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Short communication

Ambient mixing ratios of chlorofluorocarbons, hydrochlorofluorocarbons and hydrofluorocarbons in 46 Chinese cities

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ABSTRACT

Air samples in 46 cities all over China were collected in October and November 2010, and the levels of chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) were measured and are discussed in this work. In most cities, the ambient mixing ratios of CFCs were within 20% enhancements of the background values, while the levels of HCFCs and HFCs were significantly higher than the background values ($P < 0.01$). Compared with the results of previous research conducted in 2001 and other single-city studies, the levels of CFC-11, CFC-12 and CFC-113 have decreased since then, while the levels of HCFCs and HFCs have increased rapidly. The results are consistent with the fact that CFCs have been replaced by the interim replacements (HCFCs and HFCs) in compliance with the Montreal Protocol.

1. Introduction

Chlorofluorocarbons (CFCs) were first manufactured in the 1930s and then applied as refrigerants, blowing agents, aerosol propellants and solvents for different industrial and domestic use (McCulloch et al., 2003). Due to their role in stratospheric ozone depletion (Molina and Rowland, 1974; UNEP, 2003), CFCs are regulated by the Montreal Protocol (MP). Hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs), whose lifetimes are much shorter than CFCs, are used as interim replacements of CFCs, while the global warming potentials (GWPs) are quite high (IPCC/TEAP, 2005). Among them, HFCs are regulated by the Kyoto Protocol (KP).

The emissions and concentrations of these substances in China are of great interest to both the academia and policy makers. China, with a great economic and geographical disparity, is in the course of rapid industrialization, urbanization and mobilization. Most developed cities (such as Beijing, Shanghai, and Guangzhou) are located in the east coastal region. The consumption of CFCs in China was banned in mid-2007 (SEPA, 2004), while the banks still release CFCs. China is the major producer of HCFCs. In 2008, the productions of HCFC-22, HCFC-141b, and HCFC-142b accounted for 59%, 84%, and 42% of the global total, respectively (TEAP, 2011). The emissions of HFCs are undergoing a rapid growth in China (EDGAR, 2010) and are expected to keep on increasing. In general, the usages of CFCs have been decreasing while the usages of their replacements (HCFC and HFCs) have been increasing (Kim et al., 2011; Vollmer et al., 2009; Wan et al., 2009).

These substances were measured in 2001 by Barletta et al. (2006) in 45 cities in eastern and central China, and since then similar studies have been conducted in individual Chinese cities (Chan et al., 2006; Qin, 2007; Shao et al., 2011; Xiu et al., 2005). In 2001, the phase-out of CFCs in China was being carried out and CFCs were still allowed to be consumed till 2010 (China belonged to "Article 5" countries under the MP) (UNEP, 2003). Ten years passed by. In the 10 years since 2001, tremendous changes have taken place in China. Accordingly, the ambient mixing ratios of CFCs, HCFCs and HFCs might also be subject to great change. To investigate this, we measured the ambient mixing ratios of chlorofluorocarbons, hydrochlorofluorocarbons and hydrofluorocarbons in 46 cities all over China and compared our results with those of Barletta et al. (2006).

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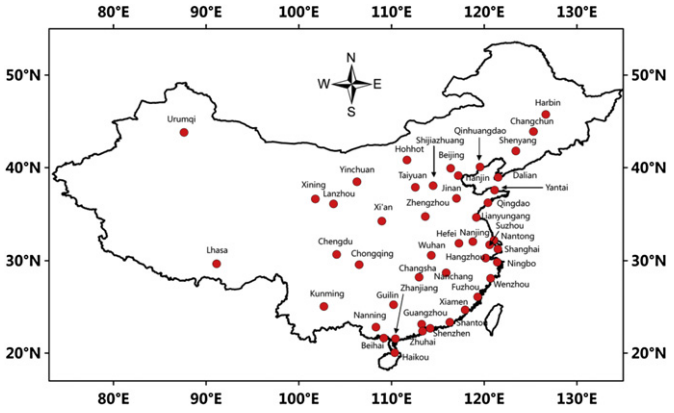

Fig. 1. Map showing the geographical locations of the sampling sites.

