Vertical distributions of non-methane hydrocarbons and halocarbons in the lower troposphere over northeast China

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A B S T R A C T
Vertical distributions of air pollutants are crucial for understanding the key processes of atmospheric transport and for evaluating chemical transport models. In this paper, we present measurements of non-methane hydrocarbons (NMHCs) and halocarbons obtained from an intensive aircraft study over northeast (NE) China in summer 2007. Most compounds exhibited a typical negative profile of decreasing mixing ratios with increasing altitude, although the gradients differed with different species. Three regional plumes with enhanced VOC mixing ratios were discerned and characterized. An aged plume transported from the northern part of the densely populated North China Plain (NCP; i.e. Beijing–Tianjin area) showed relatively higher levels of HCFC-22, 1,2-dichloroethane (1,2-DCE) and toluene. In comparison, the plume originating from Korea had higher abundances of CFC-12, tetrachloroethene (C2Cl4) and methyl chloride (CH3Cl), while regional air masses from NE China contained more abundant light alkanes. By comparing these results with the earlier PEM-West B (1994) and TRACE-P (2001) aircraft measurements, continuing declining trends were derived for methyl chloroform (CH3CCl3), tetrachloromethane (CCl4) and C2Cl4 over the greater China–northwestern Pacific region, indicating the accomplishment of China in reducing these compounds under the Montreal protocol. However, the study also provided evidence for the continuing emissions of several halocarbons in China in 2007, such as CFCs (mainly from materials in stock) and HCFCs.

1. Introduction
Volatile organic compounds (VOCs) are an important class of chemical constituents in the atmosphere. Non-methane hydrocarbons (NMHCs) are at the center of tropospheric photochemistry involving radical (i.e. ROx and HOx) cycling and propagation processes, resulting in the formation of secondary species such as surface ozone (O3). Their atmospheric oxidation products can also undergo condensed phase reactions to produce secondary organic aerosol (SOA; Kroll and Seinfeld, 2008; Hallquist et al., 2009). Long-lived halogenated hydrocarbons (halocarbons) are potent greenhouse gases and deplete stratospheric ozone, and therefore the production and consumption of many halocarbons are regulated by the Montreal Protocol and its subsequent amendments (WMO, 2002; UNEP, 2003). Consequently, information on the sources and atmospheric concentrations of VOCs is fundamental to understanding issues regarding atmospheric chemistry, regional air quality, and climate change.

China has become an important emitter for many chemically active and radiatively important air pollutants owing to the large population and fast-paced industrialization. In terms of non-methane VOCs (NMVOCs), their release from anthropogenic sources in China was estimated as approximately 23 Tg in 2006 (Zhang et al., 2009), and is expected to further increase in the following decades (Ohara et al., 2007). A number of studies based on surface measurements have been carried out in various regions of China in recent years, especially in developed areas (e.g. Liu et al., 2000,
2. Experimental

From June 20 to July 13, 2007, 16 flights were conducted over Jilin Province in NE China. A twin-engine turboprop Yun-12 aircraft served as the sampling platform. The aircraft was based at an airport (125.2°E, 43.9°N, ~245 m a.s.l.) located in the northwest of Changchun, the capital of Jilin Province. An examination of global reanalysis data suggests that during the study period, NE China was impacted by a low pressure system, and the planetary boundary layer (PBL) air primarily originated from the ocean to the south and from central eastern China (including NCP) to the southwest. More details about the aircraft missions are described elsewhere (Xue et al., 2010).

Out of 16 flight missions, 6 were carried out under sunny weather conditions, during which whole air samples were taken (the rest of the flights were conducted on cloudy days during which cloud water samples were collected). Most flights lasted 2–4 h and were centered at noon, with an average VOC sampling time of 11:50 LT (±2.7 h). A total of 88 canister samples were collected during the missions, covering a large portion of Jilin province and an altitude range of 0.5–5.5 km a.s.l. Additionally, to support analyses of the aircraft data, a total of 8 surface samples were collected in both polluted areas (i.e. Changchun, Songyuan) and clean regions (i.e. Baicheng) of Jilin during the timeframe of aircraft missions. The flight tracks and sampling locations are shown in Fig. 1.

