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Chlorofluorocarbons, hydrochlorofluorocarbons, and hydrofluorocarbons in the atmosphere of four Chinese cities

Jing Wu [a], Xuekun Fang [a], Wanyun Xu [b], Dan Wan [a], Yehong Shi [a], Shenshen Su [a], Jianxin Hu [a], Jianbo Zhang [a,*]

[a] State Key Joint Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing 100871, China
[b] Department of Atmospheric and Oceanic Sciences, School of Physics, Peking University, Beijing 100871, China

HIGHLIGHTS

- 304 air samples were collected at urban and suburban sites in four Chinese cities.
- CFC levels are approaching NH background levels, suggesting the underway phase-out.
- HCFC and HFC levels far exceed the NH background levels, indicating wide emission.
- Their yearly trends and seasonal variations were analyzed.
- By using statistical method, spatial variations and emission were also analyzed.

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ABSTRACT

From July 2009–April 2011, 304 whole-air samples were collected at urban and suburban sites in four Chinese cities. The results indicated that recent chlorofluorocarbon (CFC) concentrations in all four cities are approaching Northern Hemispheric (NH) background levels, suggesting that the phase-out of CFCs in China is underway. However, hydrochlorofluorocarbon (HCFC) and 1,1,1,2-tetrafluoroethane (HFC-134a, CH_2FCF_3) concentrations have risen far above the NH background levels. Their concentration variability is evident, suggesting significant regional emissions. One-way analysis of variance (ANOVA) and independent-sample *t*-tests were applied to analyze the spatial distributions and emissions. Monochlorodifluoromethane (HCFC-22, $CHClF_2$) levels at the urban sites were 30% higher than those observed at the suburban sites ($P < 0.05$), likely owing to larger population density in the urban areas. The largest 1-dichloro-1,1-fluoroethane (HCFC-142b, CH_3CClF_2) mean concentrations were detected in Beijing (131 and 52 pptv for urban and suburban sites, respectively), likely because of more widespread use of extruded polystyrene board. The variation in HFC-134a concentration levels in different cities was mainly related to the vehicle population. In addition, the different HCFC species exhibited significant positive correlations amongst themselves for each city ($P < 0.05$), suggesting that either they were emitted from similar or co-located sources or they shared similar emission patterns. These results are helpful to confirm the phase-out of ozone-depleting substances (ODSs) and to provide guidance for implementing effective phase-out strategies for ODSs and greenhouse gases.

1. Introduction

Chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) can release free chlorine atoms into the stratosphere and initiate catalytic cycles that induce stratospheric ozone depletion. As ozone-depleting substances (ODSs), they have been controlled successively under the Montreal Protocol and its subsequent amendments (Montzka et al., 2011). Moreover, CFCs, HCFCs, and their main substitutes, hydrofluorocarbons (HFCs), are potent greenhouse gases (GHGs). They remain in the atmosphere for a long time and efficiently absorb infrared radiation. Their global warming potentials (GWPs) are much higher than that of CO_2 (Metz et al., 2005; Solomon et al., 2007). HFCs have been controlled under the Kyoto Protocol. Furthermore, because of their global climate

* Corresponding author. Tel.: +86 10 62753438; fax: +86 10 62760755.
E-mail address: jbzhang@pku.edu.cn (J. Zhang).

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and ozone depletion effects, CFCs, HCFCs, and HFCs have become a focal point of atmospheric chemistry research.

As one of the world's fastest growing economies, China gradually became one of the largest halocarbon producers and consumers after 2000 (UNEP, 2011). Although historical HCFC emissions were relatively low in China, its annual consumption has reached 35% of the global total since 2005 (UNEP, 2005), and its annual emission has accounted for more than 20% of the global total since 2008 (Kim et al., 2010). Since then, increasing attention has been drawn to halocarbon studies of China.

The mixing ratios of CFCs, HCFCs, and HFCs are monitored continuously with more than 30 ground-based background observation stations at coastal and mountain sites worldwide (WDCGG, 2011). According to long-term observation results from these stations, the global surface mean mixing ratios of CFCs have declined significantly, while those of HCFCs and HFCs are increasing (Montzka et al., 2011). In comparison to the well-documented global background mixing ratios, there are relatively limited halocarbon observations for urban and suburban atmospheres in some individual years, even though emission sources are easy to identify in these areas (see relevant literature in Table 1). Observations of urban environments in developed countries have mostly been made from the late twentieth to early twenty-first centuries, 3–5 years after the CFC phase-out. In China, such observations have primarily focused on the more developed cities including Beijing, Shanghai, Hong Kong, and the cities of the Pearl River Delta (PRD). Extensive CFC observations have also been conducted in Taipei and Lukang. Furthermore, Barletta et al. (2006) collected 158 whole-air samples in 45 Chinese cities in 2001, providing a snapshot of the urban Chinese environment.

