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Characterization of volatile organic compounds (VOCs) in Asian and North American pollution plumes during INTEX-B: identification of specific Chinese air mass tracers

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Abstract

We present results from the Intercontinental Chemical Transport Experiment – Phase B (INTEX-B) aircraft mission conducted in spring 2006. By analyzing the mixing ratios of volatile organic compounds (VOCs) measured during the second part of the field campaign, together with kinematic back trajectories, we were able to identify five plumes originating from China, four plumes from other Asian regions, and three plumes from the United States. To identify specific tracers for the different air masses, we focused on characterizing the VOC composition of these different pollution plumes. The Chinese and other Asian air masses were significantly enhanced in carbonyl sulfide (OCS) and methyl chloride (CH_3Cl), while all CFC replacement compounds were elevated in US plumes, particularly HCFC-134a.

Although elevated mixing ratios of Halon-1211 were measured in some of the Chinese plumes, several measurements at background levels were also observed. After analyzing the VOC distribution in the Chinese pollution plumes and the correlations among selected compounds, we suggest the use of a suite of species, rather than the use of a single gas, to be used as specific tracers of Chinese air masses (namely OCS, CH_3Cl, 1,2-dichloroethane, and Halon-1211). In an era of constantly changing halocarbon usage patterns, this suite of gases best reflects new emission characteristics from China.

1 Introduction

The Intercontinental Chemical Transport Experiment – Phase B (INTEX-B) aircraft experiment was conducted in the spring of 2006. Its broad objective is to understand the behavior of trace gases and aerosols on transcontinental and intercontinental scales, and their impact on air quality and climate. The first part of INTEX-B was carried out from 4–31 March 2006 and focused on Mexico City pollution. The second part (4 April–15 May) focused on the transport, transformation and evolution of Asian pollution to North America when long-range transport of Asian pollution across the Pacific region is at a maximum (Jaffe et al., 2001; Stohl et al., 2002; Liu et al., 2003; Forster et al., 2004; Liang et al., 2004). The INTEX-B mission utilized the NASA DC-8 and the NSF/NCAR C-130. In this study we present results from the second part of INTEX-B (i.e. April/May 2006), during which the C-130 was based in Seattle and the DC-8 flew out of Honolulu and Anchorage. Among many other measurements, whole air samples were collected on board the two aircraft and were analyzed for selected volatile organic compounds (VOCs). The importance and role of VOCs on the formation of tropospheric ozone is well known (Seinfeld, 1989; Atkinson, 2000; Heard and Pilling, 2003). Briefly, ozone is produced in the troposphere by the oxidation of VOCs in the presence of sunlight and nitrogen oxides (NO_x=NO+NO_2). Ozone is a recognized greenhouse gas (Berntsen et al., 1997; Shine, 2001; IPCC, 2007) and is unhealthful at enhanced concentrations (Bell et al., 2004; Hubbell et al., 2005). Many of the measured halogenated compounds presented here are regulated under the Montreal Protocol and its subsequent amendments because of their potential to deplete stratospheric ozone (WMO, 2002; UNEP, 2003).

Other NASA field campaigns and modeling studies have focused on Asian outflow. In particular, the spring 2001 Transport and Chemical Evolution over the Pacific (TRACE-P) experiment characterized the VOC composition of Asian outflow (see Jacob et al., 2003, for an overview of the TRACE-P campaign). Several Chinese pollution plumes were encountered during TRACE-P and elevated trace gas concentrations were measured over the Yellow Sea, the Formosa Strait, and downwind of Shanghai (Blake et al., 2003; Simpson et al., 2003). However, during TRACE-P most of the air samples were collected over the western Pacific Rim region, very close to the emission sources. The Intercontinental Chemical Transport Experiment – North America Phase A (INTEX-A) experiment was conducted during the summer of 2004 to investigate the inflow and outflow of pollution over the North American continent during a period of inefficient transport over the Pacific region. The transport of Asian pollution across the Pacific is at a minimum in summer months because part of the Asian outflow is transported

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westward (Lelieveld et al., 2002; Liu et al., 2002, 2003). In addition, longer trans-Pacific transport times occur in summer (6–10 days) versus spring (1–5 days; Liang et al., 2004; Holzer et al., 2005).

By contrast, the springtime INTEX-B experiment evaluated the impact of Asian outflow on North American when the strongest outflow occurs and the VOC load reaches its maximum. During INTEX-B the DC-8 and C-130 aircraft flew over the Eastern Pacific region, along the coast of North America, and over the United States. Here we describe the identification of specific pollution plumes that originated from Asia and their comparison to air masses that originated from North America. In particular, since emissions from China have evolved during the past decade, a goal was to identify a specific sub-set of VOCs characteristic of Chinese pollution plumes that can be used as specific "tracers" for modern Chinese air masses.

2 Experimental

During the second deployment of INTEX-B a total of 2441 whole air samples (WAS) were collected on board the two aircraft (1594 from the DC-8 and 847 from the C-130) during 22 science flights. Samples were collected in 2-L electropolished stainless steel canisters equipped with a Swagelok metal bellows valve. Prior to shipping to the field the canisters were flushed with ultra-high purity (UHP) helium and subsequently evacuated to 10^{-2} Torr in the laboratory at the University of California, Irvine (UC-Irvine). Seventeen Torr of degassed ultrapure MilliQ water were added to the canisters in order to passivate the surface of the internal walls, so that the absorbance of selected compounds inside the canisters would be minimized. During the sampling the canisters were pressurized to 40 psi using a metal double bellows pump. The filling time was approximately one minute. Canisters were filled at 1–3 min intervals during ascents and descents, and every 2–8 min during horizontal flight legs. A maximum of 168 canisters were filled for each flight on the DC-8 and 72 aboard the C-130. Once filled, the canisters were shipped to our laboratory at the University of California, Irvine where – within

7 days of sample collection – they were analyzed for more than 75 gases, including nonmethane hydrocarbons, halocarbons, alkyl nitrates and sulfur compounds.

A detailed description of the analytical system is described in Colman et al. (2001). Briefly, a sample amount of 2440±3 cm^3 (STP) of the air was preconcentrated in a stainless steel loop filled with glass beads and submerged in liquid nitrogen. The sample was then heated to about 80°C, injected, and split into six different column/detector combinations using UHP helium as the carrier gas. The first column detector combination was a DB-1 column (J&W; 60 m, 0.32 mm I.D., 1 μm film thickness) output to a flame ionization detector (FID). The second was a DB-5 column (J&W; 30 m, 0.25 mm I.D., 1 μm film thickness) column connected in series to a RESTEK 1701 column (5 m, 0.25 mm I.D., 0.5 μm film thickness) and output to an electron capture detector (ECD). The third was a RESTEK 1701 column (60 m, 0.25 mm I.D., 0.50 μm film thickness) output to an ECD. The fourth combination was a PLOT column (J&W GS-Alumina; 30 m, 0.53 mm I.D.) connected in series to a DB-1 column (J&W; 5 m, 0.53 mm I.D., 1.5 μm film thickness) and output to an FID. The fifth was a DB-5ms column (J&W; 60 m, 0.25 mm I.D., 0.5 μm film thickness) output to a nitrogen phosphorus detector (NPD). The final combination was a DB-5ms column (J&W; 60 m, 0.25 mm I.D., 0.5 μm film thickness) output to a quadrupole mass spectrometer detector (MSD, HP 5973). The MSD was set to operate in selected ion monitoring (SIM) mode with one ion chosen to quantify each compound in order to achieve the maximum selectivity and to avoid potential interferences. All of the gas chromatographs and detectors used for this project were manufactured by Hewlett Packard.

