

Abstract

Using a GC/FID/MS system, we analyzed the mixing ratio levels of 16 halocarbon species in more than 100 air samples collected in 2004 from the Pearl River Delta (PRD) region of southern China. The results revealed elevated regional mixing ratios for most halocarbons, especially for HCIC = CCl₂ (trichloroethylene, TCE), CH₂Cl₂ (dichloromethane, DCM), CH₃Br (bromomethane), HCFC-22, CHCl₃ (trichloromethane), CCl₄ (tetrachloromethane), Cl₂C = CCl₂ (perchloroethylene, PCE), CH₃CCl₃ (methyl chloroform, MCF), and CFC-12. Comparisons were done with the data from TRACE-P and ALE/GAGE/AGAGE experiments, we found that the large variability in concentrations (relative standard deviation ranged from 9.31% to 96.55%) of the halocarbons suggested substantial local emissions from the PRD region in 2004. Correlations between the mixing ratio of each species and carbon monoxide (CO) were examined, and then each emission of halocarbon was quantified based on scaling the optimized CO emission inventory with the slope of the regression line fitted to each species relative to CO. The calculated results revealed that mass of CH₂Cl₂ (7.0 Gg), CH₃CCl₃ (6.7 Gg), and Cl₂C = CCl₂ (2.3 Gg) accounted for about 62.9% of total emissions, suggesting a significant contribution to halocarbon emissions from solvent use in the PRD region. Emissions of HCFC-22 (3.5 Gg), an alternative refrigerant to chlorofluorocarbons (CFCs), were about 2.3 times greater than those of CFC-12 (1.6 Gg). CFC-12 and HCFC-22 accounted for 21.5% of total emissions of halocarbons, so that the refrigerant would be the second largest source of halocarbons. However, the ratio approach found only minor emissions of other CFCs, such as CFC-11, and levels of CFC-114 and CFC-113 were close to zero. Emissions of other anthropogenic halocarbons, such as CCl₄, CHCl₃, CH₃Br, and CH₃Cl, were also estimated. Where possible, the emissions estimated from the measured ratios were compared with results from source inventory techniques, we found that both approaches gave emissions at similar magnitude for most of the halocarbons, except CFC-11. The comparison suggested that ratio method may be a useful tool for assessing regional halocarbon emissions,

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and emission uncertainty could be further reduced by incorporating both longer-term and higher-frequency observations, as well as improving the uncertainty of the CO inventory.

1 Introduction

5 The importance of halocarbons in the atmosphere has been apparent since the 1970s when Lovelock (Lovelock, 1972) measured atmospheric concentrations of chlorofluorocarbons (CFCs) using an electron capture detector and a gas chromatogram. Halocarbons, a subclass of volatile organic compounds, play an important role in the destruction of stratospheric ozone (Molina et al., 1974), some of them also function as
10 the potential greenhouse gases (Fisher et al., 1990; Lashof et al., 1990). Both of the effects have propelled halocarbons to the forefront of atmospheric chemistry research, and the great importance of halocarbons had been attached by governmental and scientific communities. Protocols, such as the Vienna Convention, the Kyoto Protocol, the Montreal Protocol, and their subsequent amendments, were developed to establish
15 mechanisms for international cooperation, with the aim of controlling and reducing the use of halocarbons (United Nations Environment Programme, 2000). Environmental agencies in many countries have prepared national emissions inventories of halocarbons; the goal of these statistical emissions estimates is to help accelerate halocarbon phase-out and reduce the impact of human activities on the environment, keeping energy efficiency and climate change objectives in mind.
20

These emissions inventories have relied primarily on bottom-up approaches, compiled based on production, end-use, and time schedule data (McCulloch et al., 1998). However, uncertainties arise if the production figures do not cover all manufacturing regions or if there are variations in the application of end-use categories. An essential
25 part of validating emissions inventories is comparison between inventory emissions derived using conventional approaches (bottom-up) and model emissions based on other databases or atmospheric measurements (top-down), because these different

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methods provide independent results (O'Doherty et al., 2004; Palmer et al., 2003b; Reimann et al., 2005; Stohl et al., 2009). On a global scale, emissions can be determined from measured atmospheric concentrations using simple two- or three-box models (Daniel et al., 2007; Montzka et al., 2009) or three-dimensional models (Hartley et al., 1993). Regional-scale emissions can be derived using observed halocarbon concentrations and a modeling back-attribution technique (Manning et al., 2003; O'Doherty et al., 2004; Stohl et al., 2010; Vollmer et al., 2009).

Recently, a simple independent technique based on the ratio between observed halocarbon concentrations and concentrations of a substance with known emissions (carbon monoxide (CO) or HCFC-22) was developed to verify and validate emission inventories of trace gases (Blake et al., 2003; Dunse et al., 2005; Millet et al., 2009; Palmer et al., 2003b; Yokouchi et al., 2005; 2006). Using such a method, halocarbon emissions estimates can be scaled with the ratio of enhancements relative to CO and CO emissions inventories. However, this method is dependent on several assumptions: (1) within a certain period of time, no chemical reaction occurs that is related to secondary production or removal of halocarbons or CO emissions, (2) the air mass over the site or the sample should represent the average emissions of anthropogenic halocarbons, (3) there are no natural or biogenic sources of any measured halocarbons, and the short term enhancement of their atmospheric mixing ratio is a sign of recent anthropogenic emissions, and (4) the bottom-up estimate of annual emissions of anthropogenic CO should be a known parameter.

While this method has been used to assess halocarbon emissions in North America, Europe, and Australia (Dunse et al., 2005; Millet et al., 2009), emissions in East Asia are of great interest to researchers because of the region's recent rapid economic development (Palmer et al., 2003b) first assessed halocarbon emissions levels in Eastern Asia using aircraft observations with the halocarbon/CO enhancement ratio method, using observational data for March–April 2001, obtained from the TRACE-P campaign; their emission estimates for methyl chloroform (CH_3CCl_3) and CFC-12 were in agreement with existing inventories, but both the carbon tetrachloride (CCl_4)

emission estimates in the PRD region, whereas the method described above would be useful for estimating halocarbon emissions in this region using these observation data.

In this study, we examined 124 whole air samples collected in October and November 2004 to perform a “top-down” validation of the halocarbon emission inventories for the PRD region. The emissions results have important implications for tracking progress towards attaining current emission control goals and future targets, as China strives to become a CFC- and HCFC-free country.

2 Observations and approaches

2.1 Sampling and analysis

Nine sites were established in the PRD region in 2004 as part of a larger-scale VOC analysis campaign (Liu et al., 2008). However, only Guangzhou (23.14° N, 113.34° E, GZ) and Xinken (22.65° N, 113.60° E, XK) were selected as intensive study sites for the current study. Figure 1 shows the geographical locations of the sampling sites.

Daily whole air samples were collected and stored in 3.2L stainless steel canisters. These inert canisters provide a useful temporary storage environment, particularly for low-polar and low boiling-point compounds such as halocarbons (Wang et al., 2000b). Before each sampling period, all canisters were cleaned using a canister cleaner (Entech 3100A, Entech, Simi Valley, CA, USA). After each sampling campaign, the canisters were shipped to our laboratory at Peking University (PKU) as quickly as possible (≤ 15 days). Due to the complexity and rapidity of variation (Chan et al., 2006) for the halocarbons in the PRD region, more than 100 VOC species and CO were simultaneously carried out for further researches. For the Laboratory analysis, a cryogenic pre-concentrator system (Entech 7100A, Entech) coupled with GC-FID/MS (Hewlett Packard 6890/5973, Hewlett Packard Co. USA) were used for analysis, and the GC-FID/MS system was equipped with two columns and two detectors. Details of the sampling and analytical methods have been described elsewhere (Liu et al., 2008; Lu

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et al., 2007) . Briefly, the C₁-C₂ non-polar halocarbons were separated on a non-polar capillary column (HP-1, 50 m × 0.32 mm ID × 1.05 μm) and quantified by a quadrupole mass spectrometer (MS, Hewlett Packard 5973) which was operated in selected ion mode. In the second injection, the C₂-C₄ alkanes, alkenes, and acetylene were separated on the same non-polar capillary column but quantified with a flame ionization detector (FID, Hewlett Packard 6890), and the C₁-C₃ semi-polar halocarbons were separated on a semi-polar column (DB-624, 60 m × 0.32 mm ID × 1.8 mm) and also quantified using a quadrupole mass spectrometer. Helium was used as the purge gas for the 7100A and as a carrier gas for gas chromatography. Column HP-1 was initially held at 40 °C for 3 min, and then raised to 140 °C at a rate of 10 °C min⁻¹ and held for 5 min. Column DB-624 was programmed from 30 °C to 180 °C at a rate of 6 °C min⁻¹ and held for 5 min at 180 °C. Three VOC compounds were used as internal standards for the calibration of our analytical system: bromochloromethane, 1,4-difluorobenzene, and 1-bromo-3-fluorobenzene.

