Science of the Total Environment 470–471 (2014) 829–834

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Estimated emissions of chlorofluorocarbons, hydrochlorofluorocarbons, and hydrofluorocarbons based on an interspecies correlation method in the Pearl River Delta region, China

Jing Wu [a], Xuekun Fang [a], Jonathan W. Martin [b], Zihan Zhai [a], Shenshen Su [a], Xia Hu [a], Jiarui Han [a], Sihua Lu [a], Chen Wang [a], Jianbo Zhang [a], Jianxin Hu [a,*]

[a] State Key Joint Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing, China
[b] Division of Analytical and Environmental Toxicology, Department of Laboratory Medicine and Pathology, University of Alberta, Edmonton, AB, Canada

HIGHLIGHTS

- The bank emissions of CFCs still exist.
- The concentrations and emissions of HCFCs and HFCs have significantly increased.
- The PRD region makes a great contribution to the China's halocarbon emissions.

ARTICLE INFO

Article history:
Received 17 July 2013
Received in revised form 19 September 2013
Accepted 22 September 2013
Available online xxxx

Editor: Xuexi Tie

Keywords:
Interspecies correlation
Emission estimation
Global warming
Ozone depletion

ABSTRACT

Although many studies have been conducted in recent years on the emissions of chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), and hydrofluorocarbons (HFCs) at the large regional (such as East Asia) and national scales, relatively few studies have been conducted for cities or metropolitan areas. In this study, 192 air samples were collected in the Pearl River Delta (PRD) region of China in November 2010. The atmospheric mixing ratios of six halocarbons were analyzed, including trichlorofluoromethane (CFC-11, CCl_3F), dichlorodifluoromethane (CFC-12, CCl_2F_2), monochlorodifluoromethane (HCFC-22, $CHClF_2$), 1,1-dichloro-1-fluoroethane (HCFC-141b, CH_3CCl_2F), 1-dichloro-1,1-fluoroethane (HCFC-142b, CH_3CClF_2), and 1,1,1,2-tetrafluoroethane (HFC-134a, CH_2FCF_3), and their emissions were estimated based on an interspecies correlation method using HCFC-22 as the reference species. The results showed no significant change in the regional concentration and emission of CFC in the past 10 years, suggesting that the continuous regional emission of CFC has had no significant effect on the CFC regional concentration in the PRD region. Concentrations and emissions of HCFCs and HFCs are significantly higher compared to previous research in the PRD region ($P < 0.05$). The largest emission was for HCFC-22, most likely due to its substitution for CFC-12 in the industrial and commercial refrigeration subsector, and the rapid development of the room air-conditioner and extruded polystyrene subsectors. The PRD's ODP-weighted emissions of the target HCFCs provided 9% (7–12%) of the national emissions for the corresponding species. The PRD's GWP-weighted emissions of the target HCFCs and HFC-134a account for 10% (7–12%) and 8% (7–9%), respectively, of the national emissions for the corresponding species, and thus are important contributions to China's total emissions.

1. Introduction

Chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), and hydrofluorocarbons (HFCs) are all man-made chemical substances used in many industrial and commercial fields, such as refrigeration, foam blowing, metered dose inhalers, and fire extinguishing, as well as solvents (Metz et al., 2005). CFCs and HCFCs are of great concern due to their high ozone depletion potential (ODP) (Montzka et al., 2011). Moreover, CFCs, HCFCs, and HFCs are greenhouse gases, and HFCs are included among the Kyoto Protocol (KP) targets (Solomon et al., 2007). Therefore, studies estimating their emissions have become the focus of academics and policy makers. Under the control of the Montreal Protocol (MP), CFCs have been phased out on a global scale (Montzka et al., 2011). The phase-out of HCFCs was requested to begin in 1996 by non-Article 5 parties (mainly developed countries), but it was not until 2013 that Article 5 parties (mainly developing countries) were requested to take action (UNEP, 2009). Influenced by phase-

* Corresponding author at: College of Environmental Sciences and Engineering, Peking University, No.5 Yiheyuan Road, Beijing 100871, China. Tel.: +86 10 62756593; fax: +86 10 62760755.
E-mail address: jianxin@pku.edu.cn (J. Hu).

0048-9697/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.scitotenv.2013.09.071

out progress and market demand, significant differences were found among countries for the emissions of CFCs, HCFCs, and HFCs (Li et al., 2011). Studying the atmospheric mixing ratios (in units of parts per trillion volume, pptv, in this paper) and emissions of these species in a particular country or region can help to track the implementation effectiveness of the MP and KP, and can provide basic information for multi-scale environmental studies and policy making.

The interspecies correlation method has been widely used in recent years, applying aircraft monitoring or high-frequency measurements at remote sites to estimate the emissions of CFCs, HCFCs, and HFCs in large regions (such as East Asia) or for entire countries (Blake et al., 2003; Kim et al., 2010; Li et al., 2011; Palmer et al., 2003; Yokouchi et al., 2005, 2006). However, the observational data from a remote background site are not suitable for estimating emissions in smaller areas using the interspecies correlation method because distinguishing the individual contribution of different source areas in the same airflow direction is difficult. An improved method was to use the interspecies correlation method, but based on local atmospheric data, as shown by Shao et al. (2011), in estimating halocarbon emissions in the Pearl River Delta (PRD) region in 2004.