Evacuated 2-L electro-polished stainless steel canisters were used for sampling. The canisters were cleaned and evacuated at the University of California, Irvine (UCI). Details of the preparation and pre-conditioning of the canisters are described by Blake et al. (1994) and Simpson et al. (2010). A sample inlet was mounted at the bottom of the aircraft, inside which an aft-facing stainless steel tube was connected with the canisters. During sampling, a stainless steel bellows valve was slightly opened and the selected canister was filled to ambient pressure in 30 s. Considering the flight parameters of the aircraft, each air sample represents a horizontal resolution of ~2 km or a vertical scale of ~120 m. After sampling, the canisters were shipped to the UCI laboratory for chemical analysis. A 5-column multiple GC system with flame ionization detection (FID), electron capture detection (ECD) and mass spectrometer detection (MSD) was deployed to identify and quantify VOC species including NMHCs, halocarbons and alkyl nitrates. Detailed descriptions of the analysis, quality assurance/quality control, and the measurement precision and accuracy for each species are given by Colman et al. (2001) and Simpson et al. (2010).

3. Results and discussion

3.1. Vertical distributions

3.1.1. NMHCs

Table 1 documents the statistics of the most abundant NMHC species for the PBL, free tropospheric (FT), and surface samples. The PBL height was chosen as 2 km a.s.l according to the mean altitude
profiles of other trace gases (i.e., SO₂, CO, and O₃; figures not shown).

The general vertical distributions are illustrated in Fig. 2 using i-pentane, propene, ethyne and benzene as examples. Log scales are used here for better clarity of the variation in the altitude profiles. As is expected, all the profiles showed a peak at the surface, which then decreased with altitude. This pattern is typical and can be explained by the interplay among surface emissions, turbulent mixing, and atmospheric processing of air masses. For relatively long-lived species like ethane and ethyne (lifetimes: weeks to months), the mixing ratios in the PBL and FT were about 30–50% and 12–34% of those at the surface, while for shorter-lived species such as butanes, pentanes and olefins (lifetimes: hours to days), the mixing ratios in the PBL were about 70% of the surface values. Examining the differences in the altitude profiles revealed that air masses from different regions and pollution conditions. In particular, a highly polluted plume from the northern part of NCP was sampled in the free troposphere during the flight on June 27 (Ding et al., 2009).

Examination of hydrocarbon pairs with similar sources but different removal rates is useful to evaluate the extent of atmospheric processing of air masses. In this work, we also assessed the altitude dependence of air mass aging by using the commonly employed C₂H₅CO and C₃H₆/C₄H₈ ratios. Both ratios showed the highest values at ground level, decreasing with the height (see Table 1). This is consistent with our expectation that air masses are more processed at higher altitudes. The mean C₂H₅CO and C₃H₆/C₄H₈ ratios (±standard deviation) for fresh air masses at the surface were 5.4 (±2.4) pptv ppbv⁻¹ and 0.59 (±0.24) pptv ppbv⁻¹, which reflect to some degree the emission characteristics of relation sources over NE China. For comparison, Xiao et al. (2007) reported a C₂H₅CO emission ratio of 4.8 pptv ppbv⁻¹ for fossil fuel combustion sources in East Asia. The average values derived for the PBL (3.2 ± 0.8 pptv ppbv⁻¹ for C₂H₅CO; 0.31 ± 0.10 pptv ppbv⁻¹ for C₃H₆/C₄H₈) and FT air (2.8 ± 1.0 pptv ppbv⁻¹ for C₂H₅CO) were also comparable to the measurement results for the TRACE-P plumes originating from “Central” (3.9 ± 1.3 pptv ppbv⁻¹ for C₂H₅CO; 0.35 ± 0.09 pptv ppbv⁻¹ for C₃H₆/C₄H₈) and “Coastal” (2.5 ± 1.2 pptv ppbv⁻¹ for C₂H₅CO; 0.19 ± 0.12 pptv ppbv⁻¹ for C₃H₆/C₄H₈) regions of China (Russo et al., 2003).