China ratified the Montreal Protocol in 1991 and phased out the production and consumption of CFCs in 2007, 2.5 years ahead of schedule (SEPA, 2007). Since then, HCFCs and HFCs have been selected as major CFC substitutes (MF, 2007). In China, monochlorodifluoromethane (HCFC-22, $CHClF_2$) is used mainly as a refrigerant for air conditioning, industry, commercial refrigeration, and related service sectors. Less than 5% of its use is by the extruded polystyrene (XPS) foam sector (MF, 2007). 1,1-Dichloro-1-fluoroethane (HCFC-141b, CH_3CCl_2F) is used in the polyurethane (PUR) foam sector and a small amount in the solvent sector (MF, 2007). The vast majority of 1-dichloro-1,1-fluoroethane (HCFC-142b, CH_3CClF_2) use is in the XPS foam sector and the remaining use is for servicing refrigeration equipment (MF, 2007). Furthermore, 1,1,1,2-tetrafluoroethane (HFC-134a, CH_2FCF_3) is used mainly as a refrigerant in the automobile air-conditioning sector (Hu et al., 2009). Regulated under the accelerated HCFC phase-out schedule of the Montreal protocol amendment, HCFC production and consumption in China will be frozen in 2013 at a baseline level equivalent to the average of the 2009 and 2010 levels and will be phased out by 2030 (UNEP, 2009).

Emission estimates have revealed that, with the phase-out of CFCs and wide HCFC and HFC use, halocarbon emission sources and levels in China have changed dramatically in the past 5 years (Wan et al., 2009). However, only limited concentration data at one semi-rural site have been reported (Yao et al., 2010, 2012; Zhang et al., 2010a; 2011). Therefore, more monitoring in urban areas is needed to reflect the atmospheric halocarbon concentrations and emission strength in urban China. Fang et al. (2012b) collected 92 samples from 46 Chinese cities in 2010. Compared to the results of Barletta et al. (2006), CFC levels have decreased to near background

Table 1
Selected halocarbon levels measured in various cities worldwide (mean mixing ratios in pptv and relative standard deviation in brackets).