Our analytical accuracy ranges from 2 to 20%, and the precision of the measurements vary by compound and by mixing ratio. For instance, the measurement precision is 1% or 1.5 pptv (whichever is larger) for the alkanes and alkynes, and 3% or 3 pptv (whichever is larger) for the alkenes. The precision of the halocarbon measurements also varies by compound and is 1% for the CFCs and CCl_4; 2–4% for the HCFCs; 5% for HFC-134a and CH_2Cl_2; and 2% for Halon-1211, methyl halides, CH_3CCl_3, C_2Cl_4, and $CHBr_3$. The measurement accuracy also varies by compound and is 2% for CFCs (except 5% for CFC-114); 10% for the HCFCs, C_2Cl_4, CH_2Cl_2, CH_3I and $CHBr_3$; and 5% for Halons, HFC-134a, CH_3CCl_3, CCl_4, CH_3Cl, CH_3Br, and hydrocarbons.

The original standard for the calibration of the NMHCs was gravimetrically prepared from National Bureau of Standards and Scott Specialty Gases standards (accuracy ±5%). These standards were used for the calibration of highly pressurized whole air standards (2000 psi) contained within aluminum cylinders. The air was then transferred from the cylinder to an electropolished stainless steel pontoon (34 L) equipped with a Swagelok metal bellows valve, after the initial addition of 17 Torr of degassed ultrapure MilliQ water. A higher degree of stability inside the pontoon has been determined for higher molecular weight hydrocarbons, alkyl nitrate, sulfur species and some of the halocarbons. During the analysis a working standard was analyzed every eight samples, and once a day a series of different standards, including primary standards, were analyzed.

In this paper we also use ozone (O_3) and carbon monoxide (CO) data measured on both airplanes. In situ CO measurements were made on the DC-8 by the differential absorption CO measurement (DACOM) instrument (Sachse et al., 1987); while a CO vacuum UV-resonance fluorescence instrument similar to that of Gerbig et al. (1999) was used on the C-130. The fast response ozone (FASTOS) instrument measured the in situ ozone along the DC-8 flight path (Pearson and Eastman, 1980), and the NCAR 4-channel chemiluminescence instrument was used to measure ozone on the C-130 (Ridley et al., 2004).

3 Results and discussion

3.1 General features

To show the general trends of the VOCs measured during this mission, the vertical profiles of ethyne (C_2H_2), carbonyl sulfide (OCS), tetrachloroethene (C_2Cl_4), methyl chloride (CH_3Cl), Halon-1211, and HFC-134a measured on board of the DC-8 and C-

130 aircraft are plotted in Fig. 1. These species have strong anthropogenic sources and a lifetime long enough to be present in remote air. Some degree of overall variability in the measured mixing ratios was observed, which is expected to be inversely related to the lifetime of each gas (Junge, 1974). Additional variability is explained by proximity to or influence by emission sources, as discussed below. Ethyne and C_2Cl_4, the most variable compounds among the ones discussed here, are the shortest lived compounds with lifetimes of approximately 3 and 16 weeks (Simpson et al., 2004; Xiao et al., 2007) compared to about one year for CH_3Cl (Khalil and Rasmussen, 1999), 2–7 years for OCS (Xu et al., 2002), 14 years for HFC-134a (McCulloch et al., 2003), and 16 years for Halon-1211 (IPCC, 2007). However, even when the overall variability is considered, we observed mixing ratios that were considerably enhanced with respect to the majority of the samples. Looking at the absolute mixing ratios of selected anthropogenic tracers measured during all flights we identified air masses recently impacted by anthropogenic emissions. Ethyne is a good tracer of general combustion, and in many samples the ethyne mixing ratio was more than double the average that was calculated for all 2441 samples collected from both aircraft (226±117 pptv), and more than four times the background values calculated as the lower 50th percentile of the INTEX-B samples not impacted by stratospheric air. The same feature can be observed for other species with strong anthropogenic sources. From our analysis we chose to identify samples with elevated mixing ratios of anthropogenic tracers (i.e. CO, ethyne, C_2Cl_4) based on enhancements in at least five consecutively collected canisters. Then, we used the kinematic back trajectories calculated by the Florida State University FLEXPART model to identify the geographical origins of the sampled air masses (Stohl et al., 1998). “Pollution plumes” were identified as air masses that had passed over source regions at low altitude (highlighted in red in Fig. 1). It can be noted that not all of the samples with elevated concentrations are included in this definition of pollution plumes, because isolated emission sources at small spatial scales can explain high VOC levels in some samples. Mixing ratios much lower than the total average were measured in several canisters (blue symbols in Fig. 1). These samples were highly enhanced in

ozone (490±150 ppbv) and – relative to the background values shown in Table 2 – were depleted in many of the CFCs (CFC-12: 490±21 pptv; CFC-11: 212±17 pptv), CFC replacements (HCFC-22: 153±8 pptv), Halon-1211 (3.42±0.41 pptv), CO (42±16 ppbv), ethane (204±155 pptv), and ethyne (37±24 pptv). The chemical composition of these 54 depleted samples indicates they were strongly influenced by stratospheric air.

The geographical origin of the identified pollution plumes and transport time was inferred using kinematic backward trajectories. Twelve total plumes were identified: five from China, four from other Asian countries (from now on simply referred to as "Asian" plumes), and three from the United States (US plumes) (Fig. 2 and Table 1). Although the analysis of the backward trajectories for three Asian plumes (#6, #7, and #9) indicates some impact of Chinese air masses (Table 1), these pollution plumes are classified as "Asian plumes".

To further support the representativeness of the identified pollution plumes, the degree of atmospheric processing of these air masses was evaluated, whereby a lower aging of air masses recently impacted by VOC sources with respect to the remaining INTEX-B samples was expected. Although different methods are used to evaluate the photochemical processing of air masses, the use of hydrocarbon pairs with common sources and different rates of removal is particularly useful to provide the so-called "photochemical clock" (Parrish et al., 1992, 2007; McKeen and Liu, 1993; McKeen et al., 1996; Ehhalt et al., 1998; de Gouw et al., 2005). In this work, we calculated the average C_2H_2/CO ratio to assess the aging of the different pollution plumes. Ethyne and CO are both emitted mainly by combustion sources and their removal from the troposphere is primarily controlled by reaction with OH with a reaction rate slow enough to easily allow their detection in the remote troposphere. However, the removal rate of ethyne is faster than CO resulting in a lifetime of about two-three weeks for C_2H_2 (Xiao et al., 2007) and about two months for CO (Logan et al., 1981). A strong correlation between these two trace gases is usually observed in the troposphere, with a C_2H_2 to CO ratio decreasing with time due to the faster removal rate of ethyne. Figure 3 illustrates how the C_2H_2/CO ratios follow the expected general trend. The lowest ratio

(0.5 pptv/ppbv) was calculated for the stratospherically influenced air, followed by the samples with no pollution plumes (1.6 pptv/ppbv), and the pollution plumes showing the highest ratios (1.8–3.5 pptv/ppbv). This further suggests the recent impact of younger polluted air masses in the 12 identified pollution plumes.