3.1.2. Halocarbons

Statistical results of the 17 measured halocarbons are given in Table 2. Fig. 3 shows the vertical profiles of selected species, namely, CFC-12, HCFC-22, CH₂Cl₂C₂H₂Cl₃, C₂Cl₆, and C₃Cl₆. Fig. 3 also shows the Northern Hemispheric background values obtained from the NOAA/ESRL halocarbons in-situ program in summer 2007, except for C₂Cl₂ which was calculated as the lower 25th percentile of the INTEX-B (Interscontinental Chemical Transport Experiment Phase B) samples not influenced by stratospheric air (Barletta et al., 2009). All of the plotted compounds generally exhibited enhanced mixing ratios compared to the background levels. Moreover, the profiles of most compounds also displayed a slight decreasing trend with altitude (see Fig. 3 and Table 2). The mixing ratios of most species in the boundary layer were evidently enhanced with respect to the PBL regional background (see Table 3), which was calculated as the median of the FT air samples not influenced by the polluted NCP plume. These results suggested that emission sources of some halocarbons still existed in NE China in 2007.

Chlorofluorocarbons (CFCs) showed elevated mixing ratios at the surface that slightly decreased with the height. Taking CFC-12 as an example, the mean surface mixing ratio (±SD) was 565 (±8) pptv, compared to 554 (±10) pptv in PBL and 547 (±12) pptv in FT. The differences are statistically significant (t-test, p < 0.01). CFCs are commonly used as refrigerants, and are also used in air conditioning and as foam blowing agents and aerosol propellants (Barletta et al., 2006). China has established the “country programme” within the framework of the Montreal Protocol for phasing out CFCs (State Environmental Protection Administration, 2000). By 2007, when this study occurred, the production and consumption of CFCs for many applications had been banned (see details in Wan et al., 2009); however, there were still some appliances using CFCs in stock in 2007, which would be gradually phased out in the following years. According to China’s framework of the Montreal Protocol for HCFCs (State Environmental Protection Administration, 2000), China has established the “country programme” within the framework of the Montreal Protocol for phasing out CFCs (State Environmental Protection Administration, 2000). By 2007, when this study occurred, the production and consumption of CFCs for many applications had been banned (see details in Wan et al., 2009). However, there were still some appliances using CFCs in stock in 2007, which would be gradually phased out in the following years (Wan et al., 2009). Therefore, the observed CFC enhancements over NE China may be due to the remaining CFC materials in storage.
Fig. 2. Vertical profiles of (a) i-pentane, (b) propene, (c) ethyne and (d) benzene over NE China. The squares at the bottom represent surface samples, and red solid circles indicate the airborne samples collected on June 27 when a highly polluted plume was sampled (Ding et al., 2009). Dashed lines together with error bars indicate the mean values and standard errors for data points in 200-m bins. Log scales are used for better clarity.

Table 2
Statistics of major halocarbons measured over NE China.a

| Name            | Formula         | Lifetimeb (years) | Surface [n = 8]c | PBL [n = 34]c | FT [n = 49]c |
|-----------------|-----------------|-------------------|-----------------|---------------|--------------|
|                 |                 |                   | Mean σ Median   | Mean σ Median | Mean σ Median |
| CFC-12          | CCl2F2          | 100               | 565 8 567       | 554 10 554    | 547 12 545    |
| CFC-11          | CCl3F           | 45                | 273 13 273      | 265 13 268    | 261 12 264    |
| CFC-113         | CCl2FCClF2      | 85                | 82 1 81         | 80 1 80       | 79 1 79       |
| CFC-114         | CCl3F3CClF3     | 300               | 16 0.8 16       | 15 0.5 15     | 15 0.4 15     |
| HFC-134a        | CH2FCClF3       | 14                | 60 14 54        | 53 7 53       | 53 9 52       |
| HFCF-22         | CHF2Cl          | 12                | 289 90 249      | 315 63 302    | 272 41 273    |
| HFCF-142b       | CHFClCClF2      | 17.9              | 29 10 25        | 40 14 37      | 31 7 29       |
| HFCF-141b       | CHFCl2CClF2     | 9.3               | 33 10 29        | 28 3 28       | 24 3 24       |
| Chloroform      | CHCl3           | 0.41              | 41 25 33        | 26 8 24       | 18 6 17       |
| Methyl chloroform | CH3CClCl      | 5                 | 18 3 17         | 17 2 17       | 17 2 16       |
| Carbon tetrachloride | CCl4         | 26                | 101 4 102       | 99 3 99       | 96 3 96       |
| Tetrachloroethene | C2Cl4           | 0.27              | 15 11 9         | 10 3 10       | 8 3 7         |
| Trichloroethene  | C2HCl            | 0.01              | 13 18 7         | 7 3 7         | 5 4 4         |
| Methyl chloride  | CH3Cl           | 1                 | 727 97 745      | 719 73 726    | 671 81 660    |
| Methyl bromide   | CH3Br           | 0.7               | 13 4 13         | 13 3 12       | 12 2 11       |
| Methyl iodide    | CH3I             | 0.02              | 2.6 1.8 2.0     | 1.4 0.5 1.3   | 0.6 0.4 0.7   |
| 1,2-DCE         | CH2ClCH2Cl       | 0.19              | 91 79 55        | 53 24 57      | 33 20 27      |

a Units are pptv.

b The atmospheric lifetimes are taken from the Scientific Assessment of Ozone Depletion (WMO, 2007).

c PBL – Planetary Boundary Layer, FT – Free Troposphere; the number of samples, n, is given in brackets.
compounds exhibited higher levels in the boundary layer than in FT (Table 2), which agrees with our knowledge on the remaining emissions. However, HCFC-22 and HCFC-142b showed higher mixing ratios in the PBL than on the ground level. We examined individually the canister data and found that most samples with elevated HCFC-22 concentrations were collected during the flight on June 27, when a plume from NCP was sampled (Ding et al., 2009; see Fig. 3). The relatively lower mixing ratios of HCFC-142b at the surface may be attributed to the specific sampling locations where there was less emission of this compound.

For other halogenated compounds, general descending vertical profiles were also observed, with the gradients varied with different species. For instance, for relatively short-lived industrial markers chloroform (CHCl₃), C₂Cl₄, trichloroethene (C₂HCl₃) and 1,2-DCE, and biofuel/biomass burning tracer CH₃Cl, negative profiles with relatively larger gradients were obtained, suggesting extensive use of these compounds and active biofuel/biomass burning activities in NE China. For CCl₄, a slight declining trend was found. While for other species such as CH₃CCl₃ and CH₃Br, the mixing ratios showed little variation with altitude, indicating success of China in controlling these substances.

3.2. Characteristics of regional plumes

An important aim of this study was to investigate the characteristics of regional air masses transported to NE China from upwind regions, especially the populated NCP. On June 27 a target plume was encountered, with highly elevated concentrations of a variety of air pollutants observed in the free troposphere (Ding et al., 2009). To determine the source region of the collected canister air samples, we computed 72-h backward trajectories using the Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT, version 4.8; Draxler and Rolph, 2010) with the Global Data Assimilation System (GDAS) meteorological data. Nine FT air samples were identified as representative of “the NCP plume” as the air parcels had passed over the northern part of NCP (i.e. Beijing–Tianjin area) at low altitudes before being sampled (see Fig. 4a). A detailed analysis of the source region and transport mechanism of this plume is given by Ding et al. (2009).

On June 29, we conducted a flight mission near the border between China and North Korea. Weather forecasting analysis suggested that easterly and southeasterly winds would dominate the air flow on that day. The purpose of this flight was to explore the chemical signatures of air masses transported from Korea. Nine canister samples were taken in the free troposphere (i.e. 2600–3100 m a.s.l.) over the border area. Backward trajectories indicated that air masses had moved slowly in the PBL over the Korea peninsula before climbing quickly off the Changbai Mountain and entering NE China (Fig. 4b). Therefore, these samples can be considered as representative of “the Korea plume”.

In addition, eight whole air samples were obtained within the boundary layer (<1500 m a.s.l.) around Changchun city during spirals over the base airport during the study period. Changchun is the capital of Jilin province and one of the largest cities in NE China. Such data can provide insights into the pollution features of VOCs over NE China.

Table 3 summarizes the average mixing ratios of major NMHCs and halocarbons measured in the identified regional plumes. To evaluate the enhancement of VOCs in the regional plumes, background VOC levels were estimated based on the FT air samples which...
were considered to be less impacted by local emissions. Regional background for the PBL air was calculated as the median of the FT samples excluding those collected in the NCP plume on June 27, while the FT background was computed as the average of the lowest 25th percentile of the FT samples not influenced by the NCP pollution. Many species were significantly enhanced in these plumes with respect to the respective background air. These compounds include most NMHCs, selected CFCs and HCFCs (e.g. CFC-12, HCFC-22 and HCFC-142b), and some combustion and industry related halides (e.g. CH₃Cl, CHCl₃, CCl₄, C₂HCl₃ and 1,2-DCE), highlighting the anthropogenic influence within these regional air masses.

Air masses that transported over large distances have undergone extensive mixing and dilution, thus the absolute mixing ratios in the pollution plumes give little information on the VOC profiles at the source regions. Enhancement ratios (ER) of VOCs with respect to relatively inert tracer such as ethyne are usually used to extract the emission profiles of the source regions (Suthawaree et al., 2010). The ER of species \( X \) relative to ethyne is given as

\[
\text{ER of } X = \frac{\text{Mixing ratio of } X}{\text{Mixing ratio of ethyne}}
\]

### Table 3

Average mixing ratios of major VOCs measured in the regional plumes.

| Species      | NCP Plume \([n = 9]\)^b | Korea plume \([n = 9]\)^b | FT\(^c\) background | NEC plumes \([n = 8]\)^b | PBL\(^c\) background |
|--------------|--------------------------|---------------------------|---------------------|--------------------------|---------------------|
| Ethane       | 1549 (250)               | 941 (71)                  | 796                 | 1756 (467)               | 891                 |
| Ethene       | 369 (94)                 | 846 (141)                 | 285                 | 1583 (634)               | 633                 |
| Ethyne       | 1088 (210)               | 813 (56)                  | 269                 | 1433 (595)               | 570                 |
| Propene      | 443 (127)                | 240 (52)                  | 99                  | 728 (373)                | 156                 |
| Propene      | 74 (17)                  | 176 (35)                  | 63                  | 225 (124)                | 131                 |
| iButane      | 115 (28)                 | 40 (11)                   | 11                  | 266 (202)                | 23                  |
| nButane      | 136 (32)                 | 67 (16)                   | 17                  | 294 (169)                | 32                  |
| iPentane     | 108 (35)                 | 32 (13)                   | 10                  | 256 (172)                | 21                  |
| nPentane     | 47 (7)                   | 24 (5)                    | 9                   | 116 (71)                 | 19                  |
| Benzene      | 410 (112)                | 304 (163)                 | 80                  | 553 (304)                | 161                 |
| Toluene      | 1929 (331)               | 790 (265)                 | 500                 | 917 (480)                | 692                 |
| CFC-12       | 550 (8)                  | 562 (6)                   | 534                 | 560 (7)                  | 545                 |
| CFC-11       | 268 (8)                  | 270 (7)                   | 244                 | 261 (16)                 | 264                 |
| CFC-113      | 79.7 (0.5)               | 80.7 (0.9)                | 78.4                | 80.3 (1.0)               | 79.0                |
| CFC-114      | 15.3 (0.2)               | 15.4 (0.2)                | 14.6                | 15.2 (0.5)               | 15.2                |
| HFC-134a     | 51.6 (2.3)               | 55.1 (3.4)                | 43.6                | 48.9 (6.5)               | 53.0                |
| HFC-22       | 341 (18)                 | 285 (15)                  | 220                 | 286 (21)                 | 257                 |
| HFC-142b     | 449 (2.1)                | 29.7 (1.3)                | 24.3                | 36.9 (13.0)              | 28.0                |
| HFC-141b     | 25.6 (2.9)               | 27.7 (2.1)                | 20.8                | 26.3 (2.0)               | 24.0                |
| CHCl₃        | 239 (5.2)                | 21.9 (4.1)                | 11.8                | 28.3 (11.4)              | 16.0                |
| CH₂Cl₂       | 17.3 (0.5)               | 18.7 (2.6)                | 14.7                | 15.9 (0.8)               | 16.0                |
| CCl₄         | 99 (1)                   | 99 (2)                    | 91                  | 100 (2)                  | 95                  |
| C₂H₃Cl₂      | 5.9 (1.1)                | 10.3 (4.8)                | 1.1                 | 7.4 (4.1)                | 3.2                  |
| C₂H₄Cl₂      | 9.3 (0.9)                | 9.6 (2.0)                 | 4.7                 | 10.6 (4.9)               | 5.9                  |
| CH₃Br        | 751 (54)                 | 735 (52)                  | 568                 | 706 (51)                 | 654                  |
| CH₃Br        | 12.1 (0.9)               | 13.7 (2.5)                | 8.9                 | 13.6 (2.6)               | 11.0                 |
| 1,2-DCE      | 63.1 (13.0)              | 36.8 (10.1)               | 13.6                | 530 (20.3)               | 22.0                 |

\(^a\) Units are pptv; standard deviations are given in parentheses. Mixing ratios enhanced with respect to the background are given in bold.