2. Experiment

2.1. Sampling description

Forty-six large cities were selected for collecting samples, including 30 provincial capitals and 16 prefecture-level cities in east coastal provinces, all of which are located in highly populated areas. The locations of the sampling sites are shown in Fig. 1. In each city, one sample was collected at 9:00 and another at 13:00 on October 27, 2010, except those at the five sites in Guangdong province where they were collected on November 27. Samples were stored in 3.2 L polished stainless steel canisters cleaned by a canister cleaner (Entech 3100A, Entech, Simi Valley, CA, USA). Samples were collected on the rooftop of buildings with a height of 5–12 floors in downtown residential and commercial areas. It is worth mentioning that samples in Barletta et al. (2006) were collected at a height of 2 m. In this study, particulate attentions were paid to avoid taking samples near noticeable halocarbon sources, such as air-conditioners, refrigerators and foams. Totally, 92 samples were collected.

2.2. Laboratory analysis

GC–MS (Varian Saturn 2100, Varian Co. USA) coupled with a cryogenic pre-concentration system (Entech 7100A, Entech Instruments Inc., USA) was used for laboratory analysis. The pre-concentration process was the same as that described by Zhang et al. (2010). Briefly, multistage traps were used in the preconcentrator to remove H_2O, CO_2 and other unwanted species. A mass spectrometer detector was used and operated in selective ion mode with electron impact ionization.

The procedures, calibration method, quality control/assurance and precision/accuracy are much the same as those in Zhang et al. (2010). Briefly, all target compounds were quantified by a multi-point external calibration method. Before analyzing the samples, humidified zero air was introduced to the analytical system to ensure its cleanliness, followed by dynamically diluted middle-concentration standard gas to check the performance of the system. TO14A (Spectra Gases, USA) and standard gas provided by National Institute of Metrology of China (NIMC) were used as the calibration gases for the CFCs, HCFCs and HFCs, respectively. Inter-comparison experiments for NIMC standard gas were done with calibration scale SIO-2005 (used for halocarbon measurements in some background sites, http://agage.eas.gatech.edu/instruments-overview.htm), and small discrepancies were found, −2.2% to 2.2% for HCFC-22, 3.4–7.6% for HCFC-141b, 0.2–3.8% for HCFC-142b, −1.6 to 3.1% for HFC-134a, −0.6 to 3.5% for HFC-152a. The measured results are presented as mixing ratios. In our chemical analysis, the precision of the halocarbon measurements was 3% for CFCs, and 6% for HCFCs and HFCs. The measurement accuracy also varied by compound and was 2% for CFCs; 6% for HCFCs. Of note is that these measured levels are just a snapshot for ambient halocarbon levels in cities all over China, and are not sufficiently representative of levels within a single city.

3. Results and discussion

3.1. General features

The descriptive statistics of the halocarbon mixing ratios together with the background values from three remote sites are shown in Table 1. Relative standard deviations (RSD) of CFCs (7–15%) were much smaller than those of HCFCs/HFCs (42–113%). The RSD of CFC-11, CFC-12, CFC-113 and CFC-114 were 15%, 7%, 8% and 11%, respectively, which is reasonable considering their long atmospheric lifetimes and their emissions mostly from the CFC banks (Wan et al., 2009). The RSD of HCFC-22, HCFC-141b and HCFC-142b were 56%, 113% and 93%, respectively. HCFCs are the major halocarbons in China (Kim et al., 2010) and are widely used in the sectors of foam blowing, refrigeration, air-conditioning and solvents. The RSD of HFCs (42–65%) were generally lower than those of HCFCs (56–113%), consistent with the fact that HFCs have been widely used in China, but in a smaller amount than HCFCs (Wan et al., 2010). The concentration variability for long-life volatile substances, such as ozone depleting substances, could be exploited as a simple indicator of significant emissions (Chang et al., 2008). Accordingly, the large variability of mixing ratios for HCFCs and HFCs indicates their significant usages and emissions in these cities.

Table 1
Measurement statistics in 46 cities (sample number = 92), together with background values from three remote sites.

Halocarbon	46 Chinese cities					Ragged point, Barbados (RPB)[a]	Trinidad head, California (THD)[a]	Mace head, Ireland (MHD)[a]
	Mean (SD)	RSD	10%	50%	90%	13.17°N, 59.43°W	41.05°N, 124.15°W	53.33°N, 9.9°W
CFC-11	268 (41)	15%	231	261	332	239.8 (0.3)	239.7 (0.3)	239.9 (0.2)
CFC-12	558 (37)	7%	525	550	599	532.5 (0.5)	532.8 (0.7)	532.5 (0.4)
CFC-113	78 (6)	8%	71	77	86	75.2 (0.2)	75.0 (0.2)	75.0 (0.2)
CFC-114	17 (2)	11%	15	17	19	14 (0.1)[b]		
HCFC-22	508 (208)	56%	277	402	863	215.5 (5.0)	222.5 (1.5)	221.4 (1.2)
HCFC-141b	57 (65)	113%	27	39	87	21.3 (0.6)	22.1 (0.3)	22.2 (0.2)
HCFC-142b	65 (60)	93%	28	41	152	21.3 (0.5)	22.2 (0.2)	22.2 (0.1)
HFC-134a	87 (57)	65%	56	74	119	61.9 (2.1)	65.4 (0.9)	65.2 (0.6)
HFC-152a	17 (7)	42%	11	16	22	6.9 (1.0)	8.8 (0.6)	8.8 (0.3)

[a] Latest data (Sep., 2010, close to our sampling period Oct./Nov., 2010) from ALE/GAGE/AGAGE. Data of CFCs except CFC-113 were form http://agage.eas.gatech.edu/data_archive/agage/gc-md/monthly and others from http://agage.eas.gatech.edu/data_archive/agage/gc-ms-medusa/monthly. These three sites were chosen for comparison due to their similar latitudes to our sampling sites (20°N–45°N).

[b] 25th percentile of TRACE-P western Pacific data collected below 1500 m in 2001 (Barletta et al., 2006; Blake et al., 2003).