The halocarbons were quantified using the prepared standard gas according to the concentrations in the range of ambient air. The working standards were periodically prepared with a static dilution of primary standard provided by D. R. Blake's group at the Department of Chemistry, University of California at Irvine, USA. All of the species' correlation coefficients of the calibration curves ranged from 0.995 to 1.000 in the experiments, indicating that the integral peak areas were proportional to the concentrations of the target compounds. The procedure chosen to define the method detection limit (MDL) was that given in the Code of Federal Regulations (40 CFR 136 Appendix B) and by the United States Environmental Protection Agency (Method TO-15, Second Edition), and the species' MDL for our experiments ranged from 2 (CHCl = CCl₂, minimum) to 8 (CHCl₂CH₂Cl, maximum) pptv.

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2.2 Method of emissions calculation

Previous studies have indicated that relative ratios between pollution enhancements of halocarbons and increases in the concentration of a trace gas should reflect the ratios of their emissions strengths over the source region, as long as they are produced from common sources and not removed during transportation processes (Dunse et al., 2005; Yokouchi et al., 2006). Thus, if the emissions of one species from a region can be determined, we can calculate the emissions of other compounds in the same dataset based simply on the ratio of pollution enhancements. In this study, CO was used as the reference compound, as inventories of CO levels are considered to be relatively well established. Additionally, the bottom-up emissions of CO in China at spatial and time scales similar to those used in this study have been studied in several inventories (Ohara et al., 2007; Streets et al., 2003, 2006b; Zhang et al., 2009).

2.2.1 Consideration of the background and the interference

There are some amounts of residual halocarbons material present in the global, it leads to the presence of background concentrations in the atmosphere and this baseline concentration is unaffected by local and regional sources (Manning et al., 2003). Baseline concentrations can vary on a timescale depending on the pollutant, some of those halocarbons may also have seasonal or annual trends (Barnes et al., 2003). These baseline concentrations should be filtered out from the observation concentrations as the halocarbon pollution enhancements, which were considered in most of the previous studies such as (Barnes et al., 2003; Blake et al., 2003; Dunse et al., 2005; Gentner et al., 2010; Hurst et al., 2006; Millet et al., 2009; Palmer et al., 2003b; Yokouchi et al., 2005, 2006), then the measurements (X) after subtracting the background values (X_0) are denoted as ΔX for each compound, where $\Delta X = X - X_0$. In fact, these studies were focus on a larger spatial scale or longer time scale than our research.

However, the data were collected over a short enough period (for about a month) of time that background concentrations do not change significantly, so that in this research

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we abandon the acquirement for pollution enhancement by subtracting the background concentrations. Furthermore, since the ratio estimate emissions are calculated from the slope of the correlation between the species, the final results are independent of whether or not a background concentration is subtracted.

For more informative, baseline concentrations over the study period for each pollutant were still shown in Table 1. To separate out the background signals during the sampling period is helpful for us to understand the halocarbon pollution enhancements in PRD region. The 20th percentile of ALE/GAGE/AGAGE data between Octobers to November 2004 was defined as the Global background values, TRACP-P backgrounds provided by B. Barletta were used for halocarbons and the 20th percentile (Barnes et al., 2003; Palmer et al., 2003b) of the datasets for the other gases were used to capture the regional background level for the halocarbons not included in TRACE-P. The lowest CO mixing ratio in South China Sea air was defined as the CO background value (Wang et al., 2005).

Additionally, because biomass fires can be both natural and man-made phenomena, any of the CO generated by such fires was regarded as non-anthropogenic in this work, because it is not typically co-located with anthropogenic halocarbon emissions. The most severe biomass burning plumes (diagnosed by $\text{CH}_3\text{CN} > 900$ pptv, Wang et al., 2007) were removed prior to calculating background levels; statistical outliers (the lower 1st percentile and the upper 99th percentile) were also removed from the dataset as abnormal values.

2.2.2 Emissions calculations

The calculations assume that there is an inherent relationship between the target gas and CO. However, there are independent variables with independent errors for halocarbon X and CO; thus, it is necessary to determine a correction slope (X/CO) with an orthogonal distance regression (ODR), in which residual distance between the data samples and orthogonal regression line is minimized (Barnes et al., 2003). We considered that the slope of the regression line between X and CO should replace the emission

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ratio, and the uncertainties for the slope of X/CO was calculated by the assuming the linear model methods, more algebraic manipulation can be found in (Cantrell, 2008). According to Sect. 2.2.1, if the emissions of CO from an area are known, then the emissions of other compounds in the same dataset can be calculated as follows:

$$E_x = E_{\text{CO}} \times (X/\text{CO}) \times (M_x/M_{\text{CO}}) \times 10^{-3} \quad (1)$$

CO and X are expressed in ppbv and pptv, respectively, and X/CO represents the molar ratio of the halocarbon gases relative to CO. Thus, the molecular weights (M_x) of the trace gases should be taken into account when we determine the mass of emissions.

The uncertainly range for halocarbon emissions is calculated using a statistical method for error propagation. Because the uncertainties of emissions are associated with the variables of X/CO and regional CO, as mentioned above for Eq. (1), the uncertainties can be simply propagated from the combination of variables in Eq. (2) as follows:

$$\sigma_x = \sqrt{\sigma_{\text{CO}}^2 * (X/\text{CO})^2 + \text{CO}^2 * \sigma_{X/\text{CO}}^2} \times (M_x/M_{\text{CO}}) \times 10^{-3} \quad (2)$$

where σ_x is the uncertainty for halocarbon emission, and σ_{CO} and $\sigma_{\Delta X/\Delta \text{CO}}$ are the uncertainties for the slope of X/CO and CO emission, respectively.

Among the anthropogenic CO emissions sources, fossil fuel-related CO is mostly emitted in urban and industrial areas, which are also large sources of halocarbons (Yokouchi et al., 2006). Biomass burning-related CO also contributes to CO pollution episodes and ΔCO , while the ratio of biomass-burning CO to halocarbons is considered to be much lower than the ratio of whole CO emissions to halocarbon (Palmer et al., 2003b). Thus, we used the fossil fuel-related CO emissions, rather than total anthropogenic CO emissions, in calculating Eq. (1). While anthropogenic CO emissions (excluding biomass burning) in Guangdong Province were estimated, using the inventory synthesis model, to range from 5900.8 Gg (in 2000, within 95% confidence intervals, overall uncertainty $\pm 185\%$) to 8693.1 Gg (in 2006, within the same 95% confidence intervals, overall uncertainty $\pm 70\%$) (Streets et al., 2006b; Zhang et al., 2009),

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CO emission estimates for the greater PRD region are relatively good as a result of detailed technology-based data, the proxy methodology of rapid technology renewal, and the rigorous compilation of energy statistics.

However, we found that there is lack of CO emissions estimates for the PRD region in 2004, even for Guangdong Province, despite many CO emissions estimation studies in the past decade that have used both bottom-up and top-down approaches to quantify integrated Chinese emissions (Allen et al., 2004; Kopacz et al., 2009; Palmer et al., 2003a; Streets et al., 2003, 2006b; Tanimoto et al., 2008; Tonooka et al., 2001; Wang et al., 2004a, b; Zhang et al., 2009). Thus, a bottom-up approach was adopted in this study for CO emission estimation. The regional CO emission inventory for the PRD region in 2004 was budgeted using the best available emissions factors and activity data. CO emissions determined by factors such as transportation, industry, residential power, and their activity data in 2004 for the PRD region were combined with the latest emission factors, according to Zhang and Zheng (Zhang et al., 2009; Zheng et al., 2009b). The result was an emission of 6996.2 (± 3761.0) Gg CO from Guangdong in 2004. Based on the provincial emissions, the CO emissions for the PRD region were spatially allocated with gross domestic product (GDP), depending on the source characteristics and grid cell size using a Geographic Information System. The results showed an estimated CO emission in the PRD region for 2004 of 3265.2 Gg with an overall uncertainty of ± 2034.5 Gg, slightly lower than the CO estimate of Zheng et al. (2009b), who reported a CO emission of 3840.6 Gg from the same region in 2006.

3 Results and discussion

3.1 Halocarbon concentration and speciation

Approximately one month of PRD data, from 4 October to 3 November 2004, was chosen for analysis. The 16 trace gases measured by GC-FID/MS, coupled with a cryogenic pre-concentrator system, were: CFC-11, CFC-12, CFC-113, CFC-114,

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HCFC-22, CH₃CCl₃, CCl₄, CHCl₃, CH₂Cl₂, CH₃Cl, CH₃Br, CCl₂ = CCl₂, CHCl = CCl₂, CHCl₂CH₂Cl, CH₃CH₂Cl, and CH₃CHClCH₂Cl. These substances were chosen for analysis because they were detectable at the limits of the GC-FID/MS analysis system at that time, and they account for more than 80% of all halocarbons in the atmosphere (Wang et al., 2000b). These samples were divided into two categories, based on daily sampling schedule. At the First, the routine ambient atmospheric air samples were collected for 60 min each, at 05:30, 07:30, and 14:00 in Guangzhou, and at 07:30 and 14:00 in Xinken. Secondly, samples to examine diurnal variation were taken every 2 h for 30 min from 06:00 to 22:00 at Guangzhou and Xinken on 9 and 21 October and 3 November 2004.

The statistical results (Table 2) showed elevated regional mixing ratios of most halocarbons, especially for HCIC = CCl₂, CH₂Cl₂, CH₃Br, HCFC-22, CHCl₃, CCl₄, Cl₂C = CCl₂, CH₃CCl₃, and CFC-12, relative to ratios from TRACE-P, ALE/GAGE/AGAGE. The results are showing that the concentrations of halocarbons were more variable in the PRD region, with only the RSD of CFC-11, CFC-12, CFC-113, and CH₃Cl being below 25%, lower than that of other halocarbons. This indicates that these four halocarbons had relatively stable sources, whereas the others may have more unexpected sources, such as emissions from stockpile leakage and unknown production or usage (Chan et al., 2006; Chan and Chu, 2007; Wang et al., 2000a). Therefore, all of the halocarbons in our study exhibited more variation in concentrations than in the global background site of the ALE/GAGE/AGAGE global network program; for example, the RSDs of HCFC-22 and CFC-12 were greater than 12% in the PRD region, but less than 1% at the AGAGE stations. Moreover, concentrations of HCFC-22 and CFC-12 were peaked at 1879 pptv and 1411 pptv, respectively, on 11 October 2004, while the global background values (see Table 1) for the two halocarbons were 158–178 pptv and 542–546 pptv, respectively. The fact that peak concentrations of both of these halocarbons in the PRD region greatly exceeded global background values indicates that there were at least occasional anthropogenic emissions of HCFC-22 and CFC-12 during the sampling period. Moreover, the median emission values of

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HCFC-22 and CFC-12 were 377 pptv and 682 pptv, respectively, which are more than 1.5 times than the background values, suggesting long-term sources of emissions for both of these halocarbons. Although the phase-out of CFC-12 under the Montreal Protocol is still in the future in the PRD regions and for all Article 5 countries, HCFC-22 has been used extensively since 2004 as an alternative to CFCs in Guangdong Province, while better substitutes are developed (Hoffman, 1990).

Table 3 compares the mixing ratios of selected halocarbons measured in the PRD region with those reported for Bristol (Rivett et al., 2003), Athens (Glavas et al., 2002), Philadelphia, Las Vegas, Marseille (Barletta et al., 2006), Beijing (Qin, 2007), Kraków (Lasa et al., 2003), Shanghai (Barletta et al., 2006), Guangzhou, Panyu, Dinghu, and Xinken (Chan et al., 2006; Chan and Chu, 2007; Chang et al., 2001, 2008). With the exception of Karachi, Pakistan, most halocarbon species had higher mixing ratios and variability in the PRD region.

3.2 Emission estimates for each halocarbon

With the respect of the high variability in halocarbons concentrations for PRD region, if there are no natural or biogenic sources for a halocarbon, the pollution episodes identified by concentration enhancements should be linked to the local emissions, and the short-term enhancement of atmospheric mixing ratios can be considered as a sign of recent anthropogenic emissions (Dunse et al., 2005; Hurst et al., 2006; Yokouchi et al., 2005). Thus, there were statistically positive relationships between X and CO were shown in Fig. 2. Uncertainty for X/CO ratio was calculated in the standard manner assuming linear model (Cantrell, 2008), and presented as the standard deviation ($\sigma_{X/CO}$). According to Eq. (1), by multiplying the X/CO ratio and 3265.2 Gg (uncertainty of ± 2034.5 Gg) CO emissions from the PRD region, regional halocarbon emissions can be calculated in Table 4, and their uncertainties determined by Eq. (2).

It is noteworthy that the correlation between some species such as CFC-113, CFC-114 and CH₃CH₂Cl and CO are not significant (Table 4). In such a case, the slope X/CO would be zero and hence Eq. (1) would give zero emissions for these species.

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In fact, the ambient mixing ratio of the above three species are much lower than the others, it is has already proven an aspect for their lower emissions. Additionally, the X/CO ratio of these species were approximately equal to zero also shown that there are few anthropogenic relative emissions since CO was taken as an anthropogenic trace gas . Furthermore, uncertainty are in same magnitude with the X/CO slope for each species, take CFC-114 as a example, more than 80% of the uncertainty for the slope. Thus there are some defects for our method to made a quantitative estimate for the three species, but the ratio estimate emission results still can be worked as a reference value for qualitative the minor emission characterization.

3.2.1 Methyl chloroform (CH_3CCl_3 , MCF)

The depleting effect of a halocarbon gas on stratospheric ozone can be expressed in terms of ozone depletion potential (ODP). However, the ODP of MCF (atmospheric lifetime 5–6 years) is only 0.12, so that the MCF plays a minor role in stratospheric ozone depletion. More important, the MCF measurements can be use in determining the behavior of the hydroxyl radical (OH) (Prinn et al., 2001, 1995). But , the ongoing emissions cast a doubt on recent reports for the strong and unexpected negative trend in OH during the 1990s, also as the previously calculated higher OH abundance in the Southern Hemisphere more than the Northern Hemisphere (Krol et al., 2003). Thus, definite conclusions about the global OH distribution and trends cannot be drawn until the emissions and distribution of MCF are better quantified (Krol et al., 2003; Millet et al., 2004).

Previous studies have shown that both the concentration and variability of MCF emissions from the PRD region are significantly greater than those from Taipei, which has a different schedule for implementing the Montreal Protocol than the Chinese mainland. These data indicate that the PRD region continues to produce MCF emissions (Chang et al., 2008). Combining the MCF/CO (0.0228 ± 0.0028 pptv ppbv⁻¹) slope with the CO emission by Eq. (1), it leads to a value of 0.4 ± 0.2 Gg for MCF emission in the

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PRD region. Comparison with the similar research for other regions, The $\Delta\text{MCF}/\Delta\text{CO}$ slopes for air samples from Korea ($0.044 \text{ pptv ppbv}^{-1}$) and Japan ($0.023 \text{ pptv ppbv}^{-1}$) (Palmer et al., 2003b) were a little higher than our measurements for the PRD region, but emissions ratios measured over the United States ($0.017 \text{ pptv ppbv}^{-1}$) and Mexico ($0.0017 \text{ pptv ppbv}^{-1}$) (Millet et al., 2009), and even from the TRACE-P missions over mainland China ($0.013 \text{ pptv ppmv}^{-1}$) (Palmer et al., 2003b), were lower than those from the PRD. Further more, according to National emissions of MCF based on consumption in 2004 were determined to be 4.8 Gg (Wan et al., 2009) in china; thus, our results indicate that Guangdong Province contributes about 14.9% of Chinese MCF emissions, as the contribution of the PRD region was 7.4%. In fact, not only PRD regional emissions but also the Chinese national MCF emissions were concerned by the scientific community. Using anthropogenic CO emissions (Palmer et al., 2003b) deduced that the anthropogenic MCF emissions from China were about 10.4 Gg, consistent with emission estimates for the “Far East,” extrapolated to be 11 Gg through 2000 by McCulloch et al. (2001a), but only 1.0 to 1.8 Gg MCF emission from Japanese and Korean MCF based on aerial survey results (Yokouchi et al., 2005).

Actually, MCF emissions around the world need to be eliminated yet. Unfortunately, not only for this study but other previous researches have observed that the continuing emissions is both from the developed world and developing countries, such as United States (Millet et al., 2009; Millet and Goldstein, 2004), Europe (Krol et al., 2003), and Japan (Palmer et al., 2003a). It was generally thought to represent the slow release from legal stockpiles accumulated prior to the ban and other unknown sources (McCulloch and Midgley, 2001b). With the implementation of MCF phase out in production and consumption for Chinese government after 2004, sales and production figures are no longer reliable proxies of emissions, it is essential need to verify the PRD regional inventory data in 2004 as providing a effective estimates method for further time . As shown in Fig. 3, our ratio estimate was agree with inventory data, it is possible because that the most of MCF is used as an industrial cleaning solvent and emitted into the atmosphere immediately after use (more details will be discussion

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in Sect. 3.3). Therefore, In situ regional atmospheric measurements could provide a reasonable method for validating actual MCF emissions estimates after the phase out period.

3.2.2 CH_2Cl_2 , $\text{CCl}_2 = \text{CCl}_2$, and $\text{CHCl} = \text{CCl}_2$

5 Chlorinated hydrocarbons, such as dichloromethane (DCM), perchloroethylene (PCE), and trichloroethylene (TCE), are used extensively in painting, dry cleaning, metal degreasing, as intermediates in the production of adhesives, foams, plastics, pharmaceuticals, and even as chemical feedstocks for the manufacturing of hydrofluorocarbons (HFCs) and related refrigerants (Olague, 2002). Other potential sources of these
10 chemicals in the atmosphere include vehicle exhaust and the combustion of coal. Non-anthropogenic fluxes of these chemicals have been identified from the ocean and biomass burning (Khalil et al., 1999), but these natural sources are not usually considered significant inputs in industrial regions. According to (McCulloch et al., 1999b), the industrial emissions of chlorinated hydrocarbons around the world ($1^\circ \times 1^\circ$ grid size)
15 can be estimated by combining three data sets: regional sales data, gross domestic products, and population distributions within each area. Moreover, Wiedmann et al. (1994) used an arbitrary factor to convert American estimates of PCE production into a global value, and (Koppmann et al., 1993; Rudolph et al., 1996) derived estimates of global emissions of DCM and PCE from their measurements. These chlorinated hydrocarbons can be oxidized by OH radicals, and all three of these chlorinated hydrocarbons have atmospheric lifetimes (158, 105, and 4.3 days for DCM, PCE, and TCE respectively) of less than 6 months (Singh et al., 1996), which is shorter than their inter-hemispheric exchange time (1.0 year) (Olague, 2002). Additionally, there are also
20 seasonal cycles without any interference from anthropogenic patterns (Simpson et al., 2004). Thus, the ratio emission estimates method could be helpful on understanding the atmospheric processes (McCulloch et al., 1999b, 1996) and their seasonal variability (Gentner et al., 2010).
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Using the correction between the CO and PCE inventories from the Forest and Atmosphere Chromatograph for Trace Species (FACTS) research at Harvard Forest, Barnes et al. (2003) derived the urban/industrial emissions of PCE from CO inventory emissions values and found that urban/industrial emissions of PCE appeared to be rising in 1998. Similarly, we used flash-sampling observations for these chlorinated hydrocarbons and CO to deduce the emissions from the PRD region on a regional scale. We first determined the X/CO ratios, which were 0.7090 ± 0.1280 , 0.1180 ± 0.0212 , and 0.4380 ± 0.0699 pptv ppbv⁻¹ for DCM, PCE and TCE respectively, and then used Eq. (1) to determine the DCM, PCE, and TCE emissions were 7.0 ± 4.6 , 2.3 ± 1.5 , and 6.7 ± 4.3 Gg from PRD region in 2004.

The slope of $\Delta\text{PCE}/\Delta\text{CO}$ for the PRD region was less than that for New York City Washington, DC, which was 0.3241 ± 0.0560 pptv ppbv⁻¹ (Barnes et al., 2003), and the emissions were also lower than in urban/industrial pollution regions in the United States from 1996 to 1997, when emissions ranged from 10.91 to 11.70 Gg (Barnes et al., 2003). According to (Olague, 2002) and (McCulloch et al., 1999b), the industrial regions of North America, Europe, and Japan are the largest sources of anthropogenic PCE emissions. Similar to these developed regions, the PRD, also known as the largest developing region in the world, is a significant new source of global PCE, with emissions from Guangdong Province already contributing 10.3% of the PCE emissions from the “Far East” (47 Gg) (McCulloch et al., 1999b), and only the PRD region (2.3 Gg) could contribute more than 4.8% of the total PCE emissions for East Asia. Among the target halocarbons in the present study, the estimated emissions of DCM, PCE, and TCE accounted for 62.9% of the total emissions. This suggests that solvents used by the electronics industry for paint removal, dry cleaning, and metal degreasing in the PRD area contribute significantly to ambient halocarbons’ concentration.

As both the DCM and TCE were not subject to the Montreal Protocol controls, they have been used extensively in developing and developed countries, so the high emissions could be found for both of these halocarbons in this study. In the mid 1990s, the United States Environmental Protection Agency (US EPA) expressed concerned about

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DCM and TCE, based on information provided by (McCulloch and Midgley, 1996), who pointed out that both of these short-lived halocarbons have non-negligible atmospheric impacts, including ozone depletion potential and global warming effects, the Chinese government should also be suggested to attach great importance to the emission of these chlorinated hydrocarbons. Unfortunately, previous study also found that Japan, one of the largest sources of DCM and TCE in eastern Asia, had estimated DCM and TCE emissions of 26.1–35.7 Gg and 18.6–21.2 Gg, respectively in 2002, based on aircraft monitoring data from Sagami Bay (Yokouchi et al., 2005). Similarly, (Millet et al., 2009) used aircraft measurements from the United States and Mexico to measure anthropogenic halocarbon emissions, and calculated a $\Delta\text{DCM}/\Delta\text{CO}$ of 0.239 (0.178 ~ 0.290) pptv/ppbv and $\Delta\text{TCE}/\Delta\text{CO}$ of 0.048 (0.036–0.059) pptv ppbv⁻¹, for emissions of 16–32 Gg and 4.8–10 Gg for DCM and TCE, respectively. Developed countries clearly have large emissions of DCM and TCE. However, with the development of transportation and the increase of industrial enterprises, the PRD region has also increased its emissions of DCM (7.0 ± 4.6 Gg) and TCE (6.7 ± 4.3 Gg).

3.2.3 Chlorofluorocarbons (CFCs)

As listed in Annex A, Group I substances in Montreal Protocol, CFC-11, CFC-12, CFC-113 and CFC-114 were also included in our research. According to the protocol, the Chinese government freeze the CFC emissions before 2004. However, consumption of CFCs by Article 5 parties was still allowed, if the end-use was considered “essential” under the terms of the protocol until 2010, when CFCs were supposed to be entirely phased out. Thus, the Chinese government committed to freeze CFC emissions at 1995–1997s levels of actual use and to begin using alternatives (Chan and Chu, 2007).

There are statistically significant corrections between the CO and CFC-11, CFC-12 (Table 4), but only weakly positive correlations can be gotten between the CO and CFC-113, CFC-114. The slopes of CFC-11/CO, CFC-12/CO, CFC-113/CO, and CFC-114/CO were 0.0222 ± 0.0048 , 0.1100 ± 0.0199 , 0.0015 ± 0.0020 , and

0.0010 ± 0.0008 pptv ppbv⁻¹, respectively. Based on these X/CO slopes, regional CO emissions and Eq. (1), the emissions of CFC-11, CFC-12, CFC-113, and CFC-114 for the PRD were 0.4, 1.6, 0.0, and 0.0 Gg, respectively. Our emission results for CFC-12 agree with the halocarbon emission estimates for the inner PRD of (Guo et al., 2009), who reported emission levels of 1.0, 1.5, and 0.9 Gg for CFC-11, CFC-12, and CFC-113, respectively, for 2001 and 2002. Among the four target CFCs, CFC-11 and CFC-12 were the most abundant substances, both of which were used as foam-blowing agents, aerosol propellants, and refrigerants before the introduction of replacements (McCulloch, 2003; McCulloch et al., 2001a, 2003). Thus, any of these products that remain in service or continue to experience minor leakage could be major sources of current CFC emissions into the atmosphere. Conversely, there were almost no emissions of CFC-113 and CFC-114 in Guangdong Province. The mean concentrations of CFC-113 (97 pptv) and CFC-114 (18 pptv) were slightly greater than background values (Tables 1 and 2).

3.2.4 Hydrochlorofluorocarbons (HCFCs)

In recent years, production and consumption of CFCs had been declined, while HCFCs, as temporary replacements for CFCs, has been increased significantly (Chan et al., 2006; Chan and Chu, 2007; Zhang et al., 2006). Here, we focus only on HCFC-22, which is a major substitute for CFC-12, the original refrigerant gas, and is commonly used in commercial refrigeration and transport. Leaks from refrigeration systems and occasional emissions from uses such as aerosol propellants, solvents, and foam-blowing agents have lead to a prevalence of HCFC-22 emissions. McCulloch et al. (2003) point out that the phase out of CFCs should have lead to a significant increase in HCFC-22 emissions starting in the early 1990s.

The HCFC-22 emissions in 2004 in the PRD region, determined by the ratio estimates method, were 3.5 ± 2.2 Gg, approximately 2.3 times the emissions of CFC-12. Because of the widespread availability of the alternative, HCFC-22, and the more

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rigorous stepped controls on CFC-12, the ratios between HCFC-22 and CFC-12 in developed areas are higher than in the PRD region (e.g., HCFC-22/CFC12 emission ratios for the United States and Japan were reported to be 5.2 and 4.3, respectively Millet et al., 2009; Yokouchi et al., 2005). These results suggest that CFC-12 must continue to be phased out and replaced with HCFC-22 in the PRD region.

3.2.5 Other halocarbons

Emission estimates and uncertainty ranges for other anthropogenic halocarbons in the PRD region are listed in Table 4. Among these halocarbons, carbon tetrachloride (CCl_4) and chloroform (CHCl_3) are used primarily as feed stocks for producing CFC-11, CFC-12, and HCFC-22 (Aucott et al., 1999; Hurst et al., 2006). About 75% of CHCl_3 in China is consumed in the pharmaceutical industry to produce HCFC-22 (Chan and Chu, 2007), and about 80–90% of CCl_4 is consumed to produce CFC-11 and CFC-12 (Simmonds et al., 1998). Because the Montreal Protocol and its various amendments have listed CCl_4 as a controlled substance, together with the continuing phase-out of CFC-11 and CFC12, large-scale production of this species has been declining rapidly. However, CHCl_3 is not regulated under the Montreal Protocol, and regional emissions continue. According to our estimates, emissions of CCl_4 and CHCl_3 from the PRD region were 1.1 ± 0.7 and 0.8 ± 0.6 Gg respectively, indicating widespread anthropogenic use of these halocarbons in this region. Based on a positive matrix factorization receptor model analysis and correlations of the mixing ratios of CCl_4 , CHCl_3 , and DCM (a solvent tracer) (Guo et al., 2009) suggested that solvents were the main source of CCl_4 in the inner PRD region, but not the most important contributor of CHCl_3 .

CH_3Br was regulated under the Montreal Protocol as an Annex E controlled substance, and emissions have been frozen in China since 2004. Our emissions estimates for CH_3Br and CH_3Cl were 0.1 ± 0.1 Gg and 0.6 ± 0.4 Gg, respectively. Similar emissions, 0.27 ± 0.06 Gg and 5.4 ± 0.4 Gg for each of CH_3Br and CH_3Cl have been reported from Japan (Yokouchi et al., 2005). In addition to anthropogenic sources, such as coal combustion and incineration, CH_3Br and CH_3Cl have also natural sources,

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including the oceans, vegetation, and biomass burning (Grimvall et al., 1995; Rhew et al., 2000). CH_3Cl , especially, can be emitted from oceanic or terrestrial biogenic processes, and can be a byproduct of biomass burning as well as exclusively anthropogenic activities (McCulloch et al., 1999a). However, no significant correction between oceanic tracers and biogenic tracers was found in the same areas, indicating that the tropical coastal belt is not likely the main CH_3Cl source in the PRD area (Guo et al., 2009). In the case of CH_3Br , the dominant anthropogenic source is from fumigant use, mostly applied in agricultural areas rather than in industry. Thus, the CO-based estimate for CH_3Br could be quite uncertain, one needs to be careful for emission results from the ratio estimate method. Additionally, the concentrations of CH_3Br (more than 20 pptv for 20th percentile of the dataset) and CH_3Cl (more than 900 pptv for 20th percentile of the dataset) in PRD were much higher than at any oceanic background sites (8.40 for CH_3Br and 486.10–535 pptv for CH_3Cl ; Table 1), further indicating that a large part of these CH_3Br and CH_3Cl emissions are not from oceanic sources.

3.3 Comparison with emission inventories

Where possible, comparisons of the enhancement ratio estimates results of the halocarbons were made with estimates from inventory techniques. However, limited data were available from the bottom-up inventory method, based on production and consumption, the available inventory information for four CFCs, CFC-11, CFC-12, CFC-113, and CFC-114, is plotted in Fig. 3. Another reason for choosing these CFC species is that they continued to be consumed prior to 1 July in 2007, according to the accelerated phase-out plan for CFCs, which includes CFC-11, CFC-12, CFC-113, CFC-114, CFC-13, and CFC-115 in China (United Nations Environment Programme (UNEP), 2004). Additionally, as reported by the State Environmental Protection Administration of China, these four CFCs accounted for more than 99% of all CFCs consumed (Wan et al., 2009). Thus, neither CFC-13 nor CFC-115 is included in this comparison. Because the studied CFCs are primarily consumed in the refrigeration, air-conditioning, foam blowing, solvent, tobacco, aerosol, and chemical industry sectors, the inventoried

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halocarbon emissions from these seven sectors were aggregated. A method developed based on the Intergovernmental Panel on Climate Change Good Practice Guidance was introduced to estimate the inventoried emissions (Wan et al., 2009).

Our enhancement ratio estimates of CFC-11 and CFC-12 were 23.4% and 165.3% of the respective inventory estimates. These results suggest a more rapid phase-out of CFC-11 than CFC-12. Also, predictions of industry inventory models that included data on annual leak rates and release profiles from the seven sectors may also have been overestimated for CFC-11, but not for CFC-12. Other explanations for the higher inventory estimates for CFC-11 may be an overestimate of the residual stock of blown-in foam, and the low inventory estimates for CFC-12 may be due to the presence of many unexpected sources of refrigeration systems in the PRD region (e.g., the number of remaining vehicles with CFC-22 charged air-conditioning systems is still uncertain).

Prior to the ban on CFC-113 and CFC-114, the primary use of both of these CFCs was as a cleansing agent for electrical and electronic components. In this manner, these species would be released directly into the atmosphere upon use; thus, it is reasonable to assume that the ratio estimates closely follow consumption. The CFC-113 and CFC-114 annual emissions from the PRD region in 2004 were 0.12 and 0.00 Gg, respectively, compared with the values of 0.04 ± 0.05 and 0.02 ± 0.02 Gg from the present study. The production and consumption of these two CFCs were much lower than those of CFC-11 and CFC-12, and they were also brought under the control of the Montreal Protocol in China before CFC-11 and CFC-12. Thus, both CFC-113 and CFC-114 were approaching zero emissions in the PRD region in 2004. The lower emission levels of these two CFCs were confirmed by both ratio and inventory estimate methods.

Since the Montreal Protocol came into effect, not only the production but also the consumption of CFCs has been declined in China. However, demand for HCFC-22 appears to be governed by organic growth, and the decreasing CFCs trends are countered by the substitution of HCFCs (McCulloch et al., 2006). Evidently, the Chinese HCFC-22 emissions are substantial (inventory estimate 33.8 Gg in 2004; Wan et al.,

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2009), but the contribution of Guangdong Province alone accounted for more than 14.5% of the national inventory estimate. The PRD, the most active region in Guangdong Province, emitted about 3.9 Gg HCFC-22, based on bottom-up estimates. Our ratio estimates were about 89% of the inventoried emissions. Thus, there was good consistency between different methods for HCFC-22 emissions, but the ratio estimation method had greater uncertainty (2.2 Gg).

Emissions inventories of MCF and CCl₄ were also aggregated sector by sector for comparison. These halocarbons were used primarily as industrial cleaning solvents, and were therefore emitted into the atmosphere immediately. As a result, the consumption data should provide a reliable estimate of emissions. The inventory consumption data suggested emissions of 0.38 and 1.14 Gg for MCF and CCl₄, respectively, which are in good agreement with the emissions results (0.35 and 1.05 Gg for MCF and CCl₄, respectively) from the enhancement ratio estimate method.

A comparison of the available species for the study period in 2004 is shown in Fig. 3. Considerable interspecies variation under the enhancement ratio technique is evident. Furthermore, linear curve fitting ($y = 0.99x + 0.19$; $R = 0.91$) of the estimated emissions for the different species and methods are also showed that the overall estimate was very close to the unbiased estimate ($y = x$). Emission estimates using two different approaches were of similar magnitude for most halocarbons (except CFC-11 and CFC-12). Thus, we are cautiously optimistic that the method used here has potential for assessing regional halocarbon emissions.

4 Conclusions

The PRD is one of the most important industrial and manufacturing regions in China and even for the world. To evaluate ambient levels and variation of halocarbons in this region, 124 whole air samples were collected from urban and rural sites in October and November 2004. Compared with corresponding global surface mixing ratios, based on ALE/GAGE/AGAGE data or other literature, the concentrations of halocarbons emitted

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from the PRD region and many other urban areas exhibited more variation and higher mixing ratios than those from background sites. The RSDs of CFC-11, CFC-12, CFC-113, CFC-114, and CH_3Cl were less than 25%. By contrast, the RSDs of HCFC-22 (more than 60%) and other halocarbon gases were significantly greater. These results indicate that emissions, mixing, and removal of anthropogenic halocarbons were still occurring in the PRD region in 2004.

Given the several assumptions listed in the introduction, local anthropogenic CO emissions can be used to deduce regional halocarbon emissions in the PRD area. Briefly, linear correlations between the enhancement of halocarbons and CO were observed by analyzing the air samples, and halocarbon emissions were deduced from the regression slopes (X/CO) and CO emissions inventories. Where possible, comparisons of these estimates were made with estimates from inventory techniques. Results showed that the ratio estimates of CFC-11 and CFC-12 were 23.4% and 165.3% of the respective inventory estimates. Very low emissions of CFC-113 and CFC-114 was detected in the PRD region in 2004, 0.04 ± 0.05 and 0.02 ± 0.02 Gg, respectively, comparing with 0.12 and 0.00 Gg from inventory estimates. As CFC consumption decreases, consumption of HCFC-22, the temporary substitute for CFCs, appears to be governed by organic growth in the region. The PRD emitted about 3.9 Gg HCFC-22, based on the bottom-up estimate for 2004, and the ratio estimate was about 89% of the inventory result. Thus, there was good consistency in HCFC-22 emissions between the different estimate methods. Similarly, the emission results from the enhancement ratio estimate and the inventory algorithm were also in good agreement for MCF and CCl_4 . Although there were no inventory data for other species for comparison with different emissions estimates, comparisons revealed similar results for many halocarbons from the ratio estimate method and the inventory technique, better is possible that the calculated results for both methods were same in order of magnitude.

Among the studied halocarbons emitted in the PRD region, the combined estimated emissions of DCM, PCE, and TCE accounted for about 63% of the total emissions, suggesting that these species are used extensively in industrial and

commercial processes. Emissions of HCFC-22 (3.5 Gg), the primary alternative refrigerant to CFCs, were about 2.3 times higher than the emission of CFC-12 (1.6 Gg) in the PRD, these refrigerants could account for about 20% of the total mass of halocarbon emissions as the second largest contributor. Moreover, emissions of other anthropogenic halocarbons (CHCl_3 , CH_3Br , and so on) from Guangdong Province were also estimated.

In conclusion, whole-air sampling analysis and atmospheric observations play an important role in assessing halocarbons emissions on a regional scale, especially in a developing with high halocarbon pollution enhancement region, such as the PRD. Comparison of independent emissions estimate results with available inventories further verified regional halocarbon emissions, and can help provide information on regional conformity to the Montreal Protocol. With more sampling sites, longer-term and higher-frequency observations, and improvements and updates to CO inventories, the uncertainty of the ratio estimates should be reduced significantly.

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Table 1. Comparison of the halocarbons' background concentrations measured from the Global background observation stations, TRACE-P field campaign, GZ, and XK.

Halocarbon X	MaceHead	CapeGrim ^b	CapeMatatula	RaggedPoint	TrinidadHead	TRACE-P ^c	XingKen ^d	GuangZhou
CFC-11	252 ^a	250	250	252	252	259	274	280
CFC-12	544	541	542	544	545	545	604	644
CFC-113	79	79	78	79	–	79	97	87
CFC-114	–	–	–	–	–	14	13	15
HCFC-22	176	158	–	–	–	–	228	381
CH ₃ CCl ₃	21	21	20	20	21	40	46	52
CCl ₄	93	91	92	93	93	99	88	207
CHCl ₃	11	6	4	6	12	9	36	50
CH ₂ Cl ₂	27	10	–	–	–	28	249	256
CH ₃ Cl	486	534	–	–	–	535	940	996
CH ₃ Br	–	–	–	–	–	8	21	21
Cl ₂ C = CCl ₂	3	1	–	–	–	5	72	55
HCIC = CCl ₂	1	–	–	–	–	–	171	224
CHCl ₂ CH ₂ Cl	–	–	–	–	–	–	9	15
CH ₃ CH ₂ Cl	–	–	–	–	–	–	8	8
CH ₃ CHClCH ₂ Cl	–	–	–	–	–	–	26	24

^a The background concentrations are in pptv.

^b The 20th percentile of ALE/GAGE/AGAGE data (<http://agage.eas.gatech.edu/data.htm>) between Octobers to November 2004 was defined as the Global background values.

^c The Lowest 25th percentile of airborne TRACE-P data collected below 1500m for the background values of Western North Pacific, we consider these results as the PRD regional background levels Barletta et al. (2006); Blake et al. (2003).

^d The lowest 20th percentile of the dataset for Guangzhou and Xinken are also shown here.

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Table 2. Describe statistics results of the halocarbons mixing ratio for PRD region, means comparison were made with TRACE-P and ALE/GAGE/AGAGE data.

Halocarbon X	PRD Regions			Guangzhou			XinKen			TRACE-P ^b			Cape Grim ^c		Mace Head		Cape Matatula		Flagged Point		Trinidad Head			
	Mea ^a	Median	RSD.	n	Mean	Median	RSD.	n	Mean	Median	RSD.	n	Mean	RSD	Mean	RSD	Mean	RSD	Mean	RSD	Mean	RSD		
CFC11	300	297	9.31%	124	304	304	8.81%	60	295	286	9.79%	49	284	12.32%	250	0.10%	252	0.31%	251	0.15%	252	0.16%	252	0.25%
CFC12	700	682	17.81%	124	739	721	18.30%	60	652	636	13.91%	49	564	6.03%	542	0.27%	545	0.15%	543	0.11%	545	0.15%	546	0.28%
CFC113	97	96	11.62%	124	92	91	5.45%	60	102	102	13.43%	49	90	11.11%	79	0.23%	79	0.28%	79	0.40%	79	0.21%	-	-
CFC114	18	16	25.02%	124	19	18	25.25%	60	16	14	20.82%	49	15	3.33%	-	-	-	-	-	-	-	-	-	-
HCFC22	464	377	62.58%	124	602	527	53.77%	60	295	272	29.85%	49	220	32.27%	158	0.86%	178	1.74%	-	-	-	-	-	-
CH3CCl3	62	56	31.46%	124	62	56	27.81%	60	61	55	35.85%	49	49	10.20%	21	1.54%	21	3.76%	20	1.48%	20	3.60%	21	1.34%
CCl4	194	201	49.52%	124	263	234	27.71%	60	110	98	29.43%	49	114	9.65%	92	0.23%	93	3.25%	92	0.36%	93	0.42%	93	0.23%
CHCl3	96	60	80.78%	124	124	103	64.91%	60	62	45	94.96%	49	48	56.25%	9	46.56%	15	30.07%	5	3.75%	6	13.50%	14	18.27%
CH2Cl2	1028	740	78.09%	124	855	637	84.69%	60	1239	1027	68.55%	49	226	102.65%	10	12.01%	34	37.64%	-	-	-	-	-	-
CH3Cl	1165	1152	18.06%	124	1180	1190	17.38%	60	1147	1104	18.95%	49	952	28.68%	590	16.63%	518	7.48%	-	-	-	-	-	-
CH3Br	47	46	56.32%	122	48	47	54.40%	60	44	44	59.21%	47	13	23.08%	-	-	-	-	-	-	-	-	-	-
CCl2 = CCl2	170	155	75.99%	124	164	157	70.28%	60	179	143	81.74%	49	129	153.49%	-	-	-	-	-	-	-	-	-	-
HClO = Cl2	467	294	96.55%	124	420	276	75.35%	60	525	346	109.21%	49	21	185.71%	-	-	-	-	-	-	-	-	-	-
CHCl2CH2Cl	34	23	90.59%	113	41	31	80.30%	60	23	12	106.10%	38	-	-	-	-	-	-	-	-	-	-	-	-
CH3CH2Cl	23	17	85.43%	120	21	16	71.38%	59	26	19	93.74%	46	-	-	-	-	-	-	-	-	-	-	-	-
CH3CHClCH2Cl	53	46	63.48%	123	56	52	59.78%	59	295	286	9.79%	49	-	-	-	-	-	-	-	-	-	-	-	-