\(^b\) NCP = North China Plain; NEC = Northeast China; the number of samples, \( n \), is given in brackets.

\(^c\) The PBL background was calculated as the median values of FT samples excluding those collected in the NCP plume the FT background levels were calculated as the averages of the lowest 25th percentile of the FT samples not influenced by the NCP pollution.

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**Fig. 4.** 72-h backward trajectories of VOC samples representative of (a) NCP plume and (b) Korea plume. The circles on the trajectories indicate 6-h intervals. The colors of trajectories indicate different samples. The NMVOC emission data was obtained from Zhang et al. (2009). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
ER(X) = \frac{\Delta[X]}{\Delta[C_2H_2]} = \frac{[X]_{ambient} - [X]_{background}}{[C_2H_2]_{ambient} - [C_2H_2]_{background}}

where brackets indicate mixing ratios. Fig. 5 shows the normalized profiles of relatively long-lived VOCs by ethyne for the regional plumes. The three regional plumes showed varied VOC profiles, indicating different characteristics of VOC emissions in the source regions. The NCP plume contained relatively high levels of HCFC-22, 1,2-DCE, and CH3Cl. Benzene has similar emission sources (i.e., incomplete combustion of fossil fuel and biomass) and also atmospheric lifetimes to ethyne. The ERs of \( \Delta \) benzene/\( \Delta C_2H_2 \) (±SD) for the regional plumes from NCP, NE China and Korea were 0.40 (±0.05), 0.47 (±0.16) and 0.41 (±0.27), respectively. These values are slightly higher than that observed at Mt. Tai (0.34) in NCP (Suthawaree et al., 2010), and also higher than those measured for urban emissions of Boston/New York (0.19–0.21) and 39 U.S. cities (~ 0.33) (Warnke et al., 2007 and references therein).

CH3Cl is commonly used as a biomass/biofuel burning tracer, and the ER of CH3Cl with respect to CO (\( \Delta \)CH3Cl/\( \Delta C_2H_2 \)) is usually used to elucidate the influence of biomass burning (Blake et al., 2003). Based on the emission factors summarized by Andreae and Merlet (2001), the emission ratios of CH3Cl/CO were found to be in the magnitude of ~ 0.62, ~ 0.27 and ~ 1.39 for the burning of savanna and grassland, biofuel and agricultural residues, respectively. According to an up-to-date compilation of emission factors for open and domestic biomass burning (Akaji et al., 2011), the CH3Cl/CO emission ratio was calculated to be ~ 0.47 for savanna fires. Suthawaree et al. (2010) reported a \( \Delta \)CH3Cl/\( \Delta C_2H_2 \) ratio of 1.88 (±1.16) for the air masses influenced by the burning of agricultural residues in central eastern China. In the present study, the average \( \Delta \)CH3Cl/\( \Delta C_2H_2 \) (±SD) were calculated as 0.58 (±0.20), 0.35 (±0.36) and 2.08 (±1.39) for the regional plumes originating from NCP, NE China and Korea. These results implied that agricultural residue burning should be an important source of VOCs in Korea peninsula, while biofuel combustion may be more important in NE China. As there is little grassland vegetation in NCP, the NCP plume should have captured reasonably well a mixture of biofuel combustion and agricultural residue burning.

3.3. Long-term changes of halocarbons in the free troposphere around China: comparison with previous aircraft measurements

To better understand long-term trends of halocarbons in the FT above China, we compared several halocarbons with earlier measurement data collected from the PEM-West B and TRACE-P aircraft missions. PEM-West B occurred in February–March 1994, while TRACE-P took place in February–April 2001. Both campaigns were conducted over the western rim of the Pacific Ocean, closely downwind of China, and aimed to characterize the composition, transport, and chemical transformation of Asian continental outflow (Hoell et al., 1997; Jacob et al., 2003). For the comparison, we bear in mind that the survey domain in the present study is located exactly over the polluted continental regions. That means if there was no decrease of emissions over the period of 2001–2007, the mixing ratios observed in the current study should be definitely higher than those obtained from TRACE-P. It’s also worth noting that the three aircraft campaigns were based on short periods of intensive sampling and limited samples, and thus the results only provide “snapshots” of the sampling domain. Finally, since some halocarbon species exhibit a pronounced latitudinal distribution, we only selected a subset of PEM-West B and TRACE-P data (i.e., 40–47°N, 2–8 km a.s.l.) for the comparison. The comparison of free tropospheric mixing ratios of selected halocarbons is given in Table 4.