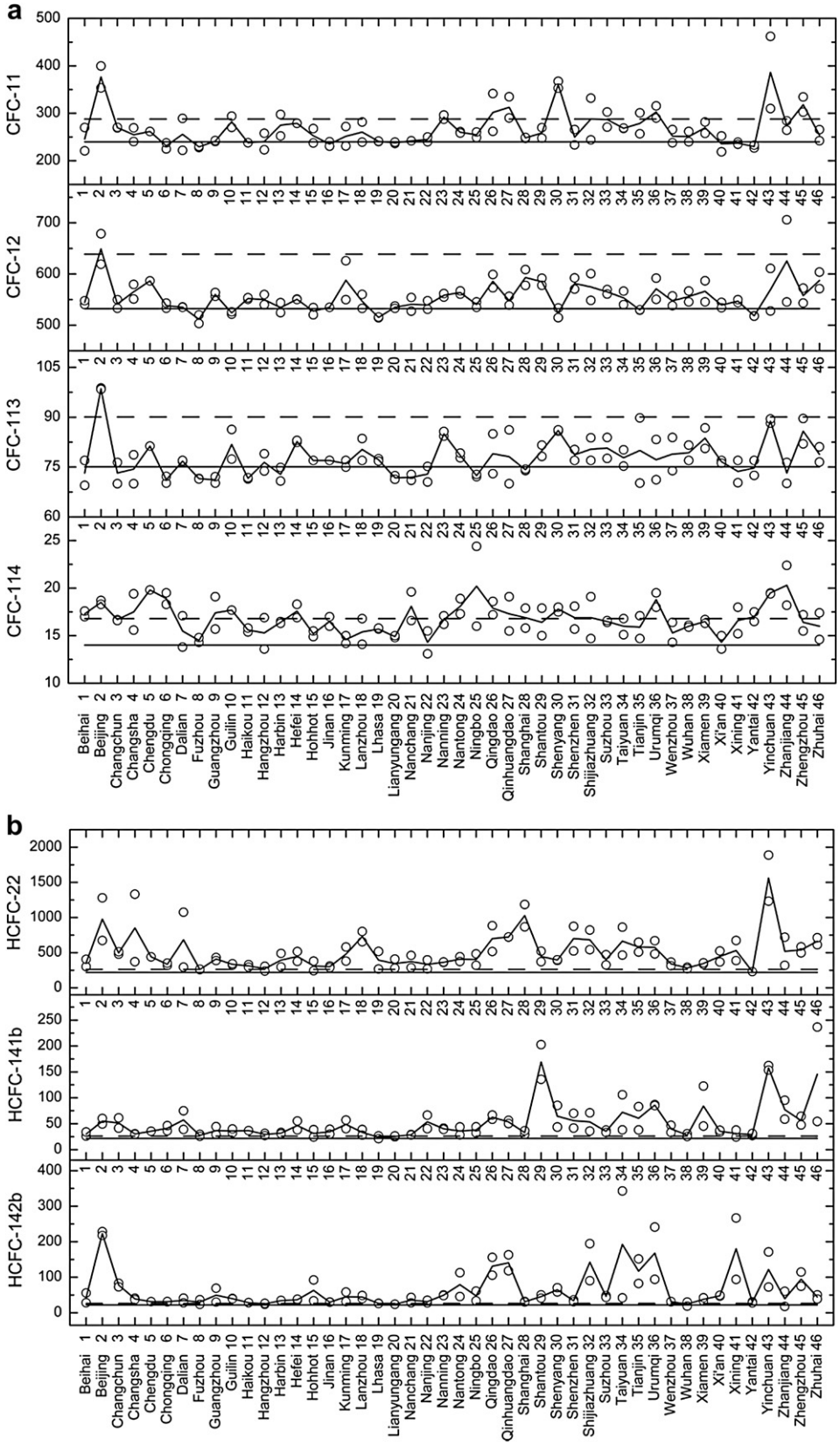

Fig. 2. Average mixing ratios (solid line) measured in the 46 cities for (a) CFCs, (b) HCFCs and (c) HFCs; each circle represents the mixing ratio of a single canister in a city; the horizontal solid line indicates the background values reported in Table 1; the horizontal dotted line is a 20% enhancement relative to background.

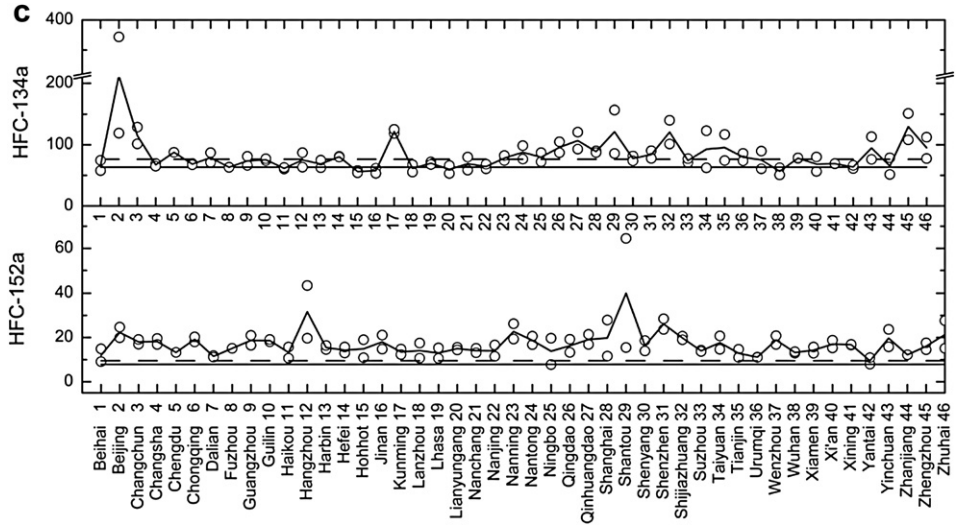

Fig. 2. (*continued*).

3.2. CFCs

From Table 1, CFCs have a negligible latitude gradient, but HCFCs and HFCs have latitude gradients of a few ppt. Therefore three background sites of similar latitude to our sampling sites (20°N–45°N) were chosen for comparison (Table 1), and halocarbon levels measured at Ragged Point, Barbados (13.17°N, 59.43°W) and Mace Head, Ireland (53.33°N, 9.90°W) were averaged to represent our background values. As for CFCs, their mixing ratios in most cities were close to the background values, as shown in Fig. 2a. The average levels of CFC-11, CFC-12 and CFC-113 in 46 Chinese cities were 28 pptv (11.8%), 25 pptv (4.7%) and 3 pptv (3.7%) higher than the background levels. Levels of CFC-11 in 9 cities and levels of CFC-12 in 2 cities were 20% or more higher than the background values. Emissions of CFC-12 in 2010 in China were estimated to be 2326 tones, only one fourth of 2001 emissions, while emissions of CFC-11 in 2010 were one half of 2001 emissions (Wan et al., 2009). This suggests that mixing ratios of CFC-12 may level off to the background level more quickly than CFC-11 in China.