Halocarbon studies	Scale	CFC-11	CFC-12	HCFC-22	HCFC-141b	HCFC-142b	HFC-134a
Guangzhou of PRD (Mar 2001), (Chan et al., 2006)	UCI	361 (26%)	720 (14%)	553 (76%)	46 (100%)	90 (166%)	36 (56%)
Guangzhou of PRD (Oct–Nov 2004), (Shao et al., 2011)	UCI	304 (9%)	739 (18%)	602 (54%)			
Guangzhou of PRD (Oct–Nov 2004, canister), (Chang et al., 2008)	UCI	310[a]	751[a]	–	–	–	–
Guangzhou of PRD (Nov 2004, *in situ*), (Chang et al., 2008)	UCI	286[a]	611[a]	–	–	–	–
Xinken of PRD (Oct–Nov 2004), (Shao et al., 2011)	UCI	295 (10%)	652 (14%)	295 (30%)			
Xinken of PRD (Nov 2004, *canister*), (Chang et al., 2008)	UCI	291[a]	638[a]				
Panyu of PRD (Sep–Dec 2001), (Chan et al., 2006)	UCI	302 (9%)	820 (80%)	274 (23%)	51 (47%)	21 (14%)	49 (29%)
Dinghu of PRD (Mar 2001), (Chan et al., 2006)	UCI	291 (5%)	580 (3%)	205 (22%)	21 (24%)	45 (273%)	19 (42%)
Wanqingsha of PRD (Oct–Dec 2007), (Zhang et al., 2010b)	TO-14A	277 (1%)	614 (1%)	438 (9%)			
PRD (Aug 2001–Dec 2002), (Guo et al., 2009)	UCI	298 (4%)	616 (3%)	304 (19%)	43 (30%)	18 (11%)	
PRD (Oct–Nov 2004), (Shao et al., 2011)	UCI	300 (9%)	700 (18%)	464 (63%)	–	–	–
PRD (Nov 2004), (Chan and Chu, 2007)[a]	UCI	274	578	214	18	17	19
Beijing (Jan 2005–Mar 2007), (Qin, 2007)	–	312 (15%)	613 (12%)	–	–	–	–
Shanghai (Jan–Feb 2001), (Barletta et al., 2006)	UCI	265 (3%)	547 (3%)				
45 cities (Jan–Feb 2001), (Barletta et al., 2006)	UCI	284 (12%)	564 (6%)	220 (32%)	20 (45%)	19 (26%)	23 (35%)
46 cities (Oct or Nov 2010), (Fang et al., 2012b)	TO-14/ NIMC/ SIO-2005	268 (15%)	558 (7%)	508 (56%)	57 (113%)	65 (93%)	87 (65%)
Hong Kong (Aug 2001–Dec 2002), (Guo et al., 2009)	UCI	294 (2%)	615 (3%)	322 (13%)	56 (23%)	32 (50%)	
Hong Kong (Oct–Dec 2007), (Zhang et al., 2010b)	TO-14A	273 (2%)	587 (1%)	574 (13%)			
Taipei (Jan 1997), (Wang et al., 1998)	UCI	283[b]	590[b]				
Taipei (Oct 1998), (Wang et al., 2000)	UCI	305[a]	722[a]				
Lukang (Apr–Oct 2004), (Lee and Chiou, 2007)	SIO-98	265 (6%)	593 (14%)				
Taipei (Nov 2005, *in situ*), (Chang et al., 2008)	UCI	279[a]	586[a]				
Lukang (Jan–Nov, 2006), (Lee and Chiou, 2008)	SIO-98	257 (14%)	577 (117%)				
Chiba, Japan (Feb 1999), (Miyoshi and Makide, 2001)	TO-14	260	640	–	–	–	–
Tokyo, Japan (1999), (Uchiyama and Hasegawa, 2000)	TO-14	279	558	752	301	68	202
Philadelphia, United States (Feb 2001), (Barletta et al., 2006)	UCI	273 (14%)	567 (12%)	–	–	–	–
Las Vegas, United States (Feb 2001), (Barletta et al., 2006)	UCI	259 (4%)	545 (9%)	–	–	–	–
Bristol, England (Aug–Sep 2000), (Pankow et al., 2003)	OGI	302 (28%)	566 (8%)	–	–	–	–
Bristol, England (Oct 2004–Dec 2005), (Khan et al., 2009)	SIO-98	255 (28%)	545 (8%)	315 (153%)	–	–	–
Krakow, Poland (Jul 1997–Sep 1999), (Rivett et al., 2003)	NPL	267 (1%)	–	–	–	–	–
Marseille, France (Jun–Jul 2001), (Barletta et al., 2006)	UCI	288 (9%)	564 (7%)	–	–	–	–

[a] The median of mixing ratios.
[b] The 10 percentiles of mixing ratios.

levels. However, HCFC and HFC levels have increased two to four times, with high HCFC-22 and HFC-134a concentrations found over the North China Plain (NCP), Yangtze River Delta (YRD), and PRD. Therefore, to accurately monitor the variation in local concentrations and emission strength, atmospheric halocarbon observations are necessary, especially in high-emission regions.

Considering previous studies, economic development levels, and climatic and geographical characteristics, Beijing, Guangzhou, Hangzhou, and Lanzhou were selected as the sampling sites for this study. In total, 304 whole-air samples were collected at urban and suburban sites in the four cities in each season from July 2009 to April 2011. The atmospheric mixing ratios were analyzed for six target halocarbons: trichlorofluoromethane (CFC-11, CCl_3F), dichlorodifluoromethane (CFC-12, CCl_2F_2), HCFC-22, -141b, -142b, and HFC-134a. The temporal change trend was examined for each substance. In addition, to study the spatial variations and emissions, some statistical methods were used, including one-way analysis of variance (ANOVA), the independent-sample *t*-test, and Pearson's correlation analysis. The results will help to confirm the effects of ODS phase-out and provide guidance for implementing effective phase-out strategies for ODSs and greenhouse gases (GHGs).

2. Methods

2.1. Sampling sites

Considering previous studies, economic development levels, and climatic and geographical characteristics, four representative cities were selected as sampling sites (see their natural and social economic indices in Table 2). Beijing, located on the northeastern edge of the NCP, is hot in the summer and cold in the winter, with an annual average temperature of 13.3 °C. It is the economic center of the NCP. Guangzhou, the economic center of the PRD, is located in southern China. It has a high annual average temperature of 23.0 °C, abundant rainfall, sufficient sunshine, and a long summer. Hangzhou is situated in the YRD, on the southeast coast of China, and experiences four distinct seasons. It is one of the top ten economically developed cities in China. Many light industries are found within several hundred kilometers of Hangzhou, in particular fluorine chemical industries (MF, 2007). Lanzhou is the geographical center of northwestern China and has a relatively low annual average temperature of 8.0 °C. The economic development and consumption levels of Lanzhou are lower than those in the other cities.

To study the local spatial distribution of the target halocarbons, we set up two sampling sites in each city: an urban site and a suburban site. Their locations are shown in Fig. 1 and Table 2. The urban site locations were in central commercial areas with relatively high population densities (Table 2), where halocarbon use might be greater. The sampling sites were located 40–50 m above ground on the rooftops of 14–18-story buildings. The suburban sites were located on high mountains or open areas that were populated sparsely (Table 2) and affected less by anthropogenic influences. All sampling sites were placed away from direct halocarbon sources, such as air conditioners and fluorine chemical plants.

2.2. Sampling and chemical analysis

All samples were collected in 3.2-L electro-polished, stainless steel, evacuated canisters. The canisters were cleaned and evacuated by a canister cleaner (Entech 3100A, Entech, USA) at Peking University before shipment to the sampling sites. During sampling, the canister valve was opened slightly over a 1-min period.

From July 2009 to April 2011, four or six sunny, windless days in a row were chosen in January, April, July, and October to represent winter, spring, summer, and autumn, respectively, with a total of 38 sampling days. On each sampling day, eight whole-air samples were simultaneously collected at the eight sampling sites at exactly 14:00 (local time), with one sample obtained at each sampling site. Therefore, a total of 304 samples were collected at the eight sampling sites on 38 different days (38 samples for each sampling site). The canisters were then shipped back to our laboratory at Peking University for analysis.

Next, 400 ml of the whole-air sample were pumped into a cryogenic pre-concentration system (Entech 7100A, Entech Instruments, USA) with multistage traps to capture and concentrate the target halocarbons. The pre-concentrated sample was flash vaporized with high-temperature nitrogen and pumped into a gas chromatography/mass spectroscopy (GC/MS) system (Varian Saturn 2100, Varian, USA) for qualitative and quantitative analyses.

TO-14A (Spectra Gases, USA) was applied as a calibration gas for CFCs, and the standard gas provided by the National Institute of Metrology of China (NIMC) was used for HCFCs and HFC-134a. The NIMC standard gas with a dilution factor of 1000 times by ultra pure nitrogen was calibrated by the standard gas reported on SIO-2005 (used for halocarbon measurements in some background sites, http://agage.eas.gatech.edu/instruments-overview.htm). The

Table 2
Natural and social economic indices of the four Chinese cities.

	Beijing	Guangzhou	Hangzhou	Lanzhou
Annual average temperature (K)[a]	286	295	290	284
Population Density of urban region in 2010 (10,000 persons km^{-2})[a]	2.20	3.08	0.24	0.58
Population Density of suburban region in 2010 (10,000 persons km^{-2})[a]	0.13	1.94	–[b]	0.01
GDP per capita in 2000 (10,000 Yuan/person)[a]	2.41	2.56	1.97	1.03
GDP per capita in 2010 (10,000 Yuan/person)[a]	7.59	8.75	6.98	3.04
Floor space of buildings under construction in 2008 (10,000 m^2)[c]	19,764	16,059	6316	1404
Vehicle population in 2010 (10,000 units)[d–g]	481[d]	215[e]	183[f]	39[g]
Location of urban sampling site	39.908°N, 116.422°E	23.130°N, 113.260°E	30.279°N, 120.130°E	36.052°N, 103.838°E
Location of suburban sampling site	39.717°N, 116.797°E	23.193°N, 113.479°E	30.199°N, 120.100°E	35.950°N, 103.944°E
Distance of the suburban site from polluted areas (km)	24	15	25	18

[a] Statistical Yearbook of each city, 2011.
[b] This site is in a large scenic spot, whose resident population is almost 0.
[c] China Statistical Yearbook for Regional Economy, 2009.
[d] Local News: http://www.askci.com/freereports/2011-03/201133175811.html. No official figures were available.
[e] Local News: http://news.gd.sina.com.cn/news/2010/12/28/1079607.html. No official figures were available.
[f] Local News: http://house.ifeng.com/loushi/hangzhou/detail_2011_02/28/4890130_0.shtml. No official figures were available.
[g] Local News: http://www.gsei.com.cn/html/xwdt/jjxw/589_126158.html. No official figures were available.

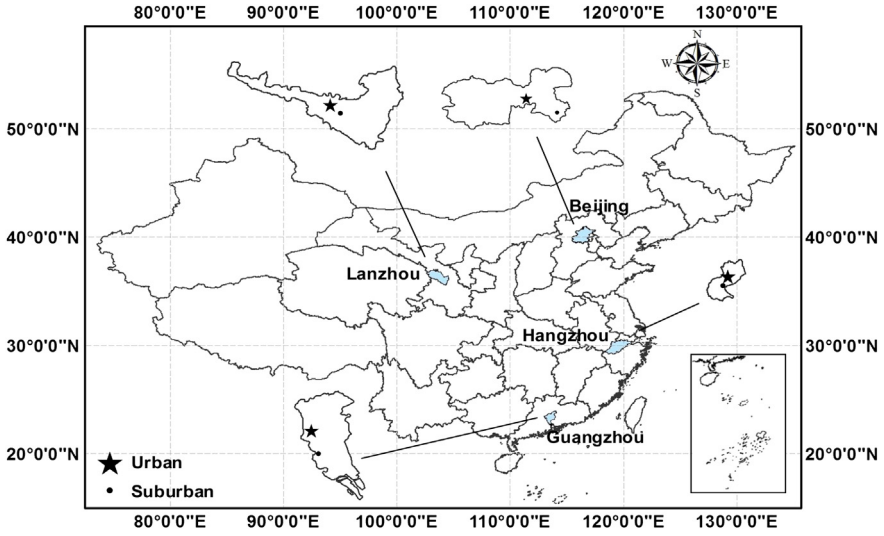

Fig. 1. Map showing the locations of the sampling sites and cities. Stars mark the urban sites and circles mark the suburban sites.

inter-comparison experiments were carried out twice in Chinese Academy of Meteorological Sciences, November 4, 2011 and November 15, 2011, respectively. In the second experiment, four parallel canisters of the diluted NIMC standard gas were calibrated, instead of only one canister in the former experiment. Therefore inter-comparison results reported here were derived from statistics in the second inter-comparison. For most species, discrepancies of only several percentages were found, 3.4–7.6% for HCFC-141b, 0.2–3.8% for HCFC-142b, −1.6–3.1% for HFC-134a, −0.6–3.5% for HFC-152a. But HCFC-22 concentration in NIMC was found to be 118.0% (average value in four canisters) of that in standard gas reported on SIO-2005, so the HCFC-22 concentration in the NIMC was revised by dividing a factor of 118.0%. In other words, HCFC-22 concentrations of ambient samples are reported on this revised NIMC scale in this study. Standard gases at five concentration levels were prepared by a dynamic dilution system (Entech 4600A, Entech Instruments, USA) to quantify the target halocarbons by a multipoint external calibration method. The dynamic dilution system can inevitably introduce uncertainties. In order to quantity the uncertainty, several standard samples of the same concentration were prepared and analyzed. The results showed very small relative standard deviations (1.68–2.10%) among the different standard samples. Therefore, we assumed that the dynamic dilution did not introduce large uncertainties. Measurement precision varied according to the compounds and was 3% for CFCs and 6% for HCFCs and HFC-134a. The measurement accuracy was 2% for CFCs and 6% for HCFCs and HFC-134a. More detailed information has been reported by Fang et al. (2012a,b).

2.3. Data analysis

All of the whole-air samples were analyzed to determine the ambient mixing ratios of the six target halocarbons. In general, common air pollutants follow a lognormal distribution (Bencala and Seinfeld, 1976; Lu, 2003; Taylor et al., 1986). Therefore, we assumed that the halocarbon ambient mixing ratios were lognormally distributed and a logarithmic transformation was required. On the basis of the air-sample analysis, descriptive statistics, including the geometric mean (GM) and geometric relative standard deviation (GRSD), were calculated and shown in Table 3. A few very high mixing ratios were found for HCFCs and HFC-134a, exceeding three times the GRSD. To a certain extent, this could be interpreted as immediate local emissions, such as from air conditioners. This also suggests that these substances are widely used and emitted at the different sampling sites. These outlier values were eliminated prior to calculations. The background concentration from the Shangdianzi site in China and the background concentrations of the Northern Hemisphere (NH) from the US National Oceanographic and Atmospheric Administration/Earth System Research Laboratory (NOAA/ESRL) are listed in Table 3.

Next, the temporal trend was analyzed for each substance, and ANOVA was applied to determine any significant differences in the

Table 3
The geometric mean (GM)[a] and geometric relative standard deviation (GRSD) of the halocarbon mixing ratios at the eight sampling sites and their comparison with monthly mean NOAA/ESRL data.

Common name	Beijing		Guangzhou		Hangzhou		Lanzhou		Shangdianzi	NOAA/ESRL[d]
	Urban	Suburban	Urban	Suburban	Urban	Suburban	Urban	Suburban		
CFC-11	261 (16%)	257 (11%)	260 (10%)	256 (8%)	260 (16%)	259 (10%)	259 (21%)	253 (15%)	243.2[b]	242
CFC-12	553 (14%)	538 (7%)	609 (20%)	573 (12%)	543 (15%)	537 (10%)	533 (10%)	533 (10%)	537.5[b]	532
HCFC-22	617 (83%)	413 (48%)	721 (62%)	526 (69%)	636 (100%)	455 (64%)	616 (70%)	398 (80%)	219.9[c]	217
HCFC-141b	40 (45%)	36 (46%)	81 (62%)	88 (60%)	61 (79%)	57 (60%)	32 (59%)	29 (43%)	–	19
HCFC-142b	131 (131%)	52 (88%)	44 (51%)	38 (33%)	44 (60%)	43 (51%)	42 (60%)	38 (87%)	21.8[c]	21
HFC-134a	110 (48%)	76 (19%)	98 (41%)	84 (48%)	90 (59%)	72 (30%)	62 (36%)	61 (31%)	–	53

[a] GM of the mixing ratios is in pptv.
[b] The CFC mixing ratios at Shangdianzi site in 2009 were given by Zhang et al. (2010a).
[c] The yearly mixing ratios of HCFC-22 and HCFC-142b at Shangdianzi site in 2010 were given by Yao et al. (2012). The yearly mean is from Jan to Sep 2010 because AGAGE stations have not yet released further data.
[d] The NOAA/ESRL data was the calculated averages of the monthly mean mixing ratios in the sampling months, which were provided from ftp://ftp.cmdl.noaa.gov/hats.

halocarbon species concentrations among the eight sampling sites (see Table 4). For halocarbons with prominent spatial variation, the eight sampling sites were divided into two groups, urban and suburban, and ANOVA was applied again to determine whether significant differences could be observed in each group (see Table 4). Furthermore, an independent-sample *t*-test was used to see if there was a significant spatial difference between the urban and suburban sites in each city (see Table 5). Moreover, the correlation among different HCFCs (Table 6) was analyzed using Pearson's correlation analysis.

3. Results and discussion

3.1. CFCs

In the atmosphere, the two most abundant CFCs are CFC-11 and CFC-12 (Montzka et al., 2011), and the total consumption of these two CFCs accounts for about 90% of the CFCs consumed in China (SEPA, 1999). Therefore, only these two CFCs were examined in this study. China has phased out CFC production and consumption since 2007 (SEPA, 2007). However, bank emissions of related products could continue to affect atmospheric CFC concentrations (Seinfeld and Pandis, 2006).

As shown in Table 3, the CFC-12 mixing ratios were two times higher than those of CFC-11. For all sampling sites, these two CFCs levels were both slightly higher than the corresponding Chinese background levels and the NH background levels, with mean CFC-11 and CFC-12 enhancements of 7% (5–8%) and 4% (0–15%), respectively, suggesting that some bank emissions still exist in China. Concentration variability can also be used to examine the relative emission strengths of halocarbons (Wang et al., 1998), and this approach has been widely used for analysis of urban halocarbon concentrations (Chang et al., 2001, 2008; Lee and Chiou, 2007, 2008; Wang et al., 1998, 2000). The concentration variability of the two CFCs in this study was lower (GRSD ranged from 7 to 22%) than for other substances at all sites, but still exceeded the variability in the remote atmosphere in China (0.74% for CFC-11, 0.48% for CFC-12; Zhang et al., 2010a), which also suggests the continuance of bank emissions in China.

Fig. 2 shows the temporal variations in CFC-11 and CFC-12 over the sampling period. The CFC-11 mixing ratios were virtually unchanged over time. For CFC-12, relatively larger temporal variations were observed at the two sites in Guangzhou, but without a seasonal or yearly trend.

Table 4
One-way analysis of variance (ANOVA) of the halocarbon mixing ratios among different groups.

		All sites ($n = 8$)	Urban sites ($n = 4$)	Suburban sites ($n = 4$)
CFC-11	*F*	0.204	–	–
	P	0.984	–	–
CFC-12	*F*	6.764	–	–
	P	0.000*	–	–
CFC-12[a]	*F*	0.587	–	–
	P	0.710	–	–
HCFC-22	*F*	5.839	0.548	2.241
	P	0.000*	0.651	0.086
HCFC-141b	*F*	31.701	26.449	50.257
	P	0.000*	0.000*	0.000*
HCFC-142b	*F*	17.312	29.311	2.230
	P	0.000*	0.000*	0.043*
HFC-134a	*F*	13.682	15.106	7.481
	P	0.000*	0.000*	0.000*

*Significant at $P < 0.05$.
[a] One-way analysis of variance of the CFC-12 mixing ratios was performed among six sampling sites, excluding the two in Guangzhou.

Table 5
Independent-sample *t*-test of the halocarbon mixing ratios at the urban site and corresponding suburban site of each city.

		Beijing	Guangzhou	Hangzhou	Lanzhou
HCFC-22	*t*	3.357	2.591	2.390	3.097
	P (2-tailed)	0.001*	0.012*	0.019*	0.003*
HCFC-141b	*t*	1.191	−0.785	0.549	1.179
	P (2-tailed)	0.238	0.435	0.585	0.242
HCFC-142b	*t*	5.046	1.406	0.133	0.739
	P (2-tailed)	0.000*	0.165	0.895	0.463
HFC-134a	*t*	5.028	1.794	2.433	1.157
	P (2-tailed)	0.000*	0.077	0.018*	0.876

*Significant at $P < 0.05$ (2-tailed).

Halocarbon levels measured in various cities worldwide are listed in Table 1 for comparison. Compared to previous findings for Beijing and Guangzhou in the similar sampling seasons (Table 1), CFC levels in each city have declined over the past ten years. We also compared our observation data to the average concentrations for 45 Chinese cities observed in 2001 (Barletta et al., 2006, Fig. 3). The CFC levels at all eight sites were significant lower than the corresponding average levels in 2001 ($P < 0.05$), except for the CFC-12 levels at the two sites in Guangzhou. The declining trend is consistent with reduced consumption (UNEP, 2005, 2011) and emissions (Wan et al., 2009; Zhang et al., 2010b).

Research in developed countries has shown that concentration variability in CFC levels has declined significantly (Hurst et al., 1998), and CFC concentrations and emissions have clearly decreased (Barnes et al., 2003; Hurst et al., 2006; Khan et al., 2009; Li et al., 2005; Uchiyama and Hasegawa, 2000) from the late twentieth to early twenty-first centuries, 3–5 years after CFC phase-out, reflecting the effectiveness of CFC restrictions under the Montreal Protocol and its amendments. The sampling for this study was conducted during a similar phase-out stage (3–5 years after CFC phase-out in China), and the CFC levels in the four Chinese cities were comparable to or lower than those of developed countries (Tables 1 and 3). Although this outcome might be related, in part, to decreasing global background levels, it also suggests that the phase-out of CFCs is progressing in China.

The ANOVA results among the eight sampling sites (Table 4) showed that CFC-11 levels had no pronounced spatial differences ($P = 0.984 > 0.05$), indicating that the low bank emissions had no significant effect on local concentrations. However, CFC-12 levels displayed significant spatial variation ($P = 0.000 < 0.001$). The least-significant difference (LSD) test was applied to make multiple comparisons of the CFC-12 levels between each pair of sites. The results indicate that the CFC-12 levels of the two sites in Guangzhou were significantly higher than those at the other sites. After eliminating the mixing ratios in Guangzhou, the ANOVA results displayed no significant spatial variation in CFC-12 ($P = 0.710 > 0.05$, see Table 4). CFC-12 was used mainly as a refrigerant for residential and mobile air-conditioning and industrial and commercial refrigeration (Wan et al., 2009). Ten years ago, when China was

Table 6
Pearson's correlation and significance (2-tailed) of HCFCs for each city.

	HCFC-22&HCFC-141b	HCFC-22&HCFC-142b	HCFC-141b&HCFC-142b
Beijing	0.601[b]	0.663[b]	0.648[b]
Guangzhou	0.430[b]	0.367[b]	0.273[a]
Hangzhou	0.368[b]	0.260[a]	0.648[b]
Lanzhou	0.585[b]	0.862[b]	0.667[b]

Statistical outliers were removed before performing the regressions.
[a] Correlation is considered significant at the 0.05 level (2-tailed).
[b] Correlation is considered significant at the 0.01 level (2-tailed).

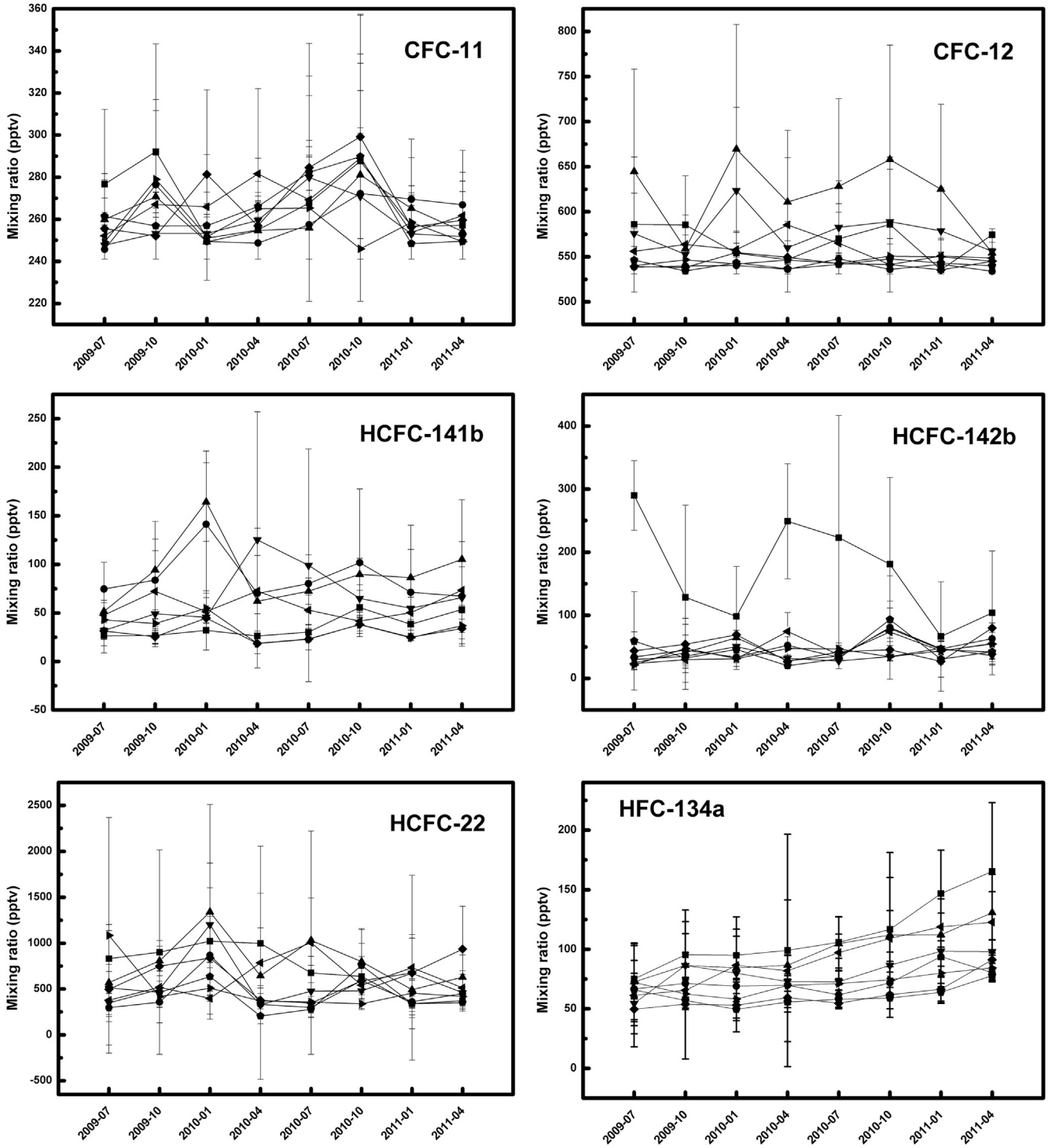

Fig. 2. The monthly variation trends for the mean mixing ratios of CFCs, HCFCs, and HFC-134a. For each sampling site, the monthly uncertainty (relative standard deviation) was calculated based on all of the mixing ratios. In each figure, different symbols indicate the eight different sampling sites. ■ and ● denote the urban and suburban sites in Beijing, respectively. ▲ and ▼ denote the urban and suburban sites in Guangzhou, respectively. ◀ and ▶ denