

# Estimate of anthropogenic halocarbon emission based on measured ratio relative to CO in the Pearl River Delta region, China

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**Abstract.** Using a GC/FID/MS system, we analyzed the mixing ratio 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 that there are elevated mixing ratios for most of halocarbons, especially for HCIC = CCl<sub>2</sub> (trichloroethylene, TCE), CH<sub>2</sub>Cl<sub>2</sub> (dichloromethane, DCM), CH<sub>3</sub> Br (bromomethane), HCFC-22, CHCl<sub>3</sub> (trichloromethane), CCl<sub>4</sub> (tetrachloromethane), Cl<sub>2</sub>C = CCl<sub>2</sub> (perchloroethylene, PCE), CH<sub>3</sub>CCl<sub>3</sub> (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 mixing ratios (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) was examined, and then the emission of each 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 CH<sub>2</sub>Cl<sub>2</sub> (7.0 Gg), CH<sub>3</sub>CCl<sub>3</sub> (6.7 Gg), and Cl<sub>2</sub>C = CCl<sub>2</sub> (2.3 Gg) accounted for about 62.9 % of total halocarbon emissions, it suggested a significant contribution 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 CFCs, such as CFC-11, and the emission of CFC-114 and CFC-113 were close to zero. Emissions of other anthropogenic halocarbons, such

as CCl<sub>4</sub>, CHCl<sub>3</sub>, CH<sub>3</sub>Br, and CH<sub>3</sub>Cl, 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 the ratio method may be a useful tool for assessing regional halocarbon emissions, and emission uncertainty could be further reduced by incorporating both longer-term and higher-frequency observations, as well as improving the accuracy of the CO inventory.

## 1 Introduction

The importance of halocarbons in the atmosphere has been recognized since the 1970s, when Lovelock measured out the ambient concentrations of chlorofluorocarbons (CFCs) using a gas chromatogram coupled with electron capture detector. As a subclass of volatile organic compounds, halocarbons play an important role in the destruction of stratospheric ozone, some of them also function as the potential greenhouse gases. Both of the two effects have propelled halocarbons to the forefront of atmospheric chemistry research. Protocols, such as the Vienna Convention, the Kyoto Protocol, the Montreal Protocol, and their subsequent amendments, were developed to establish mechanisms for international cooperation, with the aim of reducing the use of halocarbons. Environmental agencies in many countries have prepared national emissions inventories of halocarbons, and these statistical emissions estimates were used to help to accelerate the halocarbon phase-out.

These emissions inventories were relied primarily on bottom-up approaches, and compiled based on production, end-use and the time schedule data. However, uncertainties arise if the production figures do not cover all manufacturers



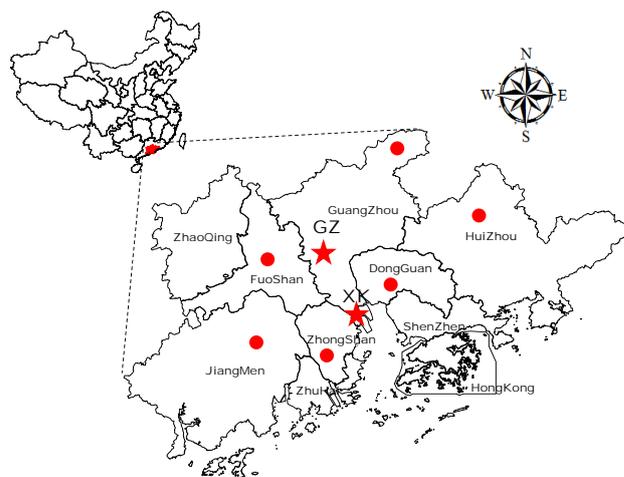
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or if there are errors in the application of end-use categories. Validating emission inventories is therefore essential by the inter-comparison between emission inventories derived from conventional approaches (bottom-up) and modeled emissions based on other databases such as atmospheric measurements (top-down). On global scale, emissions can be determined from measured atmospheric concentrations using simple box models or three-dimensional models. Regional-scale emissions can be derived using observed halocarbon concentrations and a modeling back-attribution technique.

Recently, a method based on the ratio between the halocarbons and a substance with known emissions (carbon monoxide (CO) or HCFC-22) was developed to verify emission inventories of trace gases. However, this method is dependent on several assumptions: (1) within a certain period of time, no chemical reaction occurs, (2) the air mass over the site should represent the average emissions of anthropogenic halocarbons, (3) there are no natural sources of any measured halocarbons, the short term enhancement of their atmospheric mixing ratio is due to anthropogenic emissions, and (4) the emissions of anthropogenic CO should be known.

While this method has been used to assess halocarbon emissions in North America, Europe, and Australia, emissions in East Asia were also of great interest because of the region's rapid economic development. Palmer et al. first assessed the halocarbon emissions in Eastern Asia using aircraft observations with the halocarbon/CO enhancement ratio method, by using observational data for March–April 2001, from the TRACE-P campaign; their emission estimates for methyl chloroform ( $\text{CH}_3\text{CCl}_3$ ) and CFC-12 were in agreement with existing inventories, but both the carbon tetrachloride ( $\text{CCl}_4$ ) and CFC-11 estimates were 25–50% higher than the traditional emissions inventories. Using the same methods, also estimated emissions of ethane, ethyne, propane,  $\text{CH}_3\text{Br}$ ,  $\text{CH}_3\text{Cl}$ , Halon-1211, and other long-lived halogenated species in Asian continental outflow. By using the trace gas data observed by the AGAGE program at Cape Grim, the correlations between the halocarbon gases and CO emissions are examined to deduce regional emissions. Aircraft or ground monitoring halocarbon data for Sagami Bay, Japan, Hateruma Island in East Asia, and various location in the United States and Mexico were used to estimate anthropogenic sources based on the same enhancement ratio approach.

The Pearl River Delta (PRD) region of Guangdong Province, China, the largest and most economically important metropolitan area in Southeast China, was featured by a large manufacturing industry, including the production of electronics, air conditioners, refrigerators, and automobiles. However, the rapid industrialization and urbanization of the PRD region has resulted in the deterioration of regional air quality, including high levels of volatile organic compounds (VOCs), ground-level ozone, and fine particles. Among the pollutants, halocarbons have attracted international attention, because China, as an Article 5 country under the Montreal



**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.

Protocol, is still allowed to produce and use some halocarbons under the terms of the protocol and its amendments. Many studies have shown significantly enhanced levels of most halocarbons in this region because of the increased production and extensive industrial uses. Recently, halocarbons from the greater PRD region were analyzed to apportion their sources and model their profiles. However, these studies were not conducted specifically to derive emission estimates in the PRD region.

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 measurement campaign (However, only Guangzhou (23.14° N, 113.34° E, GZ) and Xinken (22.65° N, 113.60° E, XK) were selected as intensive sites. Figure 1 shows the geographical locations of the sampling sites.

Daily whole air samples were collected and stored in 3.2 l stainless steel canisters. These inert canisters provide a useful temporary storage environment, particularly for low-polar and low boiling-point compounds such as halocarbons. Before sampling, all canisters were cleaned using a vacuum

cleaner (Entech 3100A, Entech, Simi Valley, CA, USA). After each sampling, the canisters were shipped to our laboratory at Peking University (PKU) as quickly as possible ( $\leq 15$  days). Due to the complexity and rapidity of variation for the halocarbons in the PRD region, more than 100 VOC species and CO were simultaneously analyzed for further researches. For the Laboratory analysis, a cryogenic preconcentrator system (Entech 7100A, Entech) coupled with GC-FID/MS (Hewlett Packard 6890/5973, Hewlett Packard Co. USA) were used. The GC-FID/MS system was equipped with two columns and two detectors. Details of the sampling and analytical methods have been described elsewhere. Briefly, the  $C_1$ - $C_2$  non-polar halocarbons were separated on a HP-1 column ( $50\text{ m} \times 0.32\text{ mm ID} \times 1.05\text{ }\mu\text{m}$ ) and quantified by a quadrupole mass spectrometer (MS, Hewlett Packard 5973) which was operated in selected ion mode. In the second injection, the  $C_2$ - $C_4$  alkanes, alkenes, and acetylene were separated on the same column but quantified with a flame ionization detector (FID, Hewlett Packard 6890), and the  $C_1$ - $C_3$  semi-polar halocarbons were separated on a DB-624 ( $60\text{ m} \times 0.32\text{ mm ID} \times 1.8\text{ mm}$ ) 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  $40\text{ }^\circ\text{C}$  for 3 min, and then raised to  $140\text{ }^\circ\text{C}$  at a rate of  $10\text{ }^\circ\text{C min}^{-1}$  and held for 5 min. Column DB-624 was programmed from  $30\text{ }^\circ\text{C}$  to  $180\text{ }^\circ\text{C}$  at a rate of  $6\text{ }^\circ\text{C min}^{-1}$  and held for 5 min at  $180\text{ }^\circ\text{C}$ . Three VOC compounds, bromochloromethane, 1,4-difluorobenzene, and 1-bromo-3-fluorobenzene were used as internal standards for the calibration of our analytical system.

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. The correlation coefficients of the calibration curves for target species were 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 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 ( $\text{CHCl}=\text{CCl}_2$ , minimum) to 8 ( $\text{CHCl}_2\text{CH}_2\text{Cl}$ , maximum) pptv.

## 2.2 Method of emission calculation

Previous studies have indicated that the relative ratios between the enhancements of halocarbons and the increasing of a trace gas should reflect the ratios of their emissions strengths, as long as they are emitted from common sources and not removed during transportation processes. Thus, if the emissions of one species from a region can be determined,

we can calculate out the emissions of other compounds in the same dataset based on the measured ratio of pollution enhancements. In this study, CO was used as the reference compound, as the emission inventories of CO was 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.

### 2.2.1 Consideration of the background levels and the interference

There are residual halocarbons present in the global, it leading to the background mixing ratios of halocarbons in the atmosphere and this which are unaffected by local or regional sources. The background levels may vary on a timescale depending on the species, some of the halocarbons may also have seasonal or annual patterns. These background concentrations should be filtered out from the observation concentrations as the halocarbon pollution enhancements in number of previous studies such as, then the measurements ( $X$ ) after subtracting the background values ( $X_0$ ) are denoted as  $\Delta X$  for each compound, where  $\Delta X = X - X_0$ . In fact, these studies were done on a larger spatial scale or longer time scale than our research. However, the data in this work was collected over a short enough period (for about a month) of time, the background concentrations did not change significantly, so we think it was not necessary to adopt pollution enhancement by subtracting the background concentrations. Furthermore, since the emissions are calculated from the slopes of the correlation between the species, the results were independent of whether or not a background concentration is subtracted.

For more informative, baseline concentrations over the study period for each halocarbon were still shown in Table 1. The 20-th percentile of ALE/GAGE/AGAGE data between October to November 2004 was defined as the Global background values, TRACE-P backgrounds were used for halocarbons and the 20-th-percentile of the datasets for the other gases were used to capture the regional background levels for the halocarbons that not included in TRACE-P. The lowest CO mixing ratio in South China Sea air was defined as the CO background value.

Additionally, because biomass burning could be a significant contributor to ambient CO levels and this part of CO were from local emission instead of background, therefore, the most severe biomass burning plumes (diagnosed by  $\text{CH}_3\text{CN} > 900$  pptv) were removed prior to calculating background levels, additionally, statistical outliers (the lower 1st percentile and the upper 99-th-percentile) were also removed from the dataset as abnormal values.

**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 <sup>b</sup>	CapeMatatula	RaggedPoint	TrinidadHead	TRACE-P <sup>c</sup>	XingKen <sup>d</sup>	GuangZhou
CFC-11	252 <sup>a</sup>	250	250	252	252	<b>259</b>	274	280
CFC-12	544	541	542	544	545	<b>545</b>	604	644
CFC-113	79	79	78	79	–	<b>79</b>	97	87
CFC-114	–	–	–	–	–	<b>14</b>	13	15
HCFC-22	176	158	–	–	–	<b>151</b>	228	381
CH <sub>3</sub> CCl <sub>3</sub>	21	21	20	20	21	<b>40</b>	46	52
CCl <sub>4</sub>	93	91	92	93	93	<b>99</b>	88	207
CHCl <sub>3</sub>	11	6	4	6	12	<b>9</b>	36	50
CH <sub>2</sub> Cl <sub>2</sub>	27	10	–	–	–	<b>28</b>	249	256
CH <sub>3</sub> Cl	486	534	–	–	–	<b>535</b>	940	996
CH <sub>3</sub> Br	–	–	–	–	–	<b>8</b>	21	21
Cl <sub>2</sub> C = CCl <sub>2</sub>	3	1	–	–	–	<b>5</b>	72	55
HCIC = CCl <sub>2</sub>	<b>1</b>	–	–	–	–	–	171	224
CHCl <sub>2</sub> CH <sub>2</sub> Cl	–	–	–	–	–	–	<b>9</b>	<b>15</b>
CH <sub>3</sub> CH <sub>2</sub> Cl	–	–	–	–	–	–	<b>8</b>	<b>8</b>
CH <sub>3</sub> CHClCH <sub>2</sub> Cl	–	–	–	–	–	–	<b>26</b>	<b>24</b>

<sup>a</sup> The background concentrations are in pptv.

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

<sup>c</sup> The Lowest 25-th percentile of airborne TRACE-P data collected below 1500 m 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).

<sup>d</sup> The lowest 20-th percentile of the dataset for Guangzhou and Xinken are also shown here.

## 2.2.2 Emissions calculations

The calculations assume that there is an inherent relationship between the target halocarbon 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. We considered that the slope of the regression line between  $X$  and CO should replace the emission 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. 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 following:

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

Where CO and  $X$  are expressed in the units of ppbv and pptv, respectively, and  $X/CO$  represents the molar ratio of the halocarbons relative to CO. Thus, the molecular weights ( $M_x$  and  $M_{CO}$ ) of the trace gases should be taken into account when we determine the mass of emissions,  $E_{CO}$  is the inventory emission of CO.

The uncertainty of the halocarbon emissions is calculated using error propagation method. In fact of the uncertainties of emissions are associated with the variables of  $X/CO$  and the CO emission inventory, according to the Eq. (1), the uncertainties can be propagated from the combination of

variables in Eq. (2) as:

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

where  $\sigma_x$  is the uncertainty for the estimated halocarbon emission,  $\sigma_{E_{CO}}$  and  $\sigma_{X/CO}$  are the uncertainties of  $E_{CO}$  and the  $X/CO$  slope, 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. Biomass burning-related CO also contributes to CO pollution episodes, while the ratio of biomass-burning CO to halocarbons is considered to be much lower than the ratio of whole CO emissions to halocarbons. 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, range from  $5.9 \times 10^3$  Gg (uncertain within a factor of 1.9, in 2000) to  $8.7 \times 10^3$  Gg (uncertain within a factor of 0.7, in 2006), 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 the CO emissions estimates for the PRD region in 2004 was not available, even for Guangdong Province, despite many CO emissions estimation studies in the past decade to quantify national emissions of China. Thus, a bottom-up approach was adopted in this study for the

**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 <sup>b</sup>		Cape Grim <sup>c</sup>		Mace Head		Cape Matatula		Ragged Point		Trinidad Head				
	Mea <sup>a</sup>	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	0.26%	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%	–	–	–	–	–	–
CH <sub>3</sub> CCl <sub>3</sub>	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%
CCl <sub>4</sub>	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%
CHCl <sub>3</sub>	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	9.75%	6	13.60%	14	18.27%
CH <sub>2</sub> Cl <sub>2</sub>	1028	740	78.09%	124	855	637	84.69%	60	1239	1027	68.55%	49	226	102.65%	10	12.01%	34	37.64%	–	–	–	–	–	–
CH <sub>2</sub> Cl	1165	1152	18.06%	124	1180	1190	17.38%	60	1147	1104	18.95%	49	952	28.68%	590	16.63%	518	7.48%	–	–	–	–	–	–
CH <sub>3</sub> Br	47	46	56.32%	122	48	47	54.40%	60	44	44	59.21%	47	13	23.08%	–	–	–	–	–	–	–	–	–	–
Cl <sub>2</sub> C=CCl <sub>2</sub>	170	155	75.99%	124	164	157	70.28%	60	179	143	81.74%	49	129	153.49%	–	–	–	–	–	–	–	–	–	–
HCIC=CCl <sub>2</sub>	467	294	96.55%	124	420	276	75.35%	60	525	346	109.21%	49	21	185.71%	–	–	–	–	–	–	–	–	–	–
CHCl <sub>2</sub> CH <sub>2</sub> Cl	34	23	90.59%	113	41	31	80.30%	60	23	12	106.10%	38	–	–	–	–	–	–	–	–	–	–	–	–
CH <sub>3</sub> CH <sub>2</sub> Cl	23	17	85.43%	120	21	16	71.38%	59	26	19	93.74%	46	–	–	–	–	–	–	–	–	–	–	–	–
CH <sub>3</sub> CHClCH <sub>2</sub> Cl	53	46	63.48%	123	56	52	59.78%	59	295	286	9.79%	49	–	–	–	–	–	–	–	–	–	–	–	–

<sup>a</sup> Mean and median of the mixing ratios are in pptv.

<sup>b</sup> Average extracted from TRACE-P data were provided by Barletta et al. (2006).

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

regional CO emission inventory for the PRD region in 2004, using the best available emission factors and activity data. CO emissions determined by sectors 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. The result was an emission of  $7.0 \times 10^3$  (uncertain within a factor of 0.5) 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 (GIS). The results showed an estimated CO emission in the PRD region in 2004 is  $3.3 \times 10^3 (\pm 2.0 \times 10^3)$  Gg, slightly lower than the CO estimate of Zheng et al., who reported a CO emission of  $3.8 \times 10^3$  Gg from the same region in 2006.

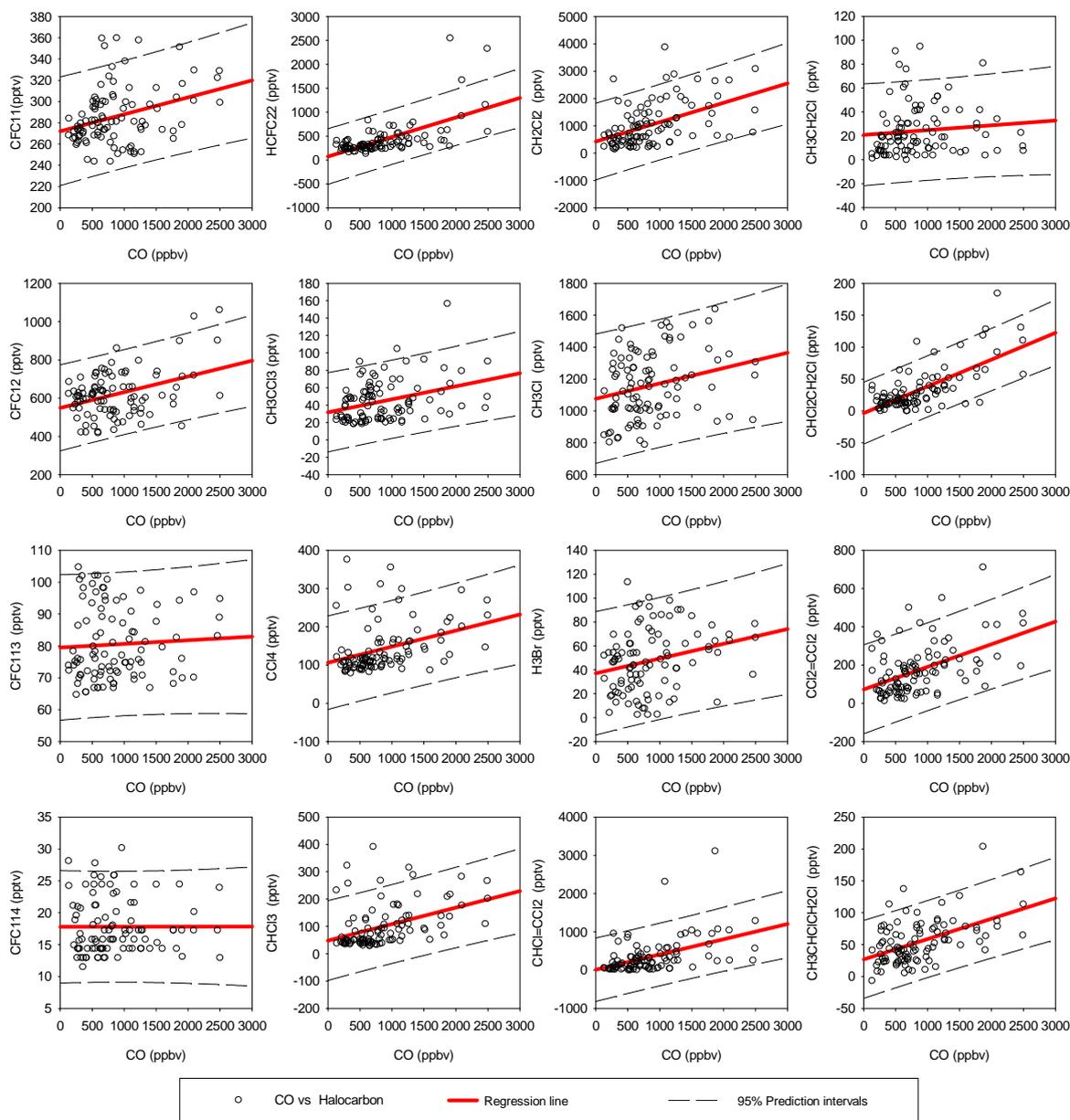
### 3 Results and discussion

#### 3.1 Halocarbon concentration and speciation

Approximately one month, from 4 October to 3 November 2004, was chosen for our analysis. The 16 halocarbons measured by GC-FID/MS, coupled with a cryogenic pre-concentrator system, were: CFC-11, CFC-12, CFC-113, CFC-114, HCFC-22, CH<sub>3</sub>CCl<sub>3</sub>, CCl<sub>4</sub>, CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>Cl, CH<sub>3</sub>Br, CCl<sub>2</sub>=CCl<sub>2</sub>, CHCl=CCl<sub>2</sub>, CHCl<sub>2</sub>CH<sub>2</sub>Cl, CH<sub>3</sub>CH<sub>2</sub>Cl, and CH<sub>3</sub>CHClCH<sub>2</sub>Cl. These substances were chosen for analysis because they were detectable at the limits of the GC-FID/MS analysis system, and they account for more than 80% of all halocarbons in the atmosphere. These samples were taken at two time intervals. 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, and the samples for 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.

Comparing to the mixing ratio obtained from TRACE-P and ALE/GAGE/AGAGE, the statistical results given in both Tables 1 and 2 showed that the regional mixing ratios of most halocarbons were elevated for their mixing ratios in PRD region, especially for HCIC=CCl<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>Br, HCFC-22, CHCl<sub>3</sub>, CCl<sub>4</sub>, Cl<sub>2</sub>C=CCl<sub>2</sub>, CH<sub>3</sub>CCl<sub>3</sub>, and CFC-12. The large concentration variability in those halocarbons suggested substantial usage and emissions in PRD region, while the variability of CFC-11 and CFC-113 were rather small. Jobson et al. reported that the magnitudes of RSD for halocarbons species are a function of loss processes as well as emissions, but the pollution enhancements and the large variability of the halocarbons confirm that there are some unexpected sources, such as emissions stockpile leakage and unknown production or usage. All 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 October 11, 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 occasional anthropogenic emissions of HCFC-22 and CFC-12 during the sampling period. Moreover, the median emission values of HCFC-22 and CFC-12 were 377 pptv and 682 pptv, respectively, which were more than 1.5 times higher than the background values, suggested that there were stronger source emissions for both of the halocarbons in PRD. 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



**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.

been used extensively since 2004 as an alternative to CFCs in Guangdong Province, while better substitutes are under development.

Table 3 compares the mixing ratios of selected halocarbons measured in the PRD region with those reported for Bristol, Athens, Philadelphia, Las Vegas, Marseille, Beijing, Kraków, Shanghai, Guangzhou, Panyu, Dinghu, and Xinken. 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 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. The positive relationships between  $X$  and CO were shown in Fig. 2 and the significance level for Pearson's Correlation coefficient ( $r$ ) were also showed in Table 4.

**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 <sub>3</sub>	
	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 %

**Table 3.** Continued.

Halocarbon Studies	CH <sub>3</sub> CCl <sub>3</sub>		CCl <sub>4</sub>		CH <sub>2</sub> Cl <sub>2</sub>		HCIC = CCl <sub>2</sub>		Cl <sub>2</sub> C = C <sub>2</sub> Cl <sub>2</sub>		CH <sub>3</sub> Cl		CH <sub>3</sub> Br	
	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 %

Uncertainty for  $X/CO$  ratio was calculated in the standard manner assuming linear model, and presented as the standard deviation ( $\sigma_{X/CO}$ ). According to Eq. (1), by multiplying the  $X/CO$  ratio and the CO inventory emissions from the PRD region in 2004, regional halocarbon emissions and their uncertainties determined by Eq. (2) were calculated and list in Table 4.

It is noteworthy that the correlation between some species such as CFC-113, CFC-114 and CH<sub>3</sub>CH<sub>2</sub>Cl and CO were 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. In fact, the ambient mixing ratio of the above three species were much lower than the others, suggesting their lower emissions. Furthermore, the uncertainties were in

same magnitude as the  $X/CO$  slopes for these species. Thus there were some defects in our method to made a quantitative estimate for the 3 species, but the emission results estimated by the measured ratios could only be used a qualitative reference.

### 3.2.1 Methyl chloroform (CH<sub>3</sub>CCl<sub>3</sub>, 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

**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.<sup>a,b,c</sup> and <sup>d</sup>

Halocarbon X	X/CO <sup>a</sup>	Uncertainty <sup>b</sup>	r <sup>c</sup>	n <sup>d</sup>	Mx (g mol <sup>-1</sup> )	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 <sub>3</sub> CCl <sub>3</sub>	0.0228	0.0028	0.550**	118	133.40	0.4	0.2
CCl <sub>4</sub>	0.0588	0.0165	0.347**	118	153.82	1.1	0.7
CHCl <sub>3</sub>	0.0604	0.0133	0.416**	118	119.38	0.8	0.6
CH <sub>2</sub> Cl <sub>2</sub>	0.7090	0.1280	0.495**	118	84.93	7.0	4.6
CH <sub>3</sub> Cl	0.0962	0.0370	0.234*	118	50.49	0.6	0.4
CH <sub>3</sub> Br	0.0121	0.0047	0.256*	115	94.94	0.1	0.1
CCl <sub>2</sub> = CCl <sub>2</sub>	0.1180	0.0212	0.352**	118	165.80	2.3	1.5
CHCl = CCl <sub>2</sub>	0.4380	0.0699	0.477**	118	131.39	6.7	4.3
CHCl <sub>2</sub> CH <sub>2</sub> Cl	0.0381	0.0042	0.723**	98	133.40	0.6	0.4
CH <sub>3</sub> CH <sub>2</sub> Cl	0.0036	0.0038	0.116	109	64.51	0.0	0.0
CH <sub>3</sub> CHClCH <sub>2</sub> Cl	0.0309	0.0056	0.497**	104	112.99	0.4	0.3
CO	–	–	–	–	28.010	3265.2	2034.5

<sup>a</sup> Statistics of the orthogonal distance regression results.

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

<sup>c</sup> *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<sup>-1</sup>). \*\* Correlation is significant at the 0.01 level (2-tailed).

<sup>d</sup> The parameter *n* is the number of effective Samples.

of the hydroxyl radical (OH). 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 than that in the Northern Hemisphere. Thus, definite conclusions about the global OH distribution and trends cannot be drawn until the emissions and distribution of MCF are better quantified.

Previous studies have shown that both the concentration and variability of MCF emissions in the PRD region are significantly greater than those from Taipei, which has a different schedule for implementing the Montreal Protocol. These data indicated that the PRD region was producing MCF emissions. Combining the MCF/CO (0.023 ± 0.003 pptv ppbv<sup>-1</sup>) slope with the CO emission by Eq. (1), it gave a value of 0.4 ± 0.2 Gg for MCF emission in the PRD region. Comparing with the similar researches in other regions, The MCF/CO slopes for air samples in Korea (0.044 pptv ppbv<sup>-1</sup>) and Japan (0.023 pptv ppbv<sup>-1</sup>) were a little higher than our measurements in the PRD region, but emissions ratios measured over the United States (0.017 pptv ppbv<sup>-1</sup>) and Mexico (0.002 pptv ppbv<sup>-1</sup>), and even from the TRACE-P missions over mainland China (0.013 pptv ppmv<sup>-1</sup>), were lower than what we measured in PRD. The National emissions of MCF based on consumption in 2004 were determined to be 4.8 Gg 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, the regional and national MCF emissions in China were concerned by using anthropogenic CO emissions, Palmer et al deduced that the anthropogenic MCF emissions from China were about 10.4 Gg, this result was consistent with emission estimates for the “Far East area” 11 Gg in 2000 by McCulloch et al., while the MCF emissions of Japanese and Korean were 1.0 to 1.8 Gg, respectively.

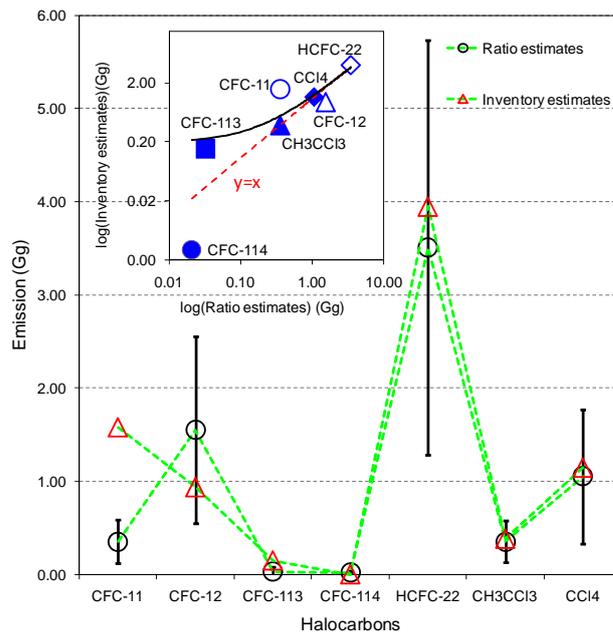
Actually, MCF emissions around the world need to be eliminated. Unfortunately, this work together with many other studies observed the continuing emissions from both the developed and developing countries, such as United States, Europe, and Japan. The emissions could be due to the slow release from legal stockpiles accumulated prior to the ban and other unknown sources. With the implementation of MCF phase out in production and consumption in China after 2004, sales and production figures were no longer reliable proxies of emissions, it is essential to verify the PRD regional inventory data in 2004 to provide an effective estimates method for further time. As shown in Fig. 3, our ratio estimate results was agree well with inventory data, it is possible because that the most of MCF was used as an industrial cleaning solvent and emitted into the atmosphere immediately after use (more details in Sect. 3.3). Therefore, in

situ measurements could be very useful for validating actual MCF emissions in the phase-out process.

### 3.2.2 $\text{CH}_2\text{Cl}_2$ , $\text{CCl}_2 = \text{CCl}_2$ , and $\text{CHCl} = \text{CCl}_2$

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. Other sources of these chemicals in the atmosphere include vehicle exhaust and the combustion of coal. Emissions of these chemicals were also found from the ocean and biomass burning, but these natural sources were usually not considered significant in industrial regions. According to, the industrial emissions of chlorinated hydrocarbons around the world ( $1^\circ \times 1^\circ$  grid size) could be estimated by using three data sets: regional sales data, gross domestic products, and population distributions within each area. Moreover, Wiedmann et al. used an arbitrary factor to convert American estimates of PCE production into a global value, Koppmann and Rudolph derived the 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, which is shorter than their inter-hemispheric exchange time (1.0 year). Thus, the ratio emission estimates method could be helpful on understanding the atmospheric processes and their seasonal variability.

Using the correction between the CO and PCE inventories, Barnes et al. derived the urban/industrial emissions of PCE from CO inventory emissions 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. We first determined the X/CO ratios, which were  $0.71 \pm 0.13$ ,  $0.12 \pm 0.02$ , and  $0.44 \pm 0.07$  pptv ppbv<sup>-1</sup> for DCM, PCE and TCE respectively, and then used Eq. (1) to calculate that the DCM, PCE, and TCE emissions were  $7.0 \pm 4.6$ ,  $2.3 \pm 1.5$ , and  $6.7 \pm 4.3$  Gg from PRD region in 2004. The slope of  $\Delta\text{PCE}/\Delta\text{CO}$  for the PRD region was smaller than that for New York City Washington, D.C, which was  $0.32 \pm 0.06$  pptv ppbv<sup>-1</sup>, and the emissions were also lower than that in urban/industrial pollution regions in the United States from 1996 to 1997, when emissions ranged from 10.9 to 11.7 Gg. According to and, 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



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

“Far East” (47.1 Gg), 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 suggested 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 halocarbons in this study. In the mid 1990s, the United States Environmental Protection Agency (US EPA) expressed concern about DCM and TCE, based on information provided by, 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 would also pay attention 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. Similarly, used aircraft measurements from the United States and Mexico to measure anthropogenic halocarbon emissions, and calculated a  $\Delta\text{DCM}/\Delta\text{CO}$  of 0.24 (0.18–0.29) pptv ppbv<sup>-1</sup> and  $\text{TCE}/\text{CO}$  of 0.05 (0.04–0.06) pptv ppbv<sup>-1</sup>, 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. With the development of transportation and the increase of industries, the PRD region had its emissions of DCM ( $7.0 \pm 4.6$  Gg) and TCE ( $6.7 \pm 4.3$  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.

There were 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  $0.02 \pm 0.00$ ,  $0.11 \pm 0.02$ ,  $0.00 \pm 0.00$ , and  $0.00 \pm 0.00$  pptv ppbv<sup>-1</sup>, 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 agreed with the halocarbon emission estimates for the inner PRD of, 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. 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. 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 led to a prevalence of HCFC-22 emissions. McCulloch et al. point out that the phase out of CFCs should have led 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  $3.5 \pm 2.2$  Gg, approximately 2.3 times as the emissions of CFC-12. Because of the widespread availability of the alternative, HCFC-22, and the more rigorous stepped controls on CFC-12, the ratios between HCFC-22 and CFC-12 in developed areas were higher than that 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). 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 were listed in Table 4. Among these halocarbons, carbon tetrachloride (CCl<sub>4</sub>) and chloroform (CHCl<sub>3</sub>) are used primarily as feed stocks for producing CFC-11, CFC-12, and HCFC-22. About 75 % of CHCl<sub>3</sub> in China was consumed in the pharmaceutical industry to produce HCFC-22, and about 80–90 % of CCl<sub>4</sub> is consumed to produce CFC-11 and CFC-12. Because the Montreal Protocol and its various amendments listed CCl<sub>4</sub> 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<sub>3</sub> is not regulated under the Montreal Protocol, and regional emissions continue. According to our estimates, emissions of CCl<sub>4</sub> and CHCl<sub>3</sub> from the PRD region were  $1.1 \pm 0.7$  and  $0.8 \pm 0.6$  Gg respectively, indicating widespread anthropogenic use of these halocarbons in this region. A study using matrix factorization receptor model analysis and correlations of the mixing ratios of CCl<sub>4</sub>, CHCl<sub>3</sub>, and DCM (a solvent tracer) suggested that solvents were the main source of CCl<sub>4</sub> in the inner PRD region, but not the most important contributor of CHCl<sub>3</sub>.

CH<sub>3</sub>Br 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<sub>3</sub>Br and CH<sub>3</sub>Cl were  $0.1 \pm 0.1$  Gg and  $0.6 \pm 0.4$  Gg, respectively. Similar emissions,  $0.3 \pm 0.06$  Gg and  $5.4 \pm 0.4$  Gg for each of CH<sub>3</sub>Br and CH<sub>3</sub>Cl have been reported from Japan. In addition to anthropogenic sources, such as coal combustion and incineration, CH<sub>3</sub>Br and CH<sub>3</sub>Cl have also natural sources, including the oceans, vegetation, and biomass burning. CH<sub>3</sub>Cl, especially, can be emitted from oceanic or terrestrial biogenic processes, biomass burning as well as many anthropogenic activities. 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<sub>3</sub>Cl source in the PRD area. In the case of CH<sub>3</sub>Br, the dominant anthropogenic source is from fumigant use, mostly applied in agricultural areas rather than in industry. Thus, the CO-based estimate for CH<sub>3</sub>Br could be quite uncertain, one needs to be careful for

emission results from the ratio estimate method. Additionally, the concentrations of  $\text{CH}_3\text{Br}$  (more than 20 pptv for 20-th-percentile of the dataset) and  $\text{CH}_3\text{Cl}$  (more than 900 pptv for 20-th-percentile of the dataset) in PRD were much higher than at any oceanic background sites (8.40 for  $\text{CH}_3\text{Br}$  and 486–535 pptv for  $\text{CH}_3\text{Cl}$ ; Table 1), further indicating that a large part of these  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{Cl}$  emissions were not from oceanic sources.

### 3.3 Comparison with emission inventories

Where possible, comparisons of the 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, were plotted in Fig. 3. Another reason for choosing these species was that the Chinese government allowed to produce the CFCs until 1 July in 2007, which include CFC-11, CFC-12, CFC-13, CFC-113, CFC-114 and CFC-115. Additionally, as reported by the Ministry of Environmental Protection of China, these four CFCs accounted for more than 99 % of all CFCs consumed. Thus, neither CFC-13 nor CFC-115 was 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 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.

Our ratio estimated emissions of CFC-11 and CFC-12 were 23.4 % and 165.3 % of the respective inventory estimates. These results suggested 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 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 lower 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  $0.04 \pm 0.05$  and  $0.02 \pm 0.02$  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 had been declined in China. However, demand for HCFC-22 appeared to be governed by organic growth, and the decreasing CFCs trends were countered by the substitution of HCFCs. Evidently, the Chinese HCFC-22 emissions were substantial (inventory estimate 33.8 Gg in 2004), 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  $\text{CCl}_4$  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  $\text{CCl}_4$ , respectively, which were in good agreement with the emissions results (0.35 and 1.05 Gg for MCF and  $\text{CCl}_4$ , respectively) from the enhancement ratio estimate method.

A comparison of the available species for the study period in 2004 was shown in Fig. 3. Considerable interspecies variation under the enhancement ratio technique was evident. Furthermore, linear curve fitting ( $y = 0.99x + 0.19$ ;  $R = 0.91$ ) of the estimated emissions for the different species and methods were 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 mixing ratio of halocarbons in PRD region 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<sub>3</sub>Cl 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 halocarbons and CO were obtained 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 were detected in the PRD region in 2004,  $0.04 \pm 0.05$  and  $0.02 \pm 0.02$  Gg, respectively, comparing with 0.1 Gg and no emission from inventory estimates. As CFC consumption decreases, consumption of HCFC-22, the temporary substitute for CFCs, appeared 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<sub>4</sub>. 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 were 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<sub>3</sub>, CH<sub>3</sub>Br, and so on) from Guangdong Province were also estimated.

In conclusion, atmospheric observations play an important role in assessing halocarbons emissions on a regional scale, especially in a fast growing region, such as the PRD. Comparison 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 ob-

servations, and improvements and updates to CO inventories, the uncertainty of the ratio estimates could be reduced significantly.

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