The mixing ratios of CFC-113 were 3 pptv (3.7%) higher than the background value ($P < 0.05$). Previous research showed that CFC-113 emissions in China were small (<0.8 kt in 2007) (Vollmer et al., 2009; Wan et al., 2009). The average level of CFC-114 was 3 pptv (20%) higher than the background value, and this enhancement may be partly associated with the measurement precision and accuracy due to its extreme low concentration. CFC-114 was mainly used in low-temperature refrigeration with low levels of consumption in the past (<0.12 kt in 1995) (SEPA, 1999). Emissions of CFC-113 and CFC-114 were expected to vanish quickly due to their phase-out schedule and short banking time, and this appears to be the case.

The results of the study of 45 cities in 2001 (Barletta et al., 2006) and other studies are cited for comparison to demonstrate the changes in the mixing ratios of halocarbons over time. Beijing (40.00°N, 116.30°E), Shanghai (31.20°N, 121.43°E) and Guangzhou (23.10°N, 113.35°E) were also selected as they represent the largest cities in northern, eastern and southeastern China, respectively. The differences in sampling method, sample numbers, time period and calibration scale require cautious comparison, and are therefore listed in Table 2. The average CFC levels in Chinese cities have decreased since 2001. For instance, the levels of CFC-11 and CFC-113 in 2010 were significantly ($P < 0.01$) lower than the 2001 values, respectively. This is corroborated by comparison with single-city research results. For example, the levels of CFC-11 and CFC-12 in Guangzhou have decreased from 361 (95) pptv to 241 (2) pptv and 720 (100) pptv to 560 (5) pptv, respectively. This change of a few hundred ppt is not explained by the small decrease in CFCs background level, which is only a few ppt (http://agage.eas.gatech.edu/data.htm). Based on the observed decrease, it is suggested that CFCs have been replaced gradually in most Chinese big cities, which is consistent with the findings of previous studies (Kim et al., 2010; Qin, 2007; Vollmer et al., 2009; Wan et al., 2009).

3.3. HCFCs

HCFCs have become widely used since the 1990s in China (Wan et al., 2009). Based on data reported to UNEP (http://ozone.unep.org/Data_Reporting/Data_Access/), in recent years, the annual consumption of HCFCs (more than 300 kt for 2010) is much larger than that of CFCs ten years ago (about 34 kt for 2001). It was not surprising that large enhancements of the mixing ratios of HCFCs were observed in the 46 cities (Fig. 2b). The average mixing ratios of HCFC-22, HCFC-141b and HCFC-142b were 508 (208) pptv, 65 (60) pptv and 87 (57) pptv, respectively, significantly higher than the background values ($P < 0.01$). These enhancements suggest their large emissions from China, which is in line with the estimated HCFC emissions. The emissions of HCFC-22, HCFC-141b and HCFC-142b in China accounted for 23%, 25% and 24% of global emissions in 2008 (Kim et al., 2010).

It is obvious that the average mixing ratios of HCFCs in Chinese cities increased during the last ten years (see Table 2). The levels of HCFC-22, HCFC-141b and HCFC-142b in this study were about 2, 2 and 3 times of those in 2001, respectively (Barletta et al., 2006). Those increases are statistically significant ($P < 0.01$). The increasing trend was also observed in Beijing and Shanghai. The emissions of HCFC-22 and HCFC-141b were estimated to increase from 11,880 tons and 2504 tons in 2001 to 117,647 tons and 18,392 tons in 2010 (Wan et al., 2009). Although the consumption of HCFCs in China will be frozen at the baseline of an average of 2009–2010 consumption in 2013 and reduced by 10% in 2015 and by 35% in 2020 under the adjustment of the MP (UNEP, 2009), their emissions will continue to increase in the next few years due to the delay between consumption and emission. Accordingly, the levels of HCFCs will grow gradually and peak in later years.

Table 2
Comparison of CFC, HCFC and HFC levels measured in Barletta et al. (2006) and other studies with this study. The time period for sampling in Barletta et al. (2006) is January and February, which is close to our sampling time October and November, which is a cool/cold time in China. No samples in Guangzhou were taken in Barletta et al. (2006), so other research results were cited.

	45 cities, China	46 cities, China	Beijing, China				Shanghai, China		Guangzhou, China		
Reference	(Barletta et al., 2006)	This study	(Xiu et al., 2005)	(Barletta et al., 2006)[a]	(Qin, 2007)	This study	(Barletta et al., 2006)[a]	This study	(Chan et al., 2006)	(Shao et al., 2011)	This study
Observation period	2001/01–2001/02	2010/10–2010/11	1999/01–2003/12	2001/01–2001/02	2005/01–2007/03	2010/10/27	2001/01–2001/02	2010/10/27	2001/03/03–03/19	2004/10–2004/11	2010/11/27
Sample number	158	92	520	3	352	2	5	2	39	60	2
Sampling	Canister	Canister	Canister	Canister	In situ/canister	Canister	Canister	Canister	Canister	Canister	Canister
Scale	UCI	TO14A/NIMC	Scott	UCI	NR[c]	TO14A/NIMC	UCI	TO14A/NIMC	UCI	UCI	TO14A/NIMC
CFC-11	284 (35)	268 (41)	893 (393)–527 (188)[b]	282–312	269 (11)–406 (1.5)[c]	377 (33)	284 (35)	248 (2)	361 (95)	304 (27)	241 (2)
CFC-12	564 (34)	558 (37)	–	625–783	562–692 (84)[c]	649 (42)	547 (18)	593 (22)	720 (100)	739 (132)	560 (5)
CFC-113	90 (10)	78 (6)	–	–	79 (1.7)–98 (34.3)[c]	99 (0)	90 (10)	74 (0)	97 (13)	92 (5)	71 (1)
CFC-114	15 (0.5)	17 (2)	–	–	–	18 (0)	15 (0.5)	17 (1)	16 (1)	19 (5)	17 (2)
HCFC-22	220 (71)	508 (208)	–	215–382	–	977 (429)	208–427	1026 (224)	553 (418)	602 (324)	409 (31)
HCFC-141b	20 (9)	57 (65)	–	–	–	55 (7)	–	33 (5)	46 (46)	–	37 (11)
HCFC-142b	19 (5)	65 (60)	–	13–31	–	223 (8)	13–33	31 (1)	90 (150)	–	49 (28)
HFC-134a	23 (8)	87 (57)	–	–	–	245 (179)	–	89 (2)	36 (20)	–	74 (10)
HFC-152a	–	17 (7)	–	–	–	22 (3)	–	20 (12)	–	–	19 (3)

[a] All values of Beijing, as well as HCFC-22 and HCFC-142b values of Shanghai were approximately extrapolated from figures 2 and 3 in literature (Barletta et al., 2006).
[b] The annual average concentration of CFC-11 decreased from 893 (393) in 1999 to 527 (188) in 2003.
[c] Minimum monthly mean to maximum monthly mean. NR represents not reported.

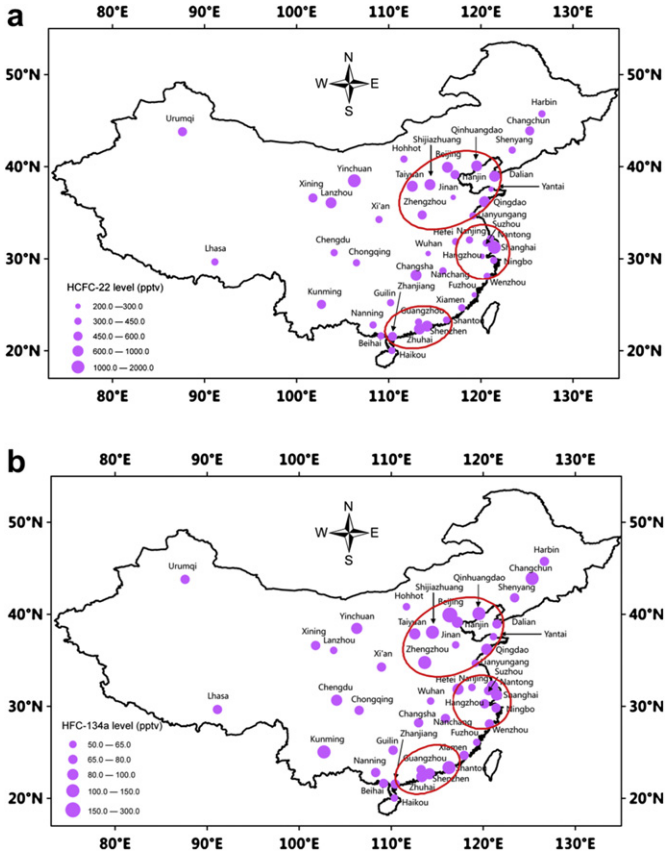

Fig. 3. Map showing the geographical distribution of ambient mixing ratios of (a) HCFC-22 and (b) HFC-134a in China. The larger the pink circle, the higher the mixing ratio. The red hollow circles display the regions with high mixing ratios. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.4. HFCs

HFCs are widely used as replacements for ODSs in developed countries and were introduced to China recently. HFC-134a is the dominant HFC consumed in China, mainly as a refrigerant for mobile air-conditioners (Wan et al., 2010). The average mixing ratio of HFC-134a measured in this study was 87 (57) pptv, higher than the background value (63.5 pptv) ($P < 0.01$) (Fig. 2c). Emissions of HFC-134a in China have been estimated to be 8.3 kt in 2008, accounting for about 5% of the major halocarbon emissions in China (Kim et al., 2011). The average mixing ratio of HFC-152a was 17 (7) pptv in this study and was significantly higher than the background value ($P < 0.01$).

It has been reported that the average HFC-134a mixing ratio in the 45 cities in 2001 was 23 (8) pptv (Barletta et al., 2006), which was significantly lower than the measured result (87 (57) pptv) in this study ($P < 0.01$). The estimated emissions of HFC-134a from China have increased from 3.9 kt in 2005 (Yokouchi et al., 2006) to 8.3 kt in 2008 (Kim et al., 2010). Nevertheless, due to the forthcoming freeze and phase-out of HCFCs in China (UNEP, 2009), it can be expected that consumption and emissions of HFC-134a and thus its mixing ratios in urban atmospheres will experience a surge if HFC-134a is selected as replacement for HCFCs in China. HFC-152a was not measured in 2001 (Barletta et al., 2006) or other studies (see Table 2), therefore no comparison was conducted.

The geographical distributions of HCFC-22 and HFC-134a mixing ratios are shown in Fig. 3. Regions with high mixing ratios of HCFC-22 and HFC-134a are North China Plain (NCP), Yangtze River Delta (YRD) and Pearl River Delta (PRD). All of these regions are highly populated areas with a relatively high rate of car ownership (NBSC, 2010), and HFC-134a mainly comes from mobile air-conditioners.

4. Conclusion

The ambient mixing ratios of CFCs in most cities were within 20% enhancement of the background values with a few exceptions. However, levels of HCFCs and HFCs surpassed the background

values to a large extent, especially HCFC-22 (508 (208) pptv for the 46 cities compared to 218.5 pptv for background). Large concentration variability of HCFCs and HFCs indicated the significant usages and emissions in the cities that were studied. Regions with high mixing ratios of HCFC-22 and HFC-134a were identified, including North China Plain (NCP), Yangtze River Delta (YRD) and Pearl River Delta (PRD).

Compared with the results of Barletta's work and other studies, ambient mixing ratios of CFC-11, CFC-12 and CFC-113 in Chinese cities have decreased since 2001. However, the levels of HCFCs and HFCs have increased rapidly. The levels of HCFC-22, HCFC-141b and HCFC-142b have grown to 2, 2 and 3 times of the corresponding values in 2001, respectively. In addition the level of HFC-134a has grown from 23 (8) pptv in 2001 to 87 (57) pptv in 2010. Based on the observed change, it is suggested that CFCs have been replaced gradually in most big Chinese cities while HCFCs/HFCs usages and emissions increased rapidly. Due to the forthcoming freeze and phase-out of HCFCs, usages and emissions of HCFCs and replacement HFCs may continue to change in subsequent years.

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