The PRD region is one of the most densely populated and highly developed metropolitan areas in China, and also features a large manufacturing industry (Streets et al., 2006). Its regional air quality has been worsened by rapid urbanization and industrialization, and halocarbon emissions in this area are of special international interest. Observational studies were widely carried out when CFCs were being phased out, as the consumption of CFCs was allowed in China until 2010 (Chan and Chu, 2007; Chan et al., 2006; Fang et al., 2012; Guo et al., 2009; Shao et al., 2011; Zhang et al., 2006a,b, 2010). A great deal has changed in the past few years, but recent halocarbon emissions have not been reported yet for the PRD region. In this study, 192 whole air samples were collected in the PRD region in November 2010, and the interspecies correlation method was applied to estimate the emissions of six halocarbons, including trichlorofluoromethane (CFC-11, CCl_3F), dichlorodifluoromethane (CFC-12, CCl_2F_2), monochlorodifluoromethane (HCFC-22, $CHClF_2$), 1,1-dichloro-1-fluoroethane (HCFC-141b, CH_3CCl_2F), 1-dichloro-1,1-fluoroethane (HCFC-142b, CH_3CClF_2), and 1,1,1,2-tetrafluoroethane (HFC-134a, CH_2FCF_3). This latest study will help to track the implementation effectiveness of the MP in this region.

2. Method

2.1. Sampling and analysis

The PRD region is located in southern China and consists of nine administrative areas in Guangdong Province, with an area of about 42,000 km^2 (Streets et al., 2006). In this region, we selected three sampling sites, including one urban site in Guangzhou (23.130°N, 113.260°E) and two rural sites in Heshan (22.711°N, 113.548°E) and Wanqingsha (22.711°N, 112.927°E), respectively (Fig. 1). All three sites were on the top of a hill or on the roof of a high building to minimize the influence of any proximate emission sources. In total, 192 air samples were collected in 3.2-L electro-polished stainless-steel canisters, which had been cleaned and evacuated by a canister cleaner (3100A; Entech, Irvine, CA, USA) before shipment to the sampling sites. The restricted grab sampler (39-RS-x; Entech), which has a 5-μm Silonite-coated metal particulate filter, was placed on the inlet of the canister to completely eliminate dust and particulate intrusion during sampling. At each sampling site, one sample was collected at 09:00 (local time) and another at 13:00 (local time) on each day between November 9 and 29, 2010. Moreover, on 3 of these days (November 19, 20, and 27) more intensive sampling was conducted, which included collection of an additional five to seven samples at each site.

A cryogenic pre-concentration system (7100A; Entech) was connected with a gas chromatography/mass spectroscopy (GC/MS) system (Saturn 2100; Varian, Palo Alto, CA, USA) to analyze the six target

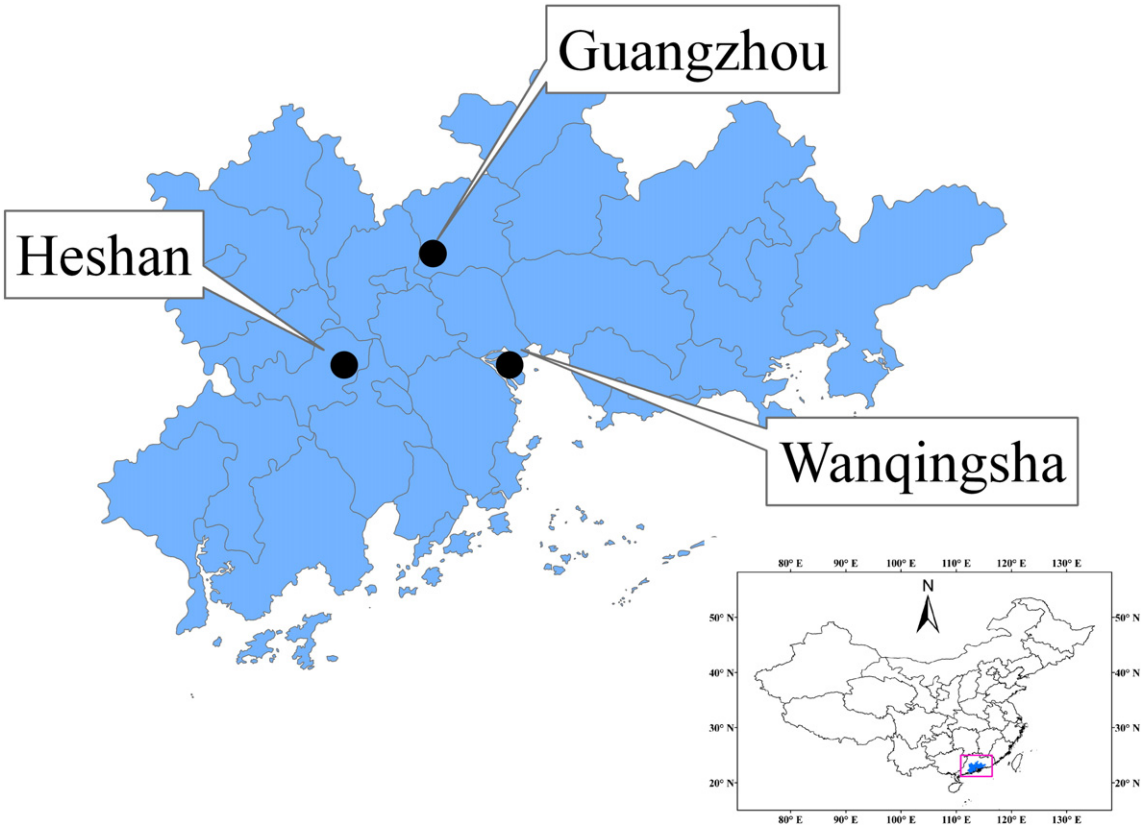

Fig. 1. Map showing the locations of three sampling sites in the PRD region. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