Under the Montreal Protocol, the production and use of CFCs have been largely reduced in China in the past decade. For example, according to Wan et al. (2009), emissions of CFC-12 have been reduced by approximately 75% and 87% in 2001 and 2007, respectively, as compared to the 1995 base level. However, this is not reflected in the atmospheric mixing ratios obtained from the three aircraft measurement campaigns. The average mixing ratio of CFC-12 measured over NE China in 2007 (547 ± 11 pptv) was even higher than those obtained from TRACE-P (535 pptv) and PEM-West B (525 pptv). As for CFC-11, the mean value observed during this study (261 ± 12 pptv) was lower than that of PEM-West B (274 pptv), but comparable to that detected from TRACE-P (259 pptv). In comparison, over the 6-year interval between TRACE-P and our study, the Northern Hemispheric background levels of CFC-12 and CFC-11 decreased by approximately 5 and 14 pptv (CFC-12 and CFC-11 data from the NOAA/ESRL halocarbons in-situ program). The relatively higher levels of CFCs recorded in 2007 may be due to the fact that our aircraft sampled air directly over the NE China continent, where CFC emissions from materials in storage remained (see Section 3.1.2). CH3CCl3 is commonly used as metal degreasing agent and in some other industrial applications (Blake et al., 2003). The Montreal protocol has since required developed countries to phase out the production of CH3CCl3, and developing countries to freeze the emissions in 2003 and finally phase it out by 2015 (UNEP, 1991). As its lifetime is relatively short compared to other ozone-depleting
halocarbons (~5 years), the atmospheric burden of CH$_3$CCl$_3$ has been rapidly declining in response to the Montreal protocol (Romashkin et al., 1999). The mixing ratios measured from TRACE-P (mean = 41 pptv) were only ~1/3 of those recorded during PEM-West B (mean = 128 pptv) (Blake et al., 2003). During the present study, substantially lower levels of CH$_3$CCl$_3$ (mean = 17 pptv) were measured over NE China, indicating the continuing decrease of CH$_3$CCl$_3$ in the atmosphere over the great northeastern Pacific region. Furthermore, comparable values were also observed in the boundary layer (mean = 17 pptv) and at the surface (mean = 18 pptv). These results demonstrated the accomplishment of China in regulating CH$_3$CCl$_3$ emissions.

Similar trends were also found for CCl$_4$ and C$_2$Cl$_4$. The main use of CCl$_4$ is as a feedstock to produce CFCs (Barletta et al., 2006). With the phase out of CFCs under regulation of the Montreal protocol, the global atmospheric mixing ratio of CCl$_4$ has been declining since 1990s (Prinn et al., 2000). From PEM-West B (1994) to TRACE-P (2001), a decrease of ~9 pptv in the CCl$_4$ mixing ratios was measured (Blake et al., 2003). In 2007, the CCl$_4$ levels in the free troposphere over NE China (mean = 96 (±17) pptv) were slightly lower than those observed from TRACE-P (mean = 99 pptv), even though the aircraft sampling was conducted immediately over the continental source region. By comparison, UCI’s global trace gas monitoring data suggests a global CCl$_4$ decline of approximately 5 pptv between 2001 and 2007 (D. R. Blake, personal communication). Together these results suggest a continuous decreasing trend of CCl$_4$ in the atmosphere over this region, and also provide indirect evidence to the banning of CFC production in China. However, the slight decreasing with altitude vertical profile also indicates small levels of CCl$_4$ emissions still appear to exist in NE China (Fig. 3d).

C$_2$Cl$_4$ is primarily used as a dry cleaning solvent and metal degreasing agent, and has been well known as a useful tracer for urban/industrial activities (Wang et al., 1995; Simpson et al. 2004) have reported a notable decline in the global atmospheric burden of C$_2$Cl$_4$ based on the long-term measurements at the remote Pacific sites from 1989 to 2002. Consistent with this, the mean C$_2$Cl$_4$ mixing ratio measured during TRACE-P was 10.6 pptv, which was substantially lower than 19.2 pptv recorded during PEM-West B (Blake et al., 2003). In the present study, the mean C$_2$Cl$_4$ level in the FT over continental NE China was even smaller at 7.9 (±6.7) pptv. The results indicated the persistent reduction of atmospheric C$_2$Cl$_4$ levels over the China-NW Pacific region. However, several samples with significantly elevated levels of C$_2$Cl$_4$ (>20 pptv) were also collected both at the surface and in the PBL (see Fig. 3e), indicating the remaining occasional use of C$_2$Cl$_4$ in NE China.

4. Summary

Whole air samples were collected during an intensive aircraft study over Jilin province in NE China in summer 2007. NMHC and halocarbon data were analyzed to investigate the vertical distributions, characteristics of regional plumes, and long-term changes of halocarbons in the free troposphere over the great China—NW Pacific region.

Almost all of the NMHCs exhibited a vertical profile of decreasing mixing ratios with the height. Most halocarbons also displayed a negative vertical trend, although the gradients varied with different species. Some halocarbons, such as CFC-12, HCFC-22, CH$_3$CCl$_3$, CCl$_4$, and C$_2$Cl$_4$, were somewhat enhanced over NE China compared to the Northern Hemispheric background levels. Three types of regional air masses transported from NCP, Korea and NE China were identified, and were characterized by comparing the VOC profiles normalized by ethyne. The plume transported from northern NCP had relatively high levels of HCFC-22, 1,2-DCE and toluene, while air masses representative of NE China air pollution contained higher abundances of ethane, propane and butanes. The plume from Korea contained more abundant CFC-12, C$_2$Cl$_4$ and CH$_3$Cl.

To derive the long-term changes of ozone-depleting halocarbons over China, the free tropospheric mixing ratios of selected halocarbon compounds were compared with earlier measurements from the PEM-West B and TRACE-P aircraft campaigns. The results verified the continuing declining trends in the atmospheric mixing ratios of CH$_3$CCl$_3$, CCl$_4$, and C$_2$Cl$_4$, demonstrating the achievements of China in regulating these halogenated compounds, though with some remaining CCl$_4$ and C$_2$Cl$_4$ emissions. The study also provided evidence of continuing emissions of CFCs (from materials in stock), CHCl$_3$ and 1,2-DCE in NE China by 2007.

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References

Akagi, S.K., Yokelson, R.J., Wiedinmyer, C., et al., 2011. Emission factors for open and domestic biomass burning for use in atmospheric models. Atmos. Chem. Phys. 11, 4039–4072.
Andreae, M.O., Merlet, P., 2001. Emission of trace gases and aerosols from biomass burning. Glob. Biogeochem. Cycles 15 (4), 955–966.
Atkinson, R., Arey, J., 2003. Atmospheric degradation of volatile organic compounds. Chem. Rev. 103, 4605–4638.

Table 4

| Species | Lifetime (years) | This study, 2007 summer (2–6 km) | TRACE-P$^b$, 2001 spring (40° N–47.5° N; 2–8 km) | PEM-West B$^b$, 1994 spring (40° N–47.5° N; 2–8 km) | Background$^c$, 2007 summer Northern Hemisphere |
|---------|-----------------|---------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| CFC-12  | 100             | 547 (11)                        | 535                                           | 525                                           | 539                                           |
| CFC-11  | 45              | 261 (12)                        | 259                                           | 274                                           | 248                                           |
| CH$_3$CCl$_3$ | 5      | 17 (2)                          | 41                                            | 128                                           | 13.4                                          |
| CCl$_4$  | 26              | 98 (17)                         | 99                                            | 107                                           | 93                                            |
| C$_2$Cl$_4$ | 0.27  | 7.9 (6.7)                       | 10.6                                          | 19.2                                          | 2.4                                            |

$^a$ Units are pptv. Standard deviation is given in parentheses for this study.

$^b$ Data from Blake et al. (2003).

$^c$ Background values of CFC-12, CFC-11, CH$_3$CCl$_3$ and CCl$_4$ are from the measurements of NOAA/ESRL halocarbons in-situ program in June–July 2007, while the background concentration of C$_2$Cl$_4$ is from the INTEX-B aircraft measurements in 2006 spring (Barletta et al., 2009).
