarbons (t < 1 day, see Table 2), including 1-pentene and isoprene, were below their detection limits in all samples except for those collected in the PBL very close to their continental sources.

Color patch plots showing the latitudinal and longitudinal variation of the concentrations of ethane and methyl chloroform are given in Plates 1 and 2, respectively. They show the spatial variation of the median trace gas mixing ratios for a latitude-longitude grid size of 2.5° by 2.5°. As expected, the highest concentrations of both ethane and CH₃CCl₃ were observed at low altitude close to the continental sources such as San Jose, California (37.3°N, 121.9°W); Anchorage, Alaska (61.2°N, 149.9°W); Tokyo, Japan (35.7°N, 139.75°E); Hong Kong (22.3°N, 114.2°E); and Guam (13.7°N, 145.0°E). Honolulu, Hawaii (21.3°N, 157.9°W), was not a "hot spot" because mission 20 had been designed specifically to study downdrafting over the Island of Hawaii, and no samples were taken in the vicinity of Honolulu. Elevated ethane concentrations were also observed in the free troposphere near the western Pacific coast and over Guam.

The lower free tropospheric sections of Plates 1 and 2 display similar features to the PBL region throughout the longitude and latitude range covered. However, in the PBL the mixing ratios of ethane (Plate 1) range from 300 to 2000 pptv and from 300 to 1500 pptv in the lower free troposphere, where smaller absolute values were observed for all hydrocarbons and halocarbons. In the middle-upper troposphere ethane ranges from 200 to 1250 pptv, indicating that the direct effect of urban centers is still less

Table 3a. Median, Average, Standard Deviation, Maximum, and Minimum Halocarbon Observations During PEM-West A

|         | CFC-12 | CFC-11 | CFC-113 | CH₃CCl₃ | CCl₄ | C₂Cl₄ |
|---------|--------|--------|---------|---------|------|-------|
| 7 - 12.7 km N=533 |        |        |         |       |      |       |
| Median  | 508    | 274    | 87.9    | 155     | 121  | 3.0   |
| Average | 508    | 274    | 87.7    | 154     | 120  | 3.3   |
| S.D.    | 5      | 5      | 3.0     | 13      | 5    | 1.7   |
| Minimum | 492    | 243    | 68.6    | 86      | 94   | 0.1   |
| Maximum | 520    | 297    | 111.5   | 205     | 168  | 25.0  |
| 2 - 7 km N=713 |        |        |         |       |      |       |
| Median  | 509    | 274    | 88.1    | 155     | 121  | 3.2   |
| Average | 509    | 273    | 88.0    | 156     | 121  | 3.9   |
| S.D.    | 7      | 5      | 2.4     | 14      | 3    | 2.5   |
| Minimum | 479    | 250    | 79.5    | 122     | 108  | 0.1   |
| Maximum | 545    | 295    | 98.3    | 232     | 131  | 16.8  |
| < 2 km N=421 |        |        |         |       |      |       |
| Median  | 509    | 274    | 89.0    | 162     | 122  | 4.6   |
| Average | 512    | 274    | 92.5    | 176     | 122  | 9.0   |
| S.D.    | 19     | 8      | 24.1    | 75      | 5    | 21.1  |
| Minimum | 487    | 252    | 77.8    | 126     | 96   | 0.9   |
| Maximum | 696    | 342    | 464.4   | 994     | 166  | 250.3 |

N, number of samples analyzed at each altitude range.
apparent. However, consistent with the high median middle-upper tropospheric ethane mixing ratios shown in Table 3, the general spread of continental influence is more extensive than in the lower free troposphere.

Altitudinal mixing ratio distributions calculated over the PEM-West A latitude and longitude range are described in Plates 3 to 10 for selected NMHCs (ethane, ethyne, propane, benzene, and i-pentane) and halocarbons (CH3CCl3, C2C14, and F-11) as three-dimensional color contour plots based on 3° by 635 m and 6.3° by 635 m latitude-altitude and longitude-altitude grids, respectively. Interpolation of the data between grid squares is achieved employing an inverse-distance weighting algorithm. These figures have much better vertical resolution than the patch plots (Plates 1 and 2) and show clearly the variable vertical extent of the influence of surface sources and trends of the different-lived gases. They provide a useful perspective for characterizing the regional large scale trace gas distribution and transport encountered during PEM-West A. However, as was stated earlier, the atmospheric sampling was neither random nor uniform (see Figures 1 and 2). Therefore, Plates 3 to 10 should always be compared with the appropriate grab-sampling distribution described in Figure 2. The nonrandom nature of the sampling strategy was especially significant for the boundary layer region, where the airport landings accounted for many samples for those altitudes. As their inclusion would strongly bias the lower-altitude distribution to overrepresent urban airport locations, 18 low-altitude airport samples were removed from the 3-D contour plot database.