halocarbons. Details on the analytical method and the associated quality control and assurance can be found in Fang et al. (2012). In brief, after concentrating the analytes using the pre-concentration system, the target halocarbons were effectively separated on a GC-Gaspro capillary column (60 m × 0.32 mm), analyzed by the ion trap mass spectrometer in SIM mode, and quantified by a multipoint external standard curve covering the concentration range of ambient air. The working standards were periodically prepared by a dynamic dilution system (4600; Entech). Primary standards were provided by TO-14A (Spectra Gases, Branchburg, NJ, USA) and the National Institute of Metrology of China (NIMC, Beijing, China).

After dilution by a factor of 1000, calibration of the NIMC standard gas in the four parallel canisters was performed by comparison against the standard gas reported on the AGAGE network calibration scales SIO-2005. The specific experimental process has been described in detail by Wu et al. (2013). Results showed that small discrepancies were observed for HCFC-141b (3.4–7.6%), HCFC-142b (0.2–3.8%), and HFC-134a (−1.6% to 3.1%). However, the HCFC-22 mean concentration for four canisters was found to be 118.0% of that in the standard gas reported on SIO-2005. Therefore, HCFC-22 concentrations of ambient samples in this study were adjusted by dividing by a factor of 118.0%. The correlation coefficients for the standard curves changed from 0.995 to 1.000. The measurement precision was 3% for CFCs and 6% for HCFCs and HFC-134a. All target halocarbons in all samples were present at mixing ratios above their detection limit. Means and relative standard deviations of the target halocarbon mixing ratios, including background data in the Northern Hemisphere (NH) provided by NOAA/ESRL (2012) are shown in Table 1.

2.2. Emission estimation

The emission of targeted halocarbons was estimated using an interspecies correlation method based on the idea that the enhancement ratio of the reference species and the target species reflects the ratio of their emission strength. This method has been widely used to estimate the emissions of halocarbons. The observational dataset used in this study was collected over a short enough period (within 21 days) when no significant changes could be observed for the background concentration of halocarbons. In addition, emissions were calculated based on the slope of the regression curve, which does not depend on whether the corresponding background concentration has been subtracted (Shao et al., 2011). Therefore, we adopted the mixing ratios rather than the enhanced mixing ratios, without subtracting the corresponding background concentrations. In this study, HCFC-22 was selected as the reference species because of its significant statistical correlation with other species and its high enhanced atmospheric mean mixing ratios above background level (Fig. 2). Emission of HCFC-22 was calculated based on production and consumption data using the bottom-up approach; see details in Supporting Information 1. HCFC-22 is used for three subsectors in the PRD region, namely, room air-conditioners, extruded polystyrene (XPS) foam, and industrial and commercial refrigeration. The results showed that the estimated emissions from these subsectors are 9.0, 0.3, and 1.4 Gg/year, respectively. The total HCFC-22 emission is 10.7 (±2.8) Gg/year (2.8 Gg/year is the uncertainties of PRD's HCFC-22 emission, see details in Supporting Information 1). The emissions of the target halocarbons were calculated according to the formula below,

$$E_x = E_{HCFC\text{-}22} \times (X/HCFC\text{-}22) \times (M_x/M_{HCFC\text{-}22}) \quad (1)$$

$$\sigma_X = \sqrt{\sigma^2_{E_{HCFC\text{-}22}} \times (X/HCFC{-}22)^2 + E^2_{HCFC\text{-}22} \times \sigma^2_{X/HCFC\text{-}22}} \times (M_X/M_{HCFC\text{-}22}) \quad (2)$$

where E and σ are emission and uncertainty, respectively, X is the target compound, and $X/HCFC\text{-}22$ is the molar ratio of the target species to HCFC-22. So the molecular mass of X and HCFC-22 (M_X and $M_{HCFC\text{-}22}$) should be considered. The slope of the regression curve was calculated using an orthogonal distance regression (ODR), which calculates the least-residual distance between the observational data and the regression line (Barnes et al., 2003). Results of the fit are shown in Table 2 and Fig. 3, and compared to two previous studies in the PRD region.

Note that our observational data were collected in autumn only, which might have introduced uncertainty. Kim et al. (2010) pointed out that the emission results should not be affected by the seasonal sampling distribution for most halocarbons because these species are emitted from industrial and commercial sources, which are expected to be fairly constant throughout the year. Therefore, interspecies ratios do not vary seasonally. Based on Kim et al.'s (2010) conclusion, one can deduce that the uncertainty introduced by the single sampling season should not be significant.