^a Mean and median of the mixing ratios are in pptv.

^b Average extracted from TRACE-P data were provided by Barletta et al. (2006).

^c ALE/GAGE/AGAGE data between Octobers to November 2004 were selected for analyzing.

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Table 3. Mixing ratios levels of selected halocarbon measured in cities around the world.

Halocarbon Studies	CFC-11		CFC-12		CFC-113		CFC-114		HCFC-22		CHCl ₃	
	Con.	Rsd	Con.	Rsd	Con.	Rsd	Con.	Rsd	Con.	Rsd	Con.	Rsd
Bristol, England (Aug–Sep 2000), Rivett et al. (2003)	301	61%	566	17%	–	–	–	–	–	–	45	56%
Philadelphia, United states (Feb 2001), Barletta et al. (2006)	273	14%	567	12%	81	4%	15	7%	–	–	27	48%
Las Vegas, United states (February 2001), Barletta et al. (2006)	259	4%	545	9%	79	3%	15	7%	–	–	28	111%
Marseille, France (Jun–Jul 2001), Barletta et al. (2006)	288	9%	564	7%	84	4%	16	25%	–	–	25	68%
Karachi, Pakistan (Dec 1998–Jan 1999), Barletta et al. (2002)	298	11%	650	19%	83	3%	14	9%	295	91%	241	232%
Kraków, Poland (Jul 1997–Sep 1999), Lasa and Sliwka (2003)	267	1%	–	–	83	2%	–	–	–	–	41	24%
Athens, Greece (Jul–Aug 2000), Glavas and Moschonas (2002)	–	–	–	–	–	–	–	–	–	–	–	–
Bristol, England (Oct 2004–Dec 2005), Khan et al. (2009)	255	28%	545	8%	–	–	–	–	315	153%	39	143%
Chinese 45 cities (Jan–Feb 2001), Barletta et al. (2006)	284	12%	564	6%	90	11%	15	3%	–	–	48	56%
Shanghai (Jan–Feb 2001), Barletta et al. (2006)	265	3%	547	3%	83	4%	14	4%	–	–	38	11%
Shanghai (Plume encountered during TRACE-P on March 2001), Barletta et al. (2006)	280	4%	566	4%	90	13%	15	1%	–	–	76	51%
Beijing, China (Jan 2005–Mar 2007), Qin (2007)	312	15%	613	12%	85	12%	–	–	–	–	–	–
Guangzhou, PRD of China (Mar 2001), Chan et al. (2006)	361	26%	720	14%	97	13%	16	6%	553	76%	181	271%
Panyu, PRD of China (Sep–Dec 2001), Chan et al. (2006)	302	9%	820	80%	97	16%	16	0%	274	23%	52	29%
Dinghu, PRD of China (Mar 2001), Chan et al. (2006)	291	5%	580	3%	93	9%	16	0%	205	22%	33	30%
Guangzhou, PRD of China (Nov 2004), Chan et al. (2008)	310	10%	751	29%	93	7%	–	–	–	–	–	–
Xinken, PRD of China (Nov 2004), Chan et al. (2008)	291	10%	638	15%	93	10%	–	–	–	–	–	–
Urban and rural site of PRD, China (Oct–Nov 2004) (This study)	300	9%	700	18%	97	12%	18	26%	464	63%	96	81%

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Table 3. Continued.

Halocarbon Studies	CH3CCl3		CCl4		CH2Cl2		HCIC = CCl2		Cl2C = C2Cl2		CH3Cl		CH3Br	
	Con.	Rsd	Con.	Rsd	Con.	Rsd	Con.	Rsd	Con.	Rsd	Con.	Rsd	Con.	Rsd
Bristol, England (Aug–Sep 2000), Rivett et al. (2003)	54	11%	98	4%	–	–	73	237%	37	259%	–	–	–	–
Philadelphia, United states (Feb 2001), Barletta et al. (2006)	50	14%	98	7%	97	55%	–	–	116	101%	–	–	–	–
Las Vegas, United states (Feb 2001), Barletta et al. (2006)	46	11%	99	3%	133	119%	–	–	159	114%	–	–	–	–
Marseille, France (Jun–Jul 2001), Barletta et al. (2006)	54	91%	107	6%	251	129%	36	156%	276	163%	–	–	–	–
Karachi, Pakistan (Dec 1998–Jan 1999), Barletta et al. (2002)	75	5%	131	33%	329	191%	–	–	68	216%	2720	57%	22	31%
Kraków, Poland (Jul 1997–Sep 1999), Lasa and Sliwka (2003)	72	14%	108	4%	–	–	–	–	–	–	–	–	–	–
Athens, Greece (Jul–Aug 2000), Glavas and Moschonas (2002)	–	–	40	50%	–	–	–	–	160	75%	–	–	–	–
Bristol, England (Oct 2004–Dec 2005), Khan et al. (2009)	25	43%	92	35%	289	134%	35	170%	34	272%	534	34%	16	47%
Chinese 45 cities (Jan–Feb 2001), Barletta et al. (2006)	49	10%	114	10%	226	103%	21	186%	129	153%	–	–	–	–
Shanghai (Jan–Feb 2001), Barletta et al. (2006)	54	17%	107	7%	648	162%	16	56%	54	31%	–	–	–	–
Shanghai (Plume encountered during TRACE-P on March 2001), Barletta et al. (2006)	51	20%	127	16%	210	69%	32	109%	56	68%	–	–	–	–
Beijing, China (Jan 2005–Mar 2007), Qin (2007)	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Guangzhou, PRD of China (Mar 2001), Chan et al. (2006)	93	55%	138	35%	–	–	234	112%	268	140%	1210	61%	–	–
Panyu, PRD of China (Sep–Dec 2001), Chan et al. (2006)	29	21%	129	27%	648	62%	656	86%	93	99%	1140	30%	–	–
Dinghu, PRD of China (Mar 2001), Chan et al. (2006)	60	35%	123	24%	–	–	84	136%	48	102%	1010	29%	–	–
Guangzhou, PRD of China (Nov 2004), Chang et al. (2008)	43	46%	156	45%	–	–	–	–	–	–	–	–	–	–
Xinken, PRD of China (Nov 2004), Chang et al. (2008)	70	70%	124	22%	–	–	–	–	–	–	–	–	–	–
Urban and rural site of PRD, China (Oct–November 2004) (This study)	62	31%	194	50%	1028	78%	467	97%	170	76%	1165	18%	47	56%

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Table 4. Halocarbons versus CO relationships measured in PRD regions during the sampling period and the their estimated emissions based on Measured ratio relative to CO.^{a,b,c,dddd}

Halocarbon <i>X</i>	<i>X</i> /CO ^a	Uncertainty ^b	<i>r</i> ^c	<i>n</i> ^d	Mx (g mol ⁻¹)	Emission (Gg)	Uncertainty (Gg)
CFC-11	0.0222	0.0048	0.416**	118	137.37	0.4	0.2
CFC-12	0.1100	0.0199	0.485**	118	120.91	1.6	1.0
CFC-113	0.0015	0.0020	0.163	118	187.38	0.0	0.0
CFC-114	0.0010	0.0008	0.006	118	170.92	0.0	0.0
HCFC-22	0.3480	0.0430	0.618**	118	86.47	3.5	2.2
CH ₃ CCl ₃	0.0228	0.0028	0.550**	118	133.40	0.4	0.2
CCl ₄	0.0588	0.0165	0.347**	118	153.82	1.1	0.7
CHCl ₃	0.0604	0.0133	0.416**	118	119.38	0.8	0.6
CH ₂ Cl ₂	0.7090	0.1280	0.495**	118	84.93	7.0	4.6
CH ₃ Cl	0.0962	0.0370	0.234*	118	50.49	0.6	0.4
CH ₃ Br	0.0121	0.0047	0.256*	115	94.94	0.1	0.1
CCl ₂ = CCl ₂	0.1180	0.0212	0.352**	118	165.80	2.3	1.5
CHCl = CCl ₂	0.4380	0.0699	0.477**	118	131.39	6.7	4.3
CHCl ₂ CH ₂ Cl	0.0381	0.0042	0.723**	98	133.40	0.6	0.4
CH ₃ CH ₂ Cl	0.0036	0.0038	0.116	109	64.51	0.0	0.0
CH ₃ CHClCH ₂ Cl	0.0309	0.0056	0.497**	104	112.99	0.4	0.3
CO	–	–	–	–	28.010	3265.2	2034.5

^a Statistics of the orthogonal distance regression results.

^b More forms appear to lead to correct estimates of the fit parameter uncertainties were discussed in Cantrell (2008).

^c *r* is the Pearson correlation coefficient of *X*/CO. * Correlation is significant at the 0.05 level (2-tailed), *X*/CO is the orthogonal distance regression slopes (pptv ppbv⁻¹). ** Correlation is significant at the 0.01 level (2-tailed).

^d The parameter *n* is the number of effective Samples.

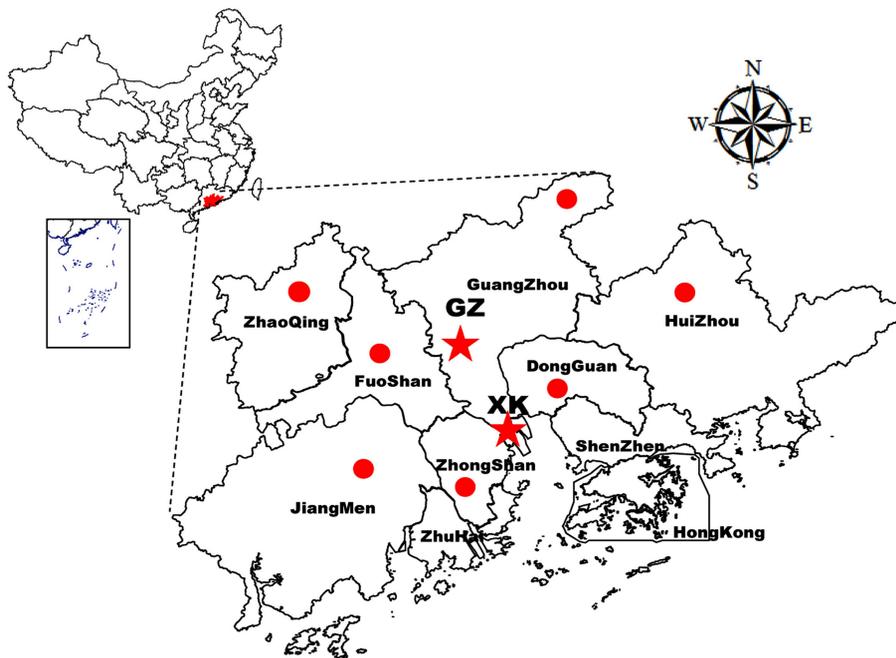


Fig. 1. Map showing the geographical locations of sampling sites and the PRD region. The star symbols indicate the intensive sites of Guangzhou (GZ) and XinKen (XK) respectively. GZ is thought to be the representative of a major metropolitan site, but XK is used to represent remote receptor site in the rapid developing region.

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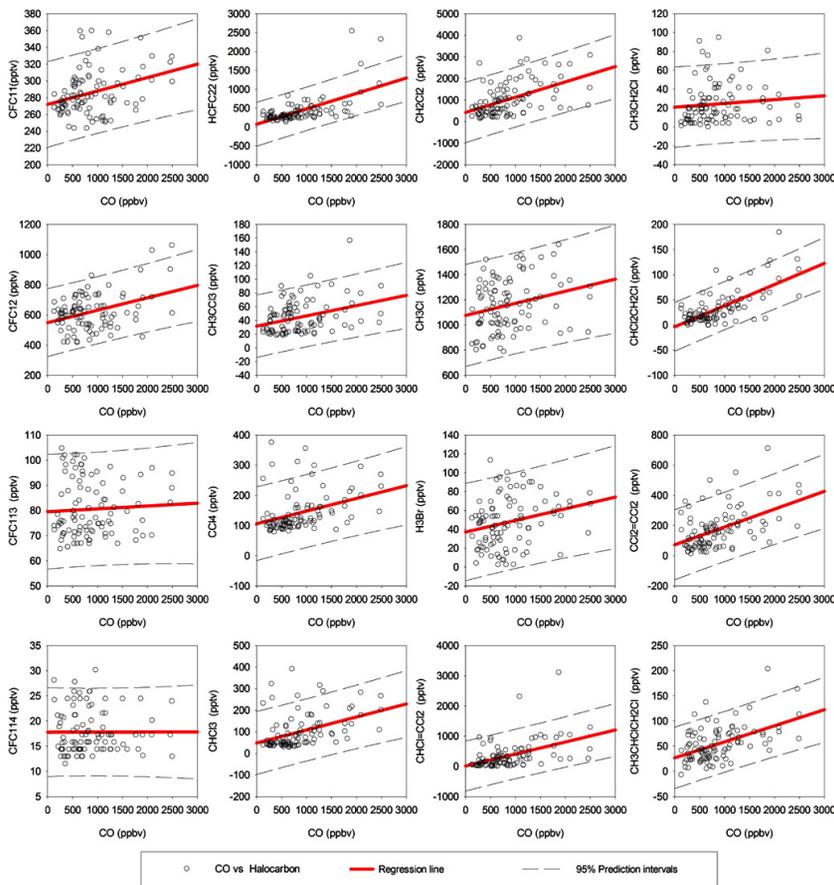


Fig. 2. Halocarbons and CO relationship of the data set. orthogonal distance regression and 95% confidence intervals were indicated by the red solid lines and the black long dash line respectively. Statistical outliers were removed prior to performing the regressions.

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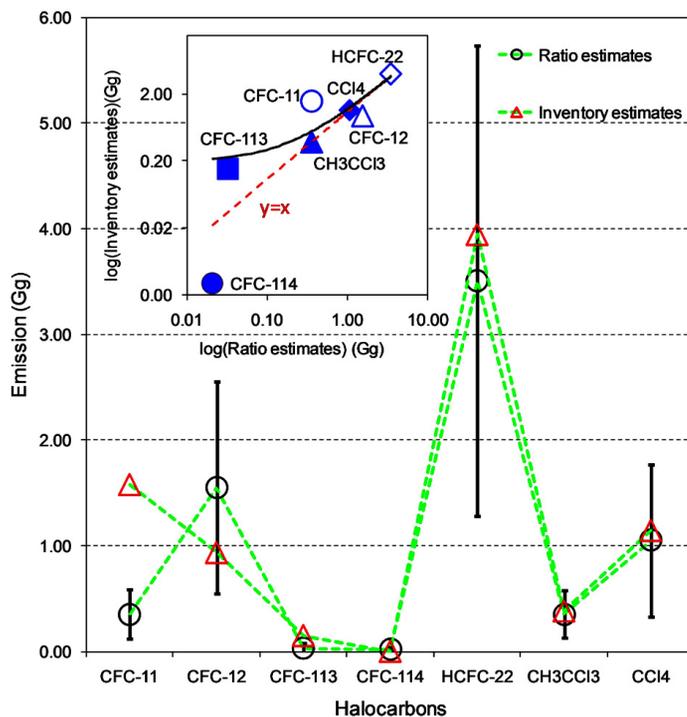


Fig. 3. Comparison of the ratio estimate emissions and inventory estimate emissions for several halocarbons from PRD region.

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