The NMHCs and halocarbons shown in Plates 3 to 10 were chosen to represent a wide range of different lifetimes and possible sources with which to interpret the large scale PEM-West A features. All the gases show relatively high concentrations near the urban source regions, but the longer-lived NMHCs such as ethane, ethyne, and propane (Plates 3, 4 and 5), show enhanced regions at all altitudes. Except for a high-altitude region between 10 and 12.5 km, relatively short-lived i-pentane (which has a lifetime of only about 5 days) quickly decayed to levels below its detection limit (Plate 7). In accord with their very long lifetimes and high background concentrations, the long-lived halocarbons, CH3CCl3 and F-11 (Plates 8 and 10, respectively) show little mixing ratio variability away from the source regions.

A feature of both the patch and the 3-D contour plots (Plates 1 to 10) is the latitudinal gradient of trace gases, with the lowest mixing ratios occurring around the equator, and increasing with latitude. The highest levels are usually above 30°N. This reflects both the proximity of continental sources at higher latitudes and the large-scale airflow regime, which featured strong continental outflow north of about 25°N in the midtroposphere and about 30°N in the upper troposphere [Bachmeier et al., this issue]. In addition, the mean cold frontal position near the Asian continent was between 20° and 40°N [Bachmeier et al., this issue]. The latitudinal trend for ethane (Plates 1 and 3) is more pronounced in the planetary boundary layer and the lower free troposphere than in the middle-upper free troposphere. This gradient was sharpened by the very clean air that was swept north to the Guam region by Typhoon Pat (mission 15) [Bachmeier et al., this issue]. The clean equatorial air to the south is also well described by the CH3CCl3 contour plot shown in Plate 8.

A longitudinal gradient is also evident, particularly for ethyne (see Plate 4) and benzene (Plate 6), where typically higher mixing ratios occur near the Asian continent, Japan, and the North American continent. Up to about 4 km (a few hundred meters
Plate 5. Propane mixing ratios in pptv as latitude-altitude and longitude-altitude 3-D contours.

Plate 6. Benzene mixing ratios in pptv as latitude-altitude and longitude-altitude 3-D contours.

above the observed boundary layer height) dome-shaped isolines are identifiable over the urban centers such as Hong Kong, Tokyo, and San Jose (e.g., Plate 9). Short-lived i-pentane (Plate 7) illustrates how the large-scale airflow transports emissions rapidly from these western Pacific source regions between 30° and 40°N up to about 3 km, followed by northeasterly advection over the Pacific.

Because of local downdrafting conditions the lower tropospheric region over the Island of Hawaii had particularly low mixing ratios for all NMHCs, comparable to the observations of background Pacific levels as shown in Plates 3 to 7. Most of the C2Cl4 observations over the Island of Hawaii (see Plate 9) were between 3 to 5 pptv instead of levels in the region of 10 pptv or higher encountered in other urban areas.

In addition to the direct vicinity of urban source regions, some remote PBL areas exhibited elevated mixing ratios. For example, elevated levels of ethane, CH3CCl3 (see Plates 1 and 2), ethyne, and propane (Plates 4 and 5), were observed around 15°N, 180°E between Hawaii and Wake Island during mission 19. Trajectory analysis suggests these urban signature gases may have originated from the Hawaiian area [Merrill, this issue]. Elevated levels of trace gases such as ethane (see Plate 1) were observed for all altitude sections along the Aleutians during mission 5 and near the eastern Chinese coast during mission 13, both of which have trajectories suggesting influence of Asian continental origin [Merrill, this issue]. Higher levels were observed near the North American and the eastern Asian coasts, with lower levels in the mid-Pacific.

Except when near urban sources, hydrocarbons such as ethane (Plate 3) have significantly more small scale structure than the much longer-lived gases such as CFC-11 (see Plate 10). This enhanced hydrocarbon structure is in addition to source locations and regional scale transport features and occurs because photochemical removal by hydroxyl is extremely important in determining the distribution of the relatively short lived NMHC species. Contributing to the relatively small scale variability in the concentrations of many of the trace gases (as seen in Plates 1-10), tropical storm Luke (mission 6) and Typhoons Mireille (mission 9) and Nat (mission 10) transported clean Pacific air north to the Japanese region. Therefore the highly structured features of the data reflect the influence of both transport and photochemistry on the complicated mix of sources and their distributions.

The ethane contours in Plate 3 show two prominent features, both at an altitude of 11 km, and exhibiting very low
Plate 7. i-Pentane mixing ratios in pptv as latitude-altitude and longitude-altitude 3-D contours.

Plate 8. CH$_3$CCl$_3$ mixing ratios in pptv as latitude-altitude and longitude-altitude 3-D contours.

Rapid Vertical and Long Range Transport

The previous discussions of Table 3b and Plates 1 to 7 revealed that a strong feature of the averaged PEM-West A data was a free-tropospheric mixing ratio enhancement, typically above 7 km. In addition, 13 out of the 18 missions show at least one vertical profile where the trace gas concentrations increase with altitude. Such observations are consistent with the earlier STRATOZ II and STRATOZ III campaigns which took place in the Atlantic [Ehhalt et al., 1985; Rudolph, 1988; Ehhalt, 1992] and with the Atmospheric Boundary Layer Expedition (ABLE) 3A, and ABLE 3B projects in Alaska and eastern Canada [Blake et al., 1992, 1994].

A typical vertical profile of ethyne up to 8 km is shown in Figure 3. This vertical ascent was made approximately 1000 km SE of Tokyo during mission 8 and exhibits enhanced ethyne mixing ratios both in the PBL and above 7 km, with relatively low concentrations at intermediate altitudes. Trajectories show that two days prior to being sampled, the air at 8 km had been transported from northern India, over central China, then southern Japan, while the cleaner lower free tropospheric air exhibited trajectories with central Pacific origins [Merrill, this issue]. An important tropospheric mechanism for the injection of such relatively high concentrations of trace gases into the middle and upper troposphere has been suggested previously by Ehhalt et al.
this latitude (see Figure 2) the feature appears to be decoupled from the sources below. Also, Plate 3 includes samples from mission 4 which were collected only a few degrees south of the enhanced mission 5 samples, but were separated by more than 40° in longitude from those from mission 5, and which have lower mixing ratios. The difference between the two missions is illustrated in Figure 4 which shows two vertical profiles of ethane. One profile, showing significantly lower ethane mixing ratios at all altitudes (0-8 km), was made during mission 4 in the Gulf of Alaska (46.8°-51.1°N and 131.7°-139.4°W), the other took place during mission 5 along the Aleutian Islands (52.6°N and 177.7°W-175.1°E). Thus the mission 5 enhancement is likely to have been a more general free tropospheric feature than it appears in the latitude-altitude plot of Plate 3, demonstrating the importance of using Figure 2 and both latitude and longitude 3-D contour plots in conjunction.

The air mass exhibiting the general enhancements observed during mission 5 has a back trajectory originating from the region of northeastern Siberia and Kamchatka [Merrill, this issue]. It also exhibits particularly high concentrations of methane [Collins et al., this issue], ethane, and propane. This composition suggests a source resembling natural gas and/or venting from oil fields. However, the lack of halocarbon data for those samples makes the source determination less certain. In addition to natural gas, it
is possible that this air mass could have originated in the region of Siberia, then spent days to weeks over the Bering Sea. At that point most of the reactive NMHCs would have been photochemically oxidized by HO, leaving the observed signature of enhanced long-lived hydrocarbons.

The potential for a typhoon to drive rapid vertical transport is illustrated for NMHCs as a large hydrocarbon-enhanced plume centered at about 22°N and 120°E over the Pacific at 12.5 km and shown for ethane, ethyne, propane, and benzene in Plates 3 to 6, respectively. This air mass was sampled at the end of mission 10 east of Taiwan and southwest of Okinawa (19.0° to 24.0°N and 120.9° to 125.7°E). Ten samples were collected in the plume and their halocarbon and hydrocarbon concentrations are shown in Tables 1a and 1b, respectively. It can be seen that methane, ethane, ethyne, propane and other nonmethane hydrocarbons were significantly enhanced above the very low concentrations associated with the air surrounding it. However, the halocarbon and hydrocarbon composition of this high-altitude plume are very similar to the background boundary layer levels employed for the Hong Kong (mission 13) and South Korea (mission 13) plumes (Tables 1a and 1b). The halocarbon concentrations associated with this plume were not enhanced and confirmed that the air mass sampled in mission 10 had not come directly from a heavily industrialized urban source area such as Tokyo or Hong Kong. This is consistent with meteorological analysis which suggests that fast convection associated with nearby Typhoon Nat, was likely to have swept surface air up to the upper troposphere [Bachmeier et al., this issue]. Thus the aged free tropospheric air at high altitude probably had a very different origin from this plume, precluding its use to represent appropriate plume background conditions.

Further evidence of typhoon activity affecting the high-altitude atmospheric trace gas composition was observed during mission 9 and can be located on the NMHC contour plots (Plates 3 to 7) as two enhanced regions between 10 and 12.5 km, centered at approximately 33°N and 130°E. The entire high-altitude portion of this mission, which took place along the perimeters of Kyushu and Shikoku, the southernmost of the four main Japanese islands (32.0°-35.2°N, 129.1°-137.0°E), exhibited enhanced NMHC mixing ratios. Transport of these gases above 10 km is attributed to the fast convective transport observed near the top of Typhoon Mireille [Newell et al., this issue] which, during mission 9, was centered approximately 50 km to the southwest of Nagasaki, Kyushu Island, Japan (32.2°N, 129.0°E). Plate 7 shows that the short-lived NMHC i-pentane (lifetime about 5 days) exhibited a greater enhancement than for the mission 10 plume, which was sampled in the same altitude range approximately 10° to the south. Dimethyl sulfide, which is a useful marker for oceanic boundary layer air, was also elevated above the free tropospheric background levels [Newell, et al. this issue]. The presence of these gases suggests that the air in this mission 10 plume was more recently in contact with the surface. The ethane enhancement seen in Figure 5 for mission 9 is relatively small in comparison to that for mission 10 and the halocarbons were not significantly enhanced; however, the NMHC concentrations indicate the influence of some combustion from the western Pacific coastal regions.

Small Scale Features

Two plumes of interest were encountered during mission 13. In the first plume, six samples were collected at 390 m altitude about 300 km off the eastern Chinese coast. Trajectory analysis indicates the air parcel came from South Korea the previous day [Merrill, this issue]. The fingerprint is shown in Tables 1a and 1b (South Korea). The second plume encounter was at 650 m over the Taiwan Strait (between China and Taiwan) during which 13 samples were collected (see eastern China plume in Tables 1a and 1b). This air parcel had been moving south along the eastern Chinese coast for the previous 5 days [Merrill, this issue]. Both plumes had enhanced CH3CC13, and C2C14 concentrations and low concentrations of short-lived alkenes compared to the alkanes and ethyne, indicating that they were urban in origin but had undergone photochemical aging for at least 2 days. The eastern China plume had propane, n-butane, and ethyne contributions...
more similar to those of Tokyo than Hong Kong. By contrast, the South Korea plume had lower ethyne and the highest propane contribution, which may indicate greater use of bottled propane for cooking and/or heating in its region of origin. However, further characterization of these two NMHC fingerprints is very difficult in the absence of source data from Korea and China.

If the two mission 13 halocarbon fingerprints are compared with those for Tokyo and Hong Kong, it can be seen that CH$_3$CCl$_3$ is the dominant halocarbon species, accounting for 50% of total halocarbons over background in the first South Korea plume and 30% in the second eastern China plume. However, the CCl$_4$ contribution of 3% to the Tokyo and Hong Kong fingerprints is very small, whereas the CCl$_4$ contribution from the South Korea and eastern China plumes was much higher at 12% and 15%, respectively. With the exception of CCl$_4$, the eastern China halocarbon fingerprint was very similar to that for Hong Kong, and the South Korea halocarbon fingerprint was more similar to that of Tokyo, probably due to the different types of industry and consumption in each region of origin.

Another plume, encountered during mission 14 at an altitude of 430 m and at a location about 500 km northeast of the Philippines, was quite different in character. As shown in Table 1a, the halocarbon fingerprint calculated from 17 plume and 2 background samples, was, except for C$_2$Cl$_4$, almost identical to that of Tokyo. Methyl chloroform was again the dominant halocarbon constituent. Trajectory analysis shows that the air parcel traveled over southern Japan and had recently been in close proximity to South Korea [Merrill, this issue]. The NMHC fingerprint in Table 1b shows that the percentage NMHC composition follows the order of atmospheric lifetime for each NMHC (Table 2), with the alkenes and shorter-lived alkanes having decayed to or near zero concentrations over background, suggesting that the air parcel had undergone substantial photochemical removal and dilution with pristine background air. This is a likely scenario because the encounter took place on the western outskirts of Typhoon Orchid. Thus, the air parcel had probably spent 2 to 3 days over the Pacific Ocean prior to being sampled [Merrill, this issue].

Comparison With Previous Work

Several sets of vertical profiles have been published describing trace gas measurements over the Atlantic and elsewhere over the Pacific Ocean [Ehhalt et al., 1985; Dickerson et al., 1987; Rudolph, 1988; Singh et al., 1988; Greenberg et al., 1990; Bonsang et al., 1991; Blake et al., 1992; Ehhalt, 1992], with four sets from the Pacific regions of northern California, Alaska, and French Polynesia. The PEM-West A project provided an opportunity to cover a large part of the northern and western Pacific, collecting the largest number of whole air samples in this region of any project to date. No hydrocarbon vertical profiles were previously available for the western Pacific region. The STRATOZ II and STRATOZ III results were published in the form of latitude-altitude profiles [Ehhalt et al., 1985; Rudolph, 1988] and took place in April - May 1980 and June 1984 over the Atlantic. Singh et al. [1988] provides a NMHC vertical profile over northern California (38°N) for February 1985, and Bonsang et al. [1991] have published NMHC profiles over the Hao atoll (18.1°S, 141.0°W) for May to June 1987. Vertical profiles over Bristol Bay, Alaska (61.1°N, 162.0°W) and the Bering Sea (58.3°N, 168.0°W) during ABLE-3A in August, 1988 were published by Blake et al. [1992].

Using data from STRATOZ and other missions, Hough [1991] developed a latitudinally averaged two-dimensional model. Comparison of the PEM-West A contours to Hough's model predicted for July and October indicates that the PEM-West A ethane measurements exhibited lower surface values between 30°N and 60°N. Ethane levels were in the range of 400 - 600 pptv compared to the 750 to 1250 pptv predicted by Hough's model. Perhaps the lower values were a result the PEM-West A flight tracks being further away from the continent compared to STRATOZ II and III which were flown in the Atlantic.

Convective activity over the equatorial region is suggested by the PEM-West A contours. Convexion associated with elevated NMHCs over the equatorial Pacific was encountered in February 1992 during the AASE II project (D. R. Blake et al., unpublished data, 1995). In addition to the lower ethane concentrations and lack of polluted equatorial convection, the observed typhoon-driven convection to the upper troposphere was not addressed by Hough's model. During PEM-West A the propane concentrations in the equatorial and subtropical regions were 50 pptv or less, while the model predicts levels of up to 250 pptv near the equatorial surface, decreasing to 50 pptv at 12 km. However, the model successfully predicts the observed enhancement in the middle-upper troposphere at latitudes above 40°N. The PEM-West A results compliment the existing data and should add significantly to the development and refinement of models.

Conclusions

The results presented here cover a suite of trace gases with lifetimes ranging from approximately 50 years to as short as a few hours (see Table 2), providing a valuable tool with which to study transport processes and the impact of Asian pollutants on the Pacific region. Data from the PEM-West A mission appear to confirm the occurrence of enhanced mixing ratios of NMHC and other trace gases in the middle-upper free troposphere is caused by convective processes, including convective outflow from the Asian continent. Cloud-driven convective activity over land and typhoon-driven convection over the ocean strongly influenced the distribution of trace gases over the northern Pacific. The collection of urban samples has established CH$_3$CCl$_3$ as a good tracer for coastal Asian industrial activity. This study also underlined the need to identify and characterize different pollution sources in Asia. This project established a three-dimensional distribution for a large suite of trace gases in a season with expected minimum continental outflow and set a good foundation for comparison with the maximum continental outflow events expected during the PEM-West B project flown in early 1994.

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