3. Results and discussion

3.1. Continued bank emissions of CFCs

As shown in Table 1, the mixing ratios of the two CFCs are both significantly higher than the corresponding NH background levels ($P < 0.05$), suggesting the continued bank emission of CFCs in the PRD region. Based on the interspecies correlation method, the emissions of CFC-11 and CFC-12 are estimated to be 0.9 (±0.4) and 1.6 (±0.5) Gg/year, respectively (Table 2). Although China phased out the production and consumption of CFCs in 2007, the residual blowing agent CFC-11 in enclosed foam will be emitted steadily throughout its life cycle (15 years). Similarly, the residual refrigerant CFC-12 in refrigeration equipment, including automobile air-conditioners, refrigerators, and freezers, will also be slowly emitted during operation and servicing (Wan et al., 2009). Furthermore, CFCs can also be used for metered

Table 1
The mean and relative standard deviation (RSD) of the target halocarbon mixing ratios in the PRD region in this study and previous studies, together with the data measured in 46 Chinese cities in 2010 and the corresponding background data in the Northern hemisphere (NH) provided by NOAA/ESRL (in pptv).

Common name	PRD for Nov 2010 in this study		PRD in Aug 2001–Dec 2002 (Guo et al., 2009)		PRD in Oct–Nov 2004 (Shao et al., 2011)		46 Chinese cities in Oct/Nov 2010 (Fang et al., 2012)		NH background data for Nov 2010[a]		NH background data in Aug 2001–Dec 2002[a]		NH background data In Oct–Nov 2004[a]	
	Mean	RSD (%)	Mean	RSD (%)	Mean	RSD	Mean	RSD (%)	Mean	RSD (%)	Mean	RSD (%)	Mean	RSD (%)
CFC-11	267	14	298	4	300	9%	268	15	241	0.09	260	0.07	255	0.08
CFC-12	590	10	616	3	700	18%	558	7	531	0.09	544	0.08	543	0.07
HCFC-22	530	29	304	19	464	63%	508	56	213	0.93	160	0.53	172	0.58
HCFC-141b	96	40	43	30	–	–	57	113	22	–	17	–	19	–
HCFC-142b	39	33	18	11	–	–	65	93	21	3.04	14	2.39	16	2.93
HFC-134a	90	32	–	–	–	–	87	65	64	–	23	–	35	–

[a] The NOAA/ESRL data were the calculated averages of the monthly mean mixing ratios and the monthly RSDs during the sampling period, which were accessed at ftp://ftp.cmdl.noaa.gov/hats. The monthly RSDs of HCFC-141b and HFC-134a were not provided on this Web site.

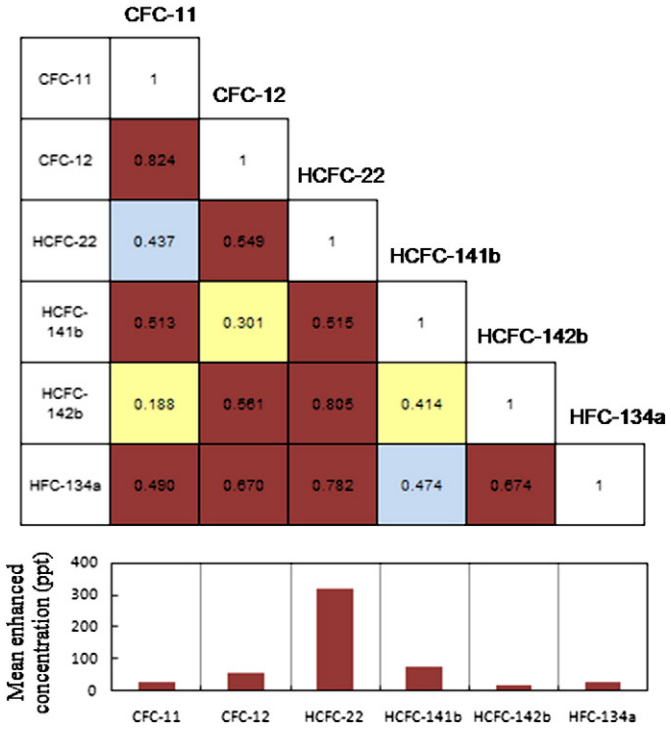

Fig. 2. Interspecies Pearson correlation coefficient (r) in the PRD region during the sampling period. Red background denotes that correlation is significant at the 0.01 level (2-tailed); blue background denotes that correlation is significant at the 0.05 level (2-tailed); yellow denotes that correlation is not significant at the 0.01 or 0.05 level (2-tailed). The lower plot shows the mean of enhanced concentrations above NH background concentration for each compound. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

dose inhalers, an exempt usage that could bring about additional emissions (SEPA, 2012).

The enhanced atmospheric mean mixing ratios above background level can be used to examine the emission strengths of a species to some extent. The mean enhanced mixing ratios of CFC-11 and CFC-12 in the PRD region in this study and previous studies were calculated based on their observational data and corresponding NH background data from Table 1. Results show that the mean enhanced atmospheric mixing ratios of CFC-11 and CFC-12 observed in this study (26 pptv and 59 pptv for CFC-11 and CFC-12, respectively) are comparable to those in previous reports (see Table S1 in the Supporting Information), suggesting that the CFC regional concentration in the PRD region has not changed significantly in recent years. Furthermore, all CFC data observed in this study were also converted to the enhanced mixing ratios by subtracting the corresponding NH background data (241 pptv and 531 pptv for CFC-11 and CFC-12, respectively), and a one-sample t-test was applied to compare these enhanced values with the mean enhanced data calculated from previous studies (see Table S1 in the Supporting Information). Results also show that the enhanced atmospheric mixing ratios of CFC-11 and CFC-12 observed in this study are comparable to those in previous reports ($P < 0.05$), further suggesting that the CFC concentration change in the PRD region was insignificant. Our 2010 estimates of CFC emissions (see Table 2) are also close to the previous two studies in 2001–2002 and in 2004 (Guo et al., 2009; Shao et al., 2011). One could deduce that the continuous regional CFC emission in the PRD region had no significant effect on the regional CFC concentration. Note that the emission magnitudes estimated by the interspecies correlation method often depend on different sampling strategies (such as sampling time, sampling sites, and sampling frequency), choice of reference species (e.g., CO and HCFC-22), and calculation methods for the slope of the regression curve and slope uncertainties (such as the ODR method and Williamson–York method). Therefore, the differences among the different estimated results could be very easily masked by these factors.

3.2. Fast-increasing emissions of HCFCs and HFC-134a

Based on the bottom-up inventory method, the emission of HCFC-22 was estimated to be 10.7 ± 2.8 Gg/year, which is much higher than the emissions of other target halocarbons estimated by the interspecies correlation method (see Table 2). Moreover, the mean mixing ratio of HCFC-22 was shown to be 530 ± 156 pptv (Table 1), with a much higher enhanced atmospheric concentration than other species (see Table S1). Our inventory estimates indicated that the major emission source of HCFC-22 is from room air-conditioners, accounting for 84% of the PRD's HCFC-22 emission. The balance of HCFC-22 emissions was 14% from the industrial and commercial refrigeration subsector, and 2% from the XPS foam subsector. This was the only estimated emission of HCFC-22 in the PRD region in 2010, and verifying our results is therefore quite difficult. Based on the Chinese emissions estimated by Wan et al. (2009), the HCFC-22 annual emission was calculated to make up 10% (8–13%) of the national HCFC-22 emissions, which is similar to the PRD contribution to the gross domestic product (GDP; 9.4%). HCFC-22 is mainly used in room air-conditioners, and the GDP is an indirect index to reflect the regional purchasing power of room air-conditioners. Therefore, the similarity in the percentage of HCFC-22 emission and GDP could verify the reliability of our estimates to some extent. In comparison, our observational data and emission estimates were both significantly higher than those for 2001–2002 and 2004 ($P < 0.05$) (Guo et al., 2009; Shao et al., 2011), in agreement with the rapidly increasing emissions in China (Wan et al., 2009) and in good agreement with the findings of Zhang et al. (2010). The increased HCFC-22 emission partly derives from its effective substitution for CFC-12 in the industrial and commercial refrigeration subsector, and

Table 2
The Pearson correlation coefficient (r) and regression slope (X/HCFC-22) between HCFC-22 and other halocarbons, and emissions of all target halocarbons from the PRD estimated in this study, together with the previously reported values for PRD and Chinese emissions (Gg/year). The ranges of emissions were the estimated uncertainties, calculated by using Eq. (2).

Common name	PRD for 2010, in this study			PRD in 2001–2002 (Guo et al., 2009)	PRD in 2004 (Shao et al., 2011)	China in 2010 (Wan et al., 2009)
	r[a]	ΔX/ΔHCFC-22	Emission			
CFC-11	0.437*	0.054 (0.028–0.080)	0.9 (0.5–1.4)	1.0 (0.7–1.3)	0.4 (0.2–0.6)	11.5
CFC-12	0.549**	0.109 (0.077–0.141)	1.6 (1.2–2.1)	1.5 (1.1–1.9)	1.6 (0.6–2.6)	2.3
HCFC-22	–[b]	–[b]	10.7 (7.9–13.5)	2.2 (1.0–3.4)	3.5 (1.3–5.7)	103.5
HCFC-141b	0.515**	0.081 (0.052–0.110)	1.2 (0.8–1.6)	0.9 (0.6–1.2)	–	16.2
HCFC-142b	0.805**	0.048 (0.043–0.053)	0.6 (0.5–0.7)	–	–	11.8 (9.9–13.8)[c]
HFC-134a	0.782**	0.103 (0.090–0.116)	1.3 (1.1–1.5)	–	–	16.1[d]

[a] *Correlation is significant at the 0.05 level (2-tailed), **Correlation is significant at the 0.01 level (2-tailed).
[b] HCFC-22 emission in this study was calculated by a bottom-up method, so no r and ΔX/ΔHCFC-22 are available for HCFC-22.
[c] Emission of HCFC-142b was extrapolated from the Chinese emission for 2009 (Fang et al., 2012). No information on the Chinese annual growth rate in 2010 can be found for the HCFC-142b emission. We assumed that the annual growth rate of HCFC-142b emission was the same as that of HCFC-141b (14.9%) derived from Wan et al. (2009).
[d] Emission of HFC-134a was calculated under the combined scenario for the mobile air-conditioners (MACs) sector (Wan et al., 2009). HFC-134a is mainly used in the MACs sector in China.

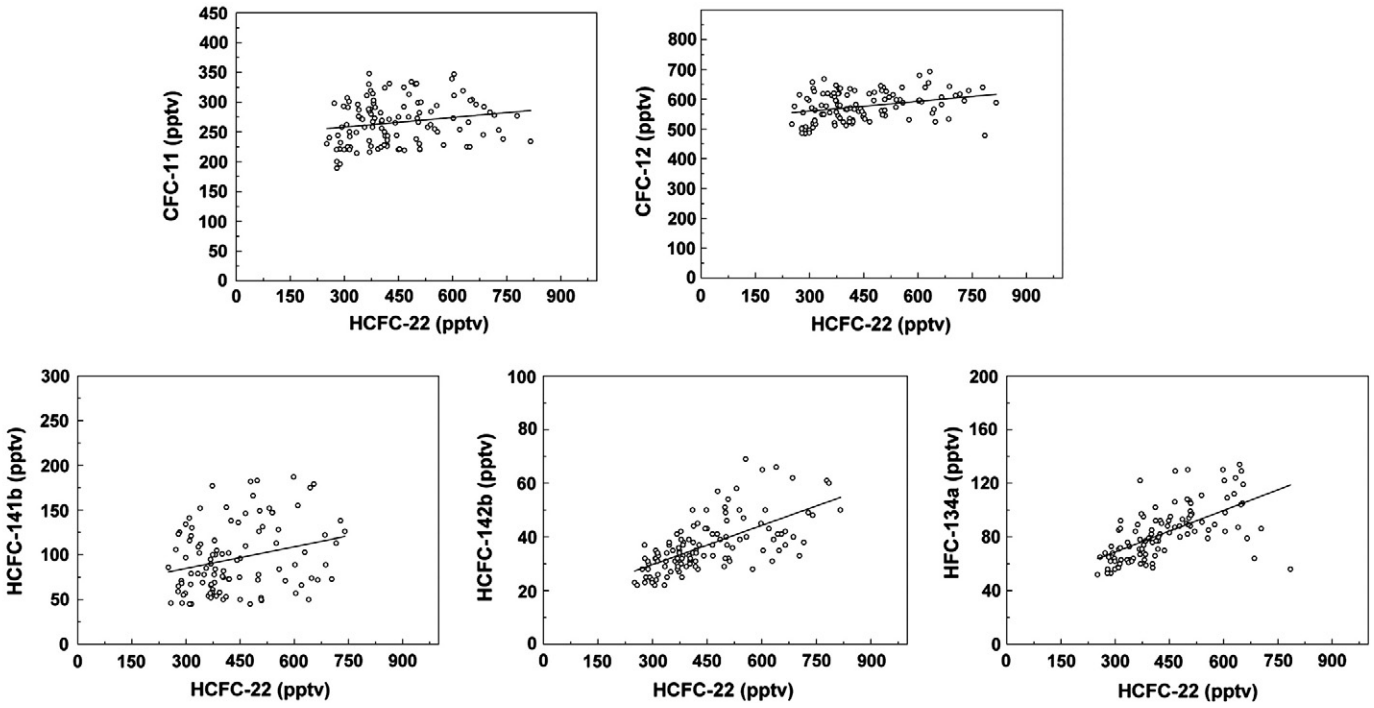

Fig. 3. Relationship between HCFC-22 and other species in the data set. Regression lines are indicated by the solid lines. Statistical outliers were removed prior to performing the regressions.

also results from the rapid development of the other two subsectors (MF, 2007).

The mean mixing ratios of HCFC-141b and HCFC-142b were 96 ± 38 pptv and 39 ± 13 pptv, respectively. These values are both significantly higher than the corresponding NH background values (see Table 1). Based on the interspecies correlation method, our 2010 PRD emission estimates for HCFC-141b and HCFC-142b were 1.2 ± 0.4 Gg/year and 0.6 ± 0.1 Gg/year, respectively (see Table 2). Our estimated result for HCFC-141b substantially exceeds that for 2001–2002 (Guo et al., 2009), and the increasing trend is consistent with the results of Wan et al. (2009).

HFC-134a is mainly used as a refrigerant in the automobile air-conditioner sector in China as a substitute for CFC-12 (Hu et al., 2009). The mean mixing ratio of HFC-134a in the PRD region was 90 ± 29 pptv, significantly higher than the corresponding NH background values (see Table 1). Based on the interspecies correlation method, our estimates for the PRD region showed that 1.3 ± 0.2 Gg/year of HFC-134a was emitted in 2010 (see Table 2). This is the first study on HFC-134a in the PRD region, confirming HFC-134a's wide usage and its effective substitution for CFC-12.

3.3. PRD's important contribution to China

Based on the Chinese emissions estimated by Wan et al. (2009), the fraction of our estimated PRD emissions to national emissions was calculated (see Table 2). Overall, the PRD emission of individual species accounts for about 5–10% of the national emission for the corresponding species, which is similar to the PRD contribution to the GDP (9.4%) and population (4.2%), except for CFC-12. The PRD's CFC-12 emission was a much larger fraction of the national emission, accounting for 71% (52–91%), in line with the significantly higher concentration of CFC-12 observed in the PRD region than in 46 Chinese cities (Fang et al., 2012). Wu et al. (2013) also observed higher CFC-12 concentration in Guangzhou than in the other three Chinese cities. CFC-12 is mainly used as a refrigerant for automobile air-conditioners, refrigerators, and freezers, together with industrial and commercial refrigeration (Wan et al., 2009). Ten years ago, when China started to phase out the production and consumption of CFCs, the PRD region had already become the manufacturing center of southern China. Its industries manufacture a wide variety of goods, including room air-conditioners, refrigerators, and automobiles (Streets et al., 2006), which results in the larger bank emission of CFC-12 in the PRD region compared with other Chinese cities. The larger local emission is also likely due to the higher demand for refrigeration products in the PRD region, resulting from the higher average annual temperatures there (China Statistics Press, 2012). Moreover, note that the fraction of CFC-12 was calculated based on the Chinese emission estimated by Wan et al. (2009) using a bottom-up method, which is the only available value in 2010. In comparison, we found that Wan et al.'s (2009) CFC-12 estimates are always lower than other studies using top-down calculation methods in the same year (Fang et al., 2012; Kim et al., 2010; Li et al., 2011). Specifically, their 2008 estimate (3.869 Gg/year) is less than that of the other two studies (Kim et al., 2010; Li et al., 2011), and their 2009 estimate (3.060 Gg/year) is also lower than the estimate (7.2 ± 1.2 Gg/year) of Fang et al. (2012). Thus, Wan et al.'s (2009) 2010 estimate may be underestimated. That is, the actual fraction of CFC-12 may be overestimated to some extent.

By summing the emissions of each target species multiplied by their corresponding ODP values or global warming potential (GWP, 100-year time horizon) values (Solomon et al., 2007; see Table S2 in the Supporting Information), the total ODP-weighted or GWP-weighted emissions of all target halocarbons in the PRD region were calculated to be 3.3 (2.3–4.5) Gg/year and 45.2 (33.1–58.9) Tg/year, respectively. The PRD's ODP-weighted or GWP-weighted emissions of the target HCFCs accounted for 9% (7–12%) and 10% (7–12%) of the national emissions for the corresponding species, respectively. The GWP-weighted emission of HFC-134a in the PRD region accounts for 8% (7–9%) of the national HFC-134a emission. These results suggest that the PRD region makes an important contribution to the halocarbon emissions in China.

4. Conclusions

In total, 192 air samples were collected in the PRD region in November 2010. Based on the observational data, emissions of six target halocarbons

were estimated using an interspecies correlation method. The results show that CFC bank emissions still exist: 0.9 (±0.4) for CFC-11 and 1.6 (±0.5) Gg/year for CFC-12. This may derive from the remaining storage in products or certain exempt usages. Also, in comparison, the deduction was made that the continuous CFC regional emission has no significant effect on the CFC regional concentration in the PRD region.

With the phase-out of CFCs, the atmospheric mixing ratios and emissions of their main substitutes, HCFCs and HFCs, in the PRD region have increased significantly. The HCFC-22 annual emission is largest among the target species (10.7 ± 2.8 Gg/year), making up 10% (8–13%) of the national HCFC-22 emissions. This was followed by emissions of HFC-134a and HCFC-141b, which accounted for 8% (7–9%) and 8% (5–10%) of the national total for the corresponding species, respectively. The PRD regional emission of HCFC-142b is smallest and makes up the smallest fraction of 5% (4–6%) of the national HCFC-142b emission. The calculated result shows that the total ODP-weighted or GWP-weighted emissions of all target halocarbons in the PRD region were 3.3 (2.3–4.5) Gg/year and 45.2 (33.1–58.9) Tg/year, respectively. The halocarbon emissions from the PRD region contribute significantly to the total emissions in China.

Conflict of interest

There are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant No. 41275156). We also thank all persons involved in sampling at the three sampling sites in the PRD region.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2013.09.071.

References

Barnes DH, Wofsy SC, Fehlau BP, Gottlieb EW, Elkins JW, Dutton GS, et al. Urban/industrial pollution for the New York City–Washington, DC, corridor, 1996–1998: 1. Providing independent verification of CO and PCE emissions inventories. J Geophys Res Atmos 2003;108:4185–98.

Blake NJ, Blake DR, Simpson IJ, Meinardi S, Swanson AL, Lopez JP, et al. NMHCs and halocarbons in Asian continental outflow during the transport and chemical evolution over the Pacific (TRACE-P) Field Campaign: comparison with PEM-West B. J Geophys Res Atmos 2003;108:8806–29.

Chan LY, Chu KW. Halocarbons in the atmosphere of the industrial-related Pearl River Delta region of China. J Geophys Res Atmos 2007;112:D04305.

Chan CY, Tang JH, Li YS, Chan LY. Mixing ratios and sources of halocarbons in urban, semi-urban and rural sites of the Pearl River Delta, South China. Atmos Environ 2006;40:7331–45.

China Statistics Press. 12-7 monthly average temperature of major cities (2011) in China Statistical Yearbook 2012. Available athttp://www.stats.gov.cn/tjsj/ndsj/2012/indexeh.htm, 2012. [accessed on Apr 4, 2013].

Fang X, Wu J, Xu J, Huang D, Shi Y, Wan D, et al. Ambient mixing ratios of chlorofluorocarbons, hydrochlorofluorocarbons and hydrofluorocarbons in 46 Chinese cities. Atmos Environ 2012;54:387–92.

Guo H, Ding AJ, Wang T, Simpson IJ, Blake DR, Barletta B, et al. Source origins, modeled profiles, and apportionments of halogenated hydrocarbons in the greater Pearl River Delta region, southern China. J Geophys Res Atmos 2009;114:D11302.