3.2 Pollution plumes

Table 2 lists the statistics calculated for the different categories of identified pollution plumes. The majority of the enhanced VOC pollution plumes were encountered over the Pacific between about 40–60° N (Fig. 2). Four of the five Chinese plumes were sampled far away from the source region: two over the Pacific ocean very close to the west coast of the United States (43–46° N; 123–126° W) and two inland – one over Oregon (44–46° N; 123° NW) and one over North Dakota (48° N; 100–103° W). The fifth Chinese plume, the four Asian plumes, and the stratospherically influenced air masses were all sampled over the Eastern Pacific region. Air masses that had recently passed at low altitude over the United States (i.e. US pollution plumes) were also encountered inland of the US Asian plumes were previously measured over North America during INTEX-A (Liang et al., 2007). For many VOCs, the mixing ratios observed during INTEX-A was considerably lower than those measured during INTEX-B. For instance, average ethane, ethyne and benzene mixing ratios of 880±190 pptv, 160±40 pptv, and 24±11 pptv were reported in 2004 for Asian plumes, versus respective averages of 1350±376 pptv, 428±209 pptv, and 105±75 pptv for all of the Asian and Chinese plumes encountered during INTEX-B. The lower VOC levels measured during INTEX-A are mainly the result of the enhanced photochemical decomposition of the VOCs during the summer, but also influenced by longer summertime transport of Asian pollution across the Pacific.

To evaluate the enhancement of the VOCs measured in the plumes, the average of the lowest 50th percentile of all of the samples collected on board of the C-130 and DC-8 aircraft was calculated (after the stratospheric samples had been removed). This is considered to represent the background of the Pacific region at the time of this sampling campaign. Compared to the 2004 background measured during INTEX-A, CO and the reported VOCs were overall not different between the two missions (when the standard deviation measured is considered), while the CFCs were higher in 2004 (Fig. 4). Long-term global monitoring networks have shown that the global tropospheric mixing ratios of the CFCs are declining with time. Therefore, the two year gap between the two missions can in part explain the observed difference. For instance, the northern hemispheric CFC-11 mixing was 253.6±0.4 pptv in August 2004 and 249.2±0.3 pptv in May 2006; CFC-12 northern hemispheric levels for the same time period declined from 534.1±0.8 pptv to 531.6±1.1 pptv (CFC-11 and CFC-12 data from the NOAA/ESRL halocarbons in situ program; NOAA/ESRL, 2008). The higher ozone measured during INTEX-A (73±17 ppbv versus 50±10 ppbv in INTEX-B) is consistent with increased photochemical activity during the summer, leading to an increase in tropospheric ozone formation. Conversely, increased photochemical activity results in lower hydrocarbon levels in summer. However, we recognize that other factors may play an important role in determining the tropospheric levels of trace gases. For instance, the effect of declining global mixing ratios must also be considered in conjunction with the enhanced or reduced photochemical activity throughout the year.

Many gases were significantly enhanced in the plumes with respect to the background air (over 2σ above background, noted in bold in Table 2). All of the plumes are enhanced in CO, CS_2, Halon-1211, HCFC-22, HCFC-141b, chloroform ($CHCl_3$), methylene chloride (CH_2Cl_2), trichloroethene (C_2HCl_3), tetrachloroethene (C_2Cl_4), methyl bromide (CH_3Br), methyl iodide (CH_3I), ethylchloride, 1,2-dichloroethane (1,2-DCE), ethane, ethyne, propane, butanes, *i*-pentane, and benzene. With the exception of CH_3Br and CH_3I, all of these species have strong (or exclusive) anthropogenic emissions, which highlight the anthropogenic influence of these air masses. Particularly interesting is the enhancement of other tracers in selected plumes. For instance, OCS and CH_3Cl were significantly higher than the background only in the Asian and Chinese plumes, while all the measured CFC replacement compounds were enhanced in the US plumes. Under the Montreal Protocol and subsequent amendments, by 1 January 1996 a complete phase out of the base levels of production and consumption was established for CFCs in developed countries, but CFCs were allowed to be produced and consumed in developing nations such as China and other Asian countries (UNEP, 2003). The average mixing ratio of the INTEX-B samples not included in the pollution plumes is not statistically different than the average background for the majority of the VOCs measured. The enhancements observed for some of the hydrocarbons in those samples are most likely the result of the presence of isolated emission sources.

Among the CFC replacements, HFC-134a appears to be particularly elevated in the air masses influenced by US emissions. An average mixing ratio of 43±5 pptv was measured in the three US plumes, representing a 24% enhancement with respect to the background of 34.6±1.1 pptv (Fig. 5). It appears that Chinese plumes #2 and #3 were diluted compared to the other plumes, with the average mixing ratios for many species not significantly different than the background (Table 3). With the exception of these two plumes, significantly higher levels of the majority of the VOCs presented here were observed in the Chinese air masses, including all the CFC replacements. Both the Asian and Chinese plumes were elevated in HCFC-134a, but with lower enhancements compared to the background: 37±2 pptv measured in the Asian plumes (7% enhancement) and, with the exclusion of the diluted Chinese plumes #2 and #3, 38±1 pptv in the Chinese air masses (10% enhancement).

3.3 Halon-1211

Halon-1211 is an anthropogenic brominated compound widely used in fire-fighting equipment. It is the most abundant halon in the atmosphere and its production and consumption is regulated under the Montreal Protocol and subsequent amendments. In particular, a complete phase out of the base levels in production and consumption of Halon-1211 was established for developed countries in 1994, while developing countries were required to reduce emissions by half – relative to the 1995–1997 base level – by 1 January 2005 (UNEP, 2003). The uncontrolled release of Halon-1211 from the large halon stocks still present is an additional important source that also needs to be considered (Montzka, 2003). Because of the long lifetime of Halon-1211 (16 years, IPCC, 2007), the reduction in production and consumption in developing countries will most likely result in a slow decrease of halons in the atmosphere. The Chinese plumes encountered during INTEX-B offer an excellent opportunity to evaluate whether the 1 January 2005 deadline is producing any change in the local and global atmospheric level of this species, and if Halon-1211 can still be considered a specific tracer for Chinese air masses as it was in previous studies such as TRACE-P (Blake et al., 2003). The highest Halon-1211 levels were measured in the Chinese plumes encountered on the C-130, with average mixing ratios of 5.19 pptv (±0.29; 24% enhancement; plume #4) and 4.65 pptv (±0.27; 11% enhancement; plume #5) compared to a background of 4.19 (±0.07) pptv (Fig. 6, Table 3). Lower average levels were measured for the remaining samples in the Chinese plumes (4.36±0.16 pptv).

Very high Halon-1211 mixing ratios were measured in ground level air samples collected on September 2005 in two major urban centers of China's Pearl River Delta region, Guangzhou and Dongguan: 31±34 pptv (6.0–160 pptv; n=42) in Guangzhou and 11±8.2 pptv (4.8–53 pptv; n=48) in Dongguan (D. R. Blake, unpublished data). The specific source responsible for these elevated mixing ratios (i.e. continuous production or release by the existing stocks) is not possible to assess from our data. The high Halon-1211 levels can be the result of continuous unregulated emissions currently happening, uncontrolled release from halon banks, or, because of the lack of information about the magnitude of Halon-1211 emissions from China before the January 2005 deadline, high levels can still be observed despite the 50% reduction called by the Montreal Protocol. The presence of high levels of Halon-1211 in Guangzhou and Dongguan 6 months prior to the INTEX-B mission and the enhanced levels measured in some air masses associated with Chinese emissions (i.e. plumes #4 and #5) suggest that Halon-1211 is still present at high levels in air masses originating from China. However, we anticipate that this species will slowly decrease its role as a "specific" Chinese tracer as suggested by the relatively low levels measured in other Chinese plumes encountered during INTEX-B. Moreover, the global average Halon-

1211 is no longer increasing in the remote troposphere. The background mixing ratio measured in 2006 for Halon-1211 by global monitoring networks was 4.16 pptv versus 4.15 pptv in 2005 (NOAA/GMD, 2008), which is in good agreement with the background of 4.19±0.07 pptv we report from the 2006 INTEX-B campaign.

3.4 Trace gas relationships

Cross correlation analysis of selected species is a useful tool to identify specific VOC sources. It is known that the most important combustion sources for OCS are coal and biofuel combustion and biomass burning (Blake et al., 2004). To isolate the biomass burning source, the OCS to CO enhancement ratio was considered. Emission ratios of 0.054 pptv/ppbv and 0.10 pptv/ppbv have been observed for "pure" biomass burning plumes (Meinardi et al., 2003; Blake et al., 2004). Higher ratios have been measured in several Chinese urban plumes (0.35–0.96 pptv/ppbv, Blake et al., 2004) where coal and biofuel combustion were the most likely sources. The analysis of correlation plots from INTEX-B pollution plumes reveal that a strong correlation was observed only in Chinese air masses, with a high coefficient of determination, R^2 (0.80–0.96) (Fig. 7). A weaker correlation was found for Asia plume #6, which was partially influenced by air masses from China (0.59 R^2; plot not shown), while a lack of correlation was observed for all the other pollution plumes (R^2 0.05–0.47; plots not shown). The enhancement ratios of OCS to CO for the five Chinese plumes range from 0.81 to 1.11 pptv/ppbv – in the high range of the Blake et al. (2004) observations of Chinese plumes – suggesting the detection of a large coal/biofuel combustion source located in China. For the other Asian plumes, the enhanced OCS mixing ratio without correlation between OCS and CO (or ethyne, R^2<0.53) indicates the presence of additional, non-combustion sources of OCS.

High mixing ratios of 1,2-dichloroethane (1,2-DCE) were measured in all of the pollution plumes, highlighting the anthropogenic origin of this compound. 1,2-DCE is used primarily as a chemical intermediate in the synthesis of other compounds (mainly vinyl chloride) or as a solvent (EPA, 1984), and is a leaded gasoline additive that is added on a mole-to-mole basis with lead (Clark et al., 1984). 1,2-Dichloroethane emissions from coal burning have also been suggested. Concentrations up to 3.51 μg m^{-3} (about 900 pptv) were measured in the gas phase of Spanish coal power station operations (Fernandez-Martinez et al., 2001). The lowest average levels were observed in the US plumes (12±1 pptv, 13±0.6 pptv, and 14±0.8 pptv), followed by the Asian plumes (15±3 to 21±8 pptv), while the highest mixing ratios were measured in the Chinese air masses. For example, both Chinese plumes #4 and #5 were particularly enhanced in 1,2-DCE, averaging 120±23 pptv in plume #4 (97–162 pptv range) and 80±36 pptv average in plume #5 (46–147 pptv range). The excellent correlation found between 1,2-DCE and the combustion tracer ethyne, the industrial solvent CH_2Cl_2, and the two coal/biomass burning tracers, OCS and CH_3Cl (Table 4) is most likely because of co-located emission sources of these species in China. The high levels observed in the Chinese plumes, and good correlations with Chinese emitted NMHCs suggest the use of 1,2-DCE, in combination with other species, as a tracer of Chinese air masses. The mixing ratios of the trace gases here suggested to be used as specific indicators of Chinese air masses (i.e. OCS, CH_3Cl, Halon-1211, 1,2-DCE), together with the ethyne/CO ratio, are reported in Fig. 8 for all the samples collected on 6 May 2006 (C-130 aircraft). A clear enhancement in all of these VOCs was observed for the Chinese pollution plumes #4 and #5 encountered during this flight.

4 Conclusions

We were able to identify 12 pollution plumes encountered during INTEX-B: five plumes originated from China, four plumes from other Asian countries, and three plumes from the United States. Four of the five Chinese plumes were sampled far away from the source region, close to the west coast of the United States or inland over the North American continent. This highlights the efficient transport of Asian air masses across the Pacific region during spring. These pollution plumes showed a higher ethyne/CO ratio with respect to the rest of the samples collected during INTEX-B and the stratospherically influenced plume, highlighting the recent impact of recently polluted air masses.

The VOC enhancement with respect to the regional background in the different plumes reflected the presence of different sources. In particular, the correlation analysis of OCS versus CO confirmed the importance of coal burning as a specific source for OCS (as opposed to biomass burning). Elevated mixing ratios of CFC replacements were measured in all of the US plumes, and in selected Chinese plumes. HFC-134a was particularly enhanced in air masses influence by US emissions. The Chinese plumes were highly enhanced in OCS, CH_3Cl, 1,2-dichloroethane, and Halon-1211. We suggest the use of this combination of gases as specific tracers for the identification of Chinese air masses as opposed to the use of a single species such as Halon-1211. We anticipate that Halon-1211 will slowly decrease its role as a "specific" Chinese tracer as suggested by the relatively low levels measured in some of the Chinese plumes encountered during INTEX-B.

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Table 1. Summary of INTEX-B pollution plumes.

	Transport time (days)[a]	Geographical origin[a]	Number of samples	Aircraft – Flight date
Chinese plumes				
Plume # 1	7	China	5	DC8 – 17 April 2006
Plume # 2	5	China	29	DC8 – 12 May 2006
Plume # 3	7	China	6	DC8 – 15 May 2006
Plume # 4	5	China	6	C130 – 1 May 2006
Plume # 5	7	China	7	C130 – 1 May 2006
Asian plumes				
Plume # 6	7-9	Japan/Korea/China	15	DC8 – 25 April 2006
Plume # 7	3–5	Korea/Taiwan/China	10	DC8 – 7 May 2006
Plume # 8	5–7	Japan	8	DC8 – 7 May 2006
Plume # 9	7	South Asia/China	8	DC8 – 23 April 2006
US Plumes				
Plume # 10	2	Washington/Idaho/Montana	23	C130 – 24 April 2006
Plume # 11	2	California/Oregon/Washington	17	C130 – 3 May 2006
Plume # 12	2	Washington/Oregon	14	DC8 – 15 May 2006

[a] Transport time and geographical origin were estimated using kinematic backtrajectories.

Table 2. Average mixing ratio (pptv, unless otherwise specified; ±1-sigma SD) measured in pollution plumes, in background air (see text for explanation), and in the remaining samples during INTEX-B. Mixing ratios enhanced with respect to the background (±2-sigma SD) are reported in bold. 1,2-DCE = 1,2 dichloroethane.

	Background	Chinese plumes	Asian plumes	US plumes	C130-DC8[a]
Ozone, ppbv	50 (10)	**84 (29)**	**73 (16)**	63 (7)	65 (24)
CO, ppbv	113 (16)	**184 (49)**	**181 (21)**	**166 (22)**	131 (25)
OCS	472 (11)	**548 (62)**	**519 (19)**	465 (19)	486 (19)
CS_2	3.5(1.0)	**12.7 (8.9)**	**6.7 (3.5)**	**10.2 (6.0)**	**6.7 (5.0)**
CFC-12	526 (4)	529 (5)	529 (6)	531 (5)	529 (5)
CFC-11	247 (3)	248 (4)	250 (3)	250 (2)	248 (3)
CFC-113	76.5 (0.8)	77.4 (0.9)	77.1 (1.3)	77.7 (0.7)	77.2 (1.0)
CFC-114	14.7 (0.1)	14.8 (0.2)	14.8 (0.2)	14.8 (0.1)	14.8 (0.2)
Halon-1211	4.19 (0.07)	**4.49 (0.31)**	**4.38 (0.10)**	**4.37 (0.19)**	4.27 (0.11)
H-2402	0.47 (0.01)	0.48 (0.01)	0.48 (0.02)	0.49 (0.01)	0.48 (0.01)
H-1301	3.03 (0.04)	3.06 (0.07)	3.06 (0.06)	**3.12 (0.06)**	3.09 (0.09)
HFC-134a	34.6 (1.1)	36.1 (4.0)	36.7 (1.9)	**42.8 (5.3)**	36.0 (1.9)
HCFC-22	170 (3)	**181 (11)**	**180 (4)**	**185 (11)**	173 (5)
HCFC-142b	15.6 (0.4)	**17.0 (1.3)**	16.4 (0.6)	**17.3 (1.0)**	16.0 (0.6)
HCFC-141b	18.1 (0.5)	**19.9 (2.3)**	**19.9 (0.7)**	**20.1 (1.1)**	18.7 (0.8)
$CHCl_3$	8.4 (1.2)	**14.9 (6.0)**	**12.4 (1.5)**	**12.5 (1.5)**	9.8 (1.9)
CCl_4	93 (1)	95 (2)	94 (2)	94 (1)	94 (2)
CH_2Cl_2	30.1 (4.4)	**54.2 (24.4)**	**48.8 (7.4)**	**44.0 (8.4)**	35.7 (7.3)
C_2HCl_3	0.26 (0.12)	**1.57 (1.90)**	**1.46 (1.17)**	**1.58 (1.82)**	0.50 (0.40)
C_2Cl_4	2.92 (0.93)	**5.92 (4.76)**	**5.73 (1.90)**	**9.43 (4.76)**	4.30 (1.71)
CH_3Cl	535 (14)	**604 (57)**	**584 (21)**	548 (13)	554 (25)
CH_3Br	7.6 (0.3)	**8.9 (1.1)**	**8.8 (0.5)**	**10.9 (10.2)**	8.0 (0.7)
CH_3I	0.05 (0.03)	**0.12 (0.10)**	**0.19 (0.17)**	**0.28 (0.22)**	**0.16 (0.16)**
$CHBr_3$	0.38 (0.13)	0.63 (0.26)	**0.81 (0.52)**	**0.94 (0.24)**	0.62 (0.33)
Ethylchloride	3.30 (0.81)	**11.40 (8.48)**	**7.44 (1.84)**	**6.58 (1.60)**	4.66 (1.84)
1,2-DCE	8.6 (2.3)	**39.7 (34.67)**	**18.4 (5.36)**	**13.1 (1.06)**	**11.6 (4.24)**
Ethane	839 (206)	**1319 (407)**	**1391 (319)**	**1608 (306)**	1144 (377)
Ethene	7 (3)	**17 (85)**	10 (6)	**117 (136)**	**24 (61)**
Ethyne	144 (48)	**453 (228)**	**396 (85)**	**356 (104)**	218 (100)
Propane	107 (57)	**358 (262)**	**276 (110)**	**505 (232)**	**225 (163)**
i-Butane	11 (4)	**41 (37)**	**29 (11)**	**66 (46)**	**20 (18)**
n-Butane	14 (6)	**64 (116)**	**48 (19)**	**166 (143)**	**30 (33)**
i-Pentane	7 (3)	**32 (95)**	**16 (7)**	**139 (127)**	**14 (23)**
n-Pentane	6 (3)	**20 (40)**	11 (5)	**60 (54)**	10 (15)
Benzene	22 (9)	**124 (79)**	**82 (30)**	**82 (32)**	**41 (27)**
Toluene	5 (3)	**22 (67)**	10 (5)	**75 (73)**	**10 (14)**

[a] The samples collected within the pollution plumes and the stratospherically influenced air masses have been excluded.

Table 3. Average mixing ratio (pptv, unless otherwise indicated) of the five Chinese pollution plumes. The one sigma standard deviation is reported in parenthesis. ND = below detection limit.

	Background	Plume #1	Plume #2	Plume #3	Plume #4	Plume #5
Ozone, ppbv	50 (10)	64 (4)	81 (39)	63 (5)	108 (9)	110 (13)
CO, ppbv	113 (16)	173 (25)	156 (44)	177 (47)	273 (24)	238 (42)
OCS	472 (11)	524 (24)	522 (47)	533 (44)	649 (22)	599 (47)
CS_2	3.5(1.0)	13.8 (3.3)	10.4 (7.4)	4.2 (0.9)	29.3 (10.1)	15.0 (5.2)
CFC-12	526 (4)	530 (7)	529 (5)	523 (3)	530 (3)	531 (5)
CFC-11	247 (3)	252 (4)	248 (3)	243 (1)	250 (3)	249 (1)
CFC-113	76.5 (0.8)	78.3 (0.9)	77.1 (0.8)	76.8 (0.5)	78.3 (0.9)	77.9 (0.6)
CFC-114	14.7 (0.1)	14.9 (0.1)	14.8 (0.2)	14.7 (0.1)	15.0 (0.2)	14.8 (0.2)
Halon-1211	4.19 (0.07)	4.39 (0.10)	4.36 (0.17)	4.35 (0.14)	5.19 (0.29)	4.65 (0.27)
H-2402	0.47 (0.01)	0.49 (0.01)	0.48 (0.01)	0.48 (0.01)	0.48 (0.01)	0.48 (0.01)
HFC-134a	34.6 (1.1)	36.9 (1.2)	35.1 (1.1)	34.7 (0.8)	38.9 (0.5)	38.2 (0.8)
HCFC-22	170 (3)	181 (5)	175 (6)	174 (4)	201 (5)	191 (9)
HCFC-142b	15.6 (0.4)	16.7 (0.5)	16.4 (0.7)	15.9 (0.7)	19.7 (1.0)	18.4 (1.1)
HCFC-141b	18.1 (0.5)	19.9 (0.8)	18.3 (0.7)	18.5 (0.5)	25.4 (1.4)	22.9 (1.9)
$CHCl_3$	8.4 (1.2)	13.4 (1.7)	11.0 (3.0)	13.2 (3.1)	28.7 (4.5)	22.1 (5.4)
CCl_4	93 (1)	97 (2)	93 (2)	94 (1)	97 (2)	97 (2)
CH_2Cl_2	30.1 (4.4)	50.7 (9.6)	37.9 (9.3)	44.0 (6.0)	113.2 (13.3)	82.4 (20.5)
C_2HCl_3	0.26 (0.12)	1.70 (0.85)	0.59 (0.34)	0.50 (0.15)	5.72 (0.85)	2.89 (1.11)
C_2Cl_4	2.92 (0.93)	6.52 (1.18)	3.88 (1.33)	4.20 (0.96)	12.82 (12.0)	9.51 (2.12)
CH_3Cl	535 (14)	610 (28)	573 (32)	571 (29)	720 (30)	658 (52)
CH_3Br	7.6 (0.3)	9.3 (1.0)	8.2 (0.5)	8.2 (0.4)	11.0 (0.9)	10.1 (1.2)
CH_3I	0.05 (0.03)	0.10 (0.02)	0.06 (0.04)	0.03 (0.01)	0.34 (0.06)	0.28 (0.07)
$CHBr_3$	0.38 (0.13)	0.84 (0.17)	0.57 (0.28)	0.40 (0.08)	0.82 (0.11)	0.75 (0.10)
Ethylchloride	3.30 (0.81)	7.94 (2.87)	6.20 (3.08)	7.42 (2.28)	29.73 (7.89)	23.11 (8.62)
1,2-DCE	8.6 (2.3)	24.3 (7.39)	19.3 (11.38)	24.0 (9.89)	119.6 (23.39)	80.2 (35.99)
Ethane	839 (206)	1265 (82)	1116 (292)	1091 (226)	2025 (82)	1790 (180)
Ethene	7 (3)	ND	13 (8)	ND	36 (15)	12 (4)
Ethyne	144 (48)	408 (108)	313 (156)	372 (161)	949 (112)	711 (200)
Propane	107 (57)	244 (60)	223 (162)	168 (60)	851 (64)	737 (99)
i-Butane	11 (4)	28 (11)	28 (18)	18 (6)	99 (9)	64 (17)
n-Butane	14 (6)	43 (18)	49 (44)	27 (10)	144 (11)	99 (22)
i-Pentane	7 (3)	17 (4)	22 (11)	10 (4)	83 (13)	45 (13)
n-Pentane	6 (3)	12 (3)	16 (11)	6 (1)	47 (5)	27 (7)
Benzene	22 (9)	102 (34)	78 (49)	67 (36)	300 (33)	214 (67)
Toluene	5 (3)	14 (3)	6 (2)	9 (3)	66 (23)	22 (6)

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Table 4. Coefficient of determination and slope calculated for 1,2-dichloroethane versus ethyne, C_2HCl_3, OCS, and CH_3Cl. NC = No Correlation ($R^2 < 0.50$).

	1,2-Dichloroethane vs:			
	Ethyne R^2 (slope)	C_2HCl_3 R^2 (slope)	OCS R^2 (slope)	CH_3Cl R^2 (slope)
Chinese Plumes				
Plume # 1	0.83 (13.31)	0.97 (0.11)	0.89 (3.08)	0.82 (3.49)
Plume # 2	0.93 (13.20)	0.89 (0.03)	0.85 (3.82)	0.77 (2.50)
Plume # 3	0.98 (16.11)	0.64 (0.01)	0.96 (4.35)	0.64 (2.32)
Plume # 4	0.93 (4.64)	NC	0.93 (0.89)	0.82 (1.18)
Plume # 5	0.95 (5.41)	0.97 (0.03)	0.90 (1.25)	0.99 (1.44)

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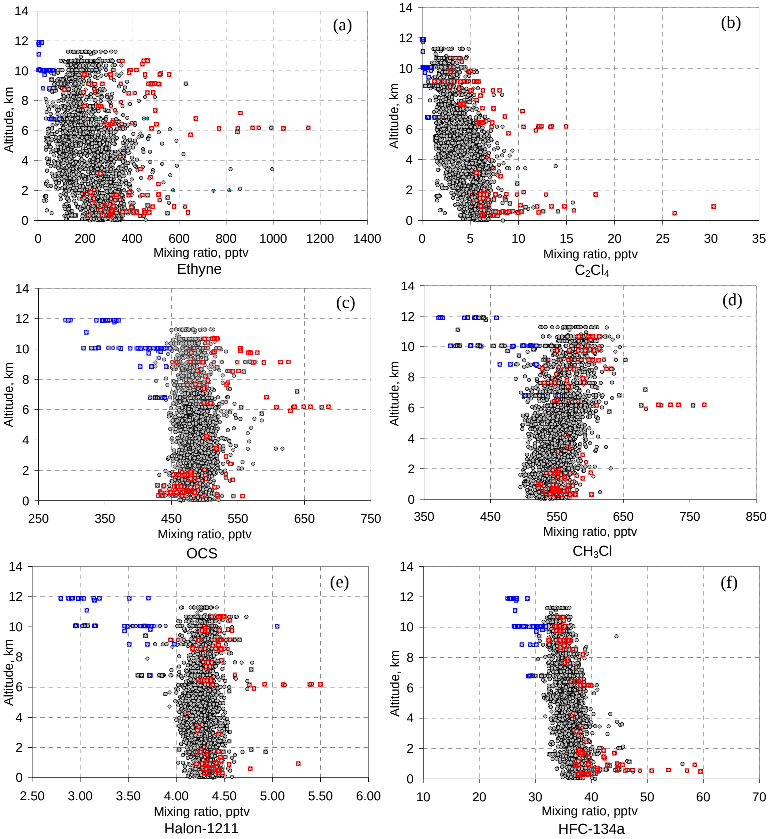

Fig. 1. Vertical profiles of **(a)** ethyne, **(b)** C_2Cl_4, **(c)** OCS, **(d)** CH_3Cl, **(e)** Halon-1211, and **(f)** HFC-134a measured during the second phase of INTEX-B (4 April–15 May 2006). Samples included in pollution plumes are highlighted in red; stratospherically influenced air masses are indicated in blue.

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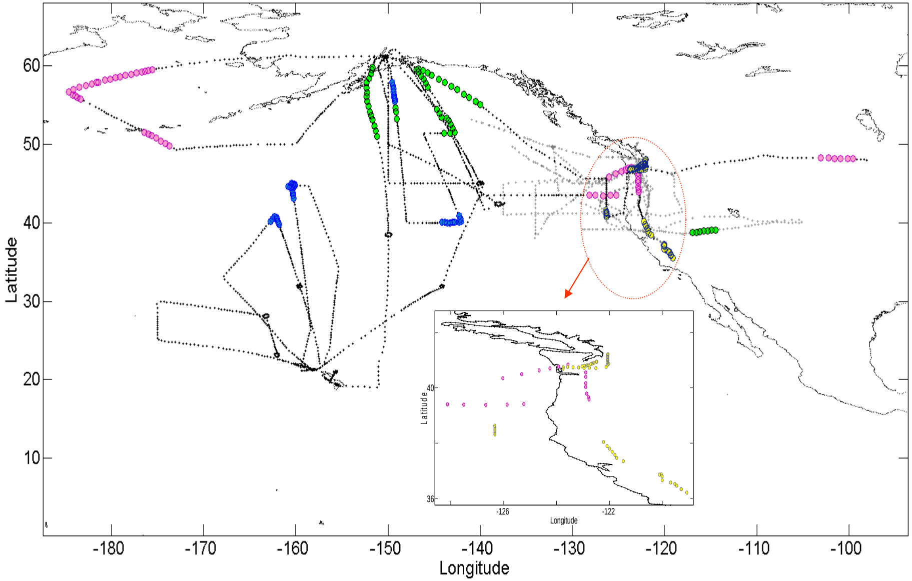

Fig. 2. Geographical location where the different pollution plumes were sampled by the DC-8 and C-130 aircraft. Colored circles represent the canisters collected within the different plumes: pink filled circles for Chinese plumes; blue circles for Asian plumes; yellow circles for US plumes; green circles for stratospherically influenced air masses.

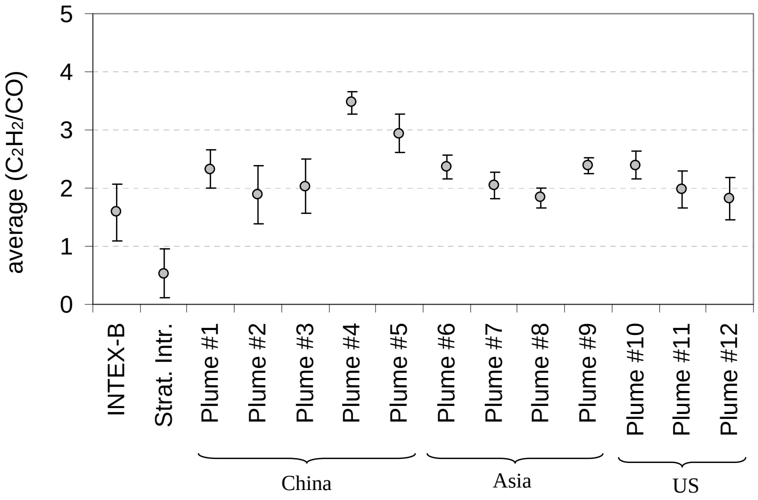

Fig. 3. Average ethyne/CO ratio calculated for the different pollution plumes, for the stratospherically influenced air masses, and for the remaining samples collected.

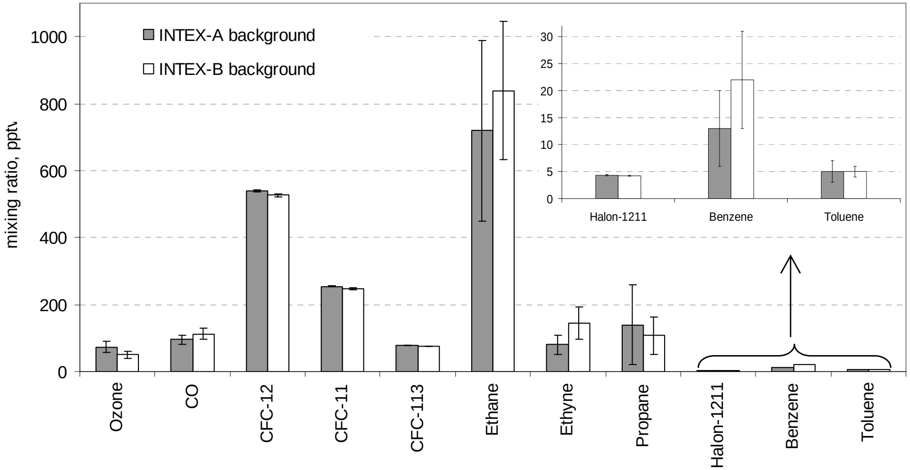

Fig. 4. Comparison between the background levels for selected species measured during INTEX-B and INTEX-A (see text for explanation on background calculation).

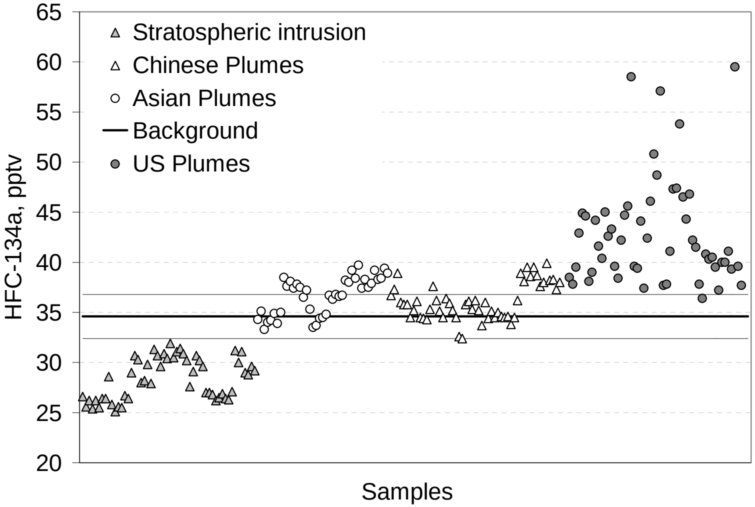

Fig. 5. HCFC-134a mixing ratios measured in the different pollution plumes identified. The 2-σ SD calculated for the background is reported by the thin black lines above and below the thick background line.

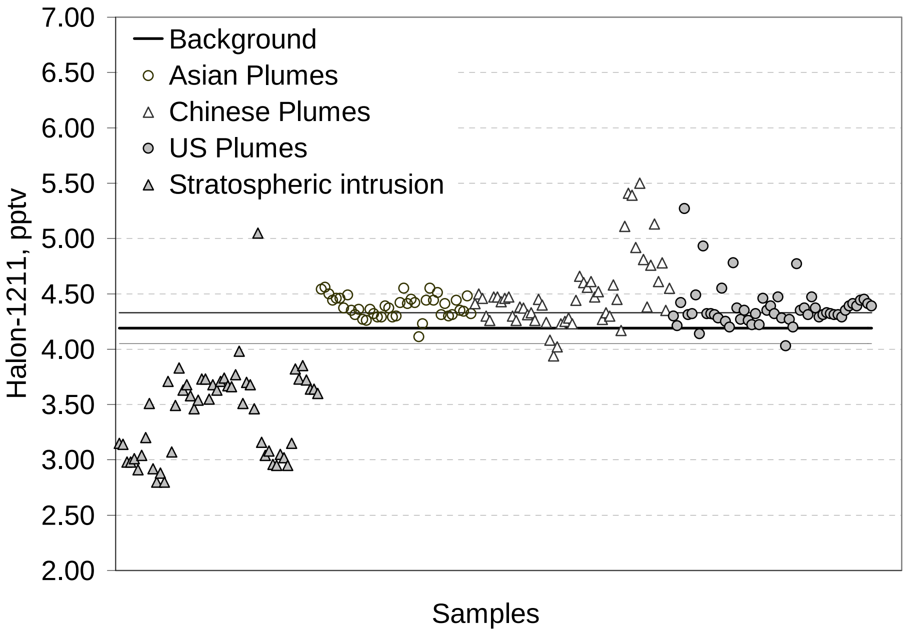

Fig. 6. Halon-1211 mixing ratios measured in the different pollution plumes identified. The 2-σ SD calculated for the background is reported by the thin black lines above and below the thick background line.

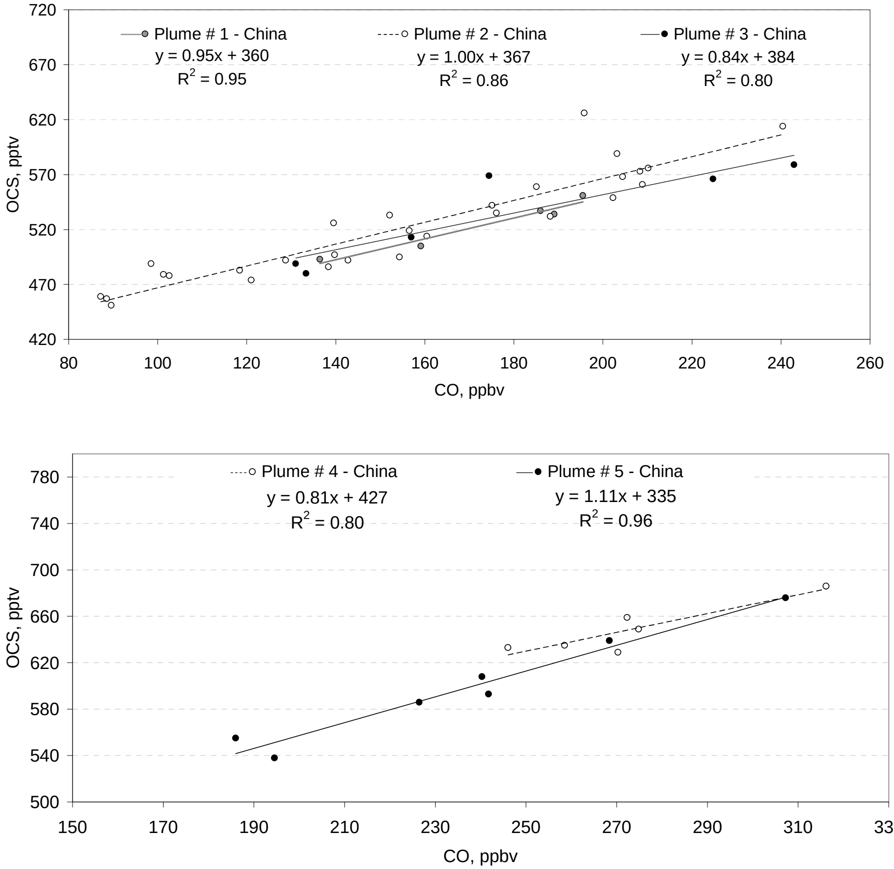

Fig. 7. Correlation plots of OCS verses CO for the five Chinese plumes identified during INTEX-B.

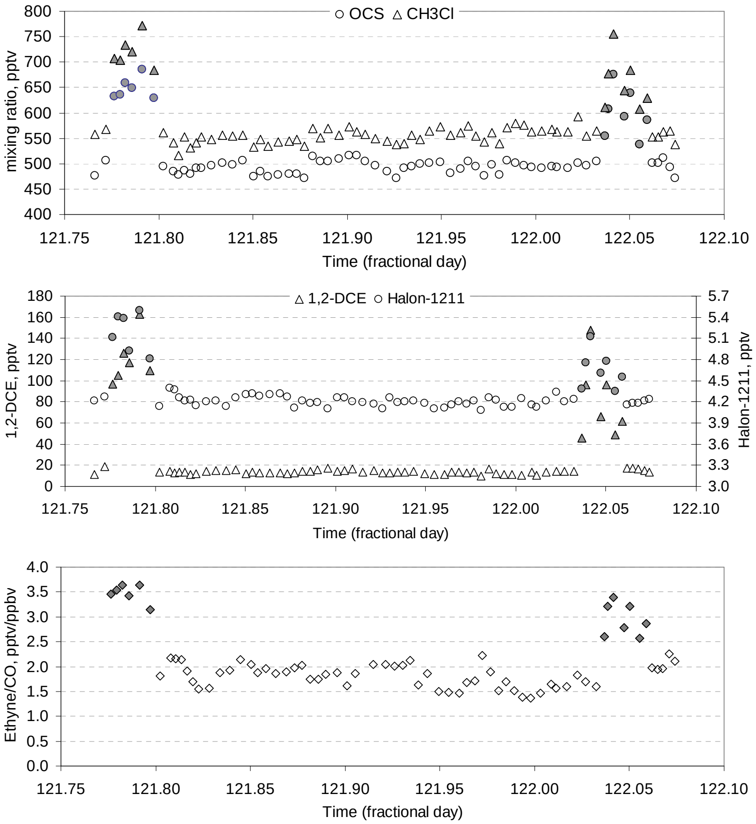

Fig. 8. Mixing ratios of the suggested indicators of Chinese air masses measured on 6 May 2006 (C-130 aircraft). The six samples collected at the beginning of the flight corresponding to pollution plume #4, and the seven samples collected at the end of the flight corresponding to pollution plume #5 are indicated with filled symbols.