Hu J, Wan D, Li C, Zhang J, Yi X. Forecasting of consumption and emission of HFC-134a used in automobile air conditioner sector in China. Adv Clim Chang Res 2009;5:1–6. [in Chinese].

Kim J, Li S, Kim KR, Stohl A, Muhle J, Kim SK, et al. Regional atmospheric emissions determined from measurements at Jeju Island, Korea: halogenated compounds from China. Geophys Res Lett 2010;37:L12801.

Li S, Kim J, Kim KR, Muhle J, Kim SK, Park MK, et al. Emissions of halogenated compounds in East Asia determined from measurements at Jeju Island, Korea. Environ Sci Technol 2011;45:5668–75.

Metz B, Kuijpers L, Solomon S, Andersen SO, Davidson O, Pons J, et al. IPCC/TEAP special report on safeguarding the ozone layer and the global climate system: issues related to hydrofluorocarbons and perfluorocarbons. UK: IPCC/TEAP, Cambridge University Press; 2005.

MF (Multilateral Fund Secretariat). Study on the strategy for the long term management of HCFCs in China, the multilateral fund for the implementation of the Montreal Protocol. Available at:http://www.multilateralfund.org/sites/51/Document%20Library2/1/51inf3.pdf, 2007.

Montzka SA, Reimann S, Engel A, Kruger K, O'Doherty S, Sturges WT, et al. Ozone-depleting substances (ODSs) and related chemicals. Scientific assessment in ozone depletion: 2010, chapter 1. Global ozone research and monitoring project-report no. 52Geneva, Switzerland: World Meteorological Organization; 2011. [http://ozone.unep.org/Assessment_Panels/SAP/Scientific_Assessment_2010/index.shtml].

NOAA/ESRL Global Monitoring Division. ftp://ftp.cmdl.noaa.gov/hats, 2012. [accessed on Sept 5, 2012].

Palmer PI, Jacob DJ, Mickley LJ, Blake DR, Sachse GW, Fuelberg HE, et al. Eastern Asian emissions of anthropogenic halocarbons deduced from aircraft concentration data. J Geophys Res Atmos 2003;108:4753–9.

SEPA (State Environmental Protection Administration). http://www.ozone.org.cn/sylm/tzgg/201203/t20120306_16509.html, 2012. [accessed on Sept 18, 2012].

Shao M, Huang D, Gu D, Lu S, Chang C, Wang J. Estimate of anthropogenic halocarbon emission based on measured ratio relative to CO in the Pearl River Delta region, China. Atmos Chem Phys 2011;11:5011–25.

Solomon S, Qin D, Manning M, Alley RB, Berntsen T, Bindoff NL, et al. Technical summary. In: Solomon S, Qin D, Manning M, Chen Z, Marquis M, Averyt KB, Tignor M, Miller HL, editors. Climate change 2007: the physical science basis, contribution of working group I to the fourth assessment report of the intergovernmental panel on climate change. Cambridge, UK and New York, NY, USA: IPCC, Cambridge University Press; 2007.

Streets DG, Yu C, Bergin MH, Wang XM, Carmichael GR. Modeling study of air pollution due to the manufacture of export goods in China's Pearl River Delta. Environ Sci Technol 2006;40:2099–107.

UNEP (United Nations Environment Programme). Handbook for the Montreal Protocol on substances that deplete the ozone layer. United Nations environment programmeeighth ed. 2009. [Available at http://ozone.unep.org/Publications/MP_Handbook/MP-Handbook-2009.pdf].

Wan D, Xu JH, Zhang JB, Tong XC, Hu JX. Historical and projected emissions of major halocarbons in China. Atmos Environ 2009;43:5822–9.

Wu J, Fang X, Xu W, Wan D, Shi Y, Su S, et al. Chlorofluorocarbons, hydrochlorofluorocarbons, and hydrofluorocarbons in the atmosphere of four Chinese cities. Atmos Environ 2013;75:83–91.

Yokouchi Y, Inagaki T, Yazawa K, Tamaru T, Enomoto T, Izumi K. Estimates of ratios of anthropogenic halocarbon emissions from Japan based on aircraft monitoring over Sagami Bay, Japan. J Geophys Res Atmos 2005;110:D06301.

Yokouchi Y, Taguchi S, Saito T, Tohjima Y, Tanimoto H, Mukai H. High frequency measurements of HFCs at a remote site in East Asia and their implications for Chinese emissions. Geophys Res Lett 2006;33:L21814.

Zhang F, Wang XM, Li L, Yi Z, Zhou L, Donald RB, et al. Recent levels and trends of trace chlorofluorocarbons (CFCs) in the Pearl River Delta region. Earth Environ 2006a;34:19–24. [in Chinese].

Zhang F, Wang X, Li Z, Li L, Chen Z, Chen L, et al. Preliminary investigation on levels and trends of atmospheric chlorodifuoromethane (HCFC-22) in the Pearl River Delta. Acta Sci Circumst 2006b;26:987–91. [in Chinese].

Zhang YL, Guo H, Wang XM, Simpson IJ, Barletta B, Blake DR, et al. Emission patterns and spatiotemporal variations of halocarbons in the Pearl River Delta region, southern China. J Geophys Res Atmos 2010;115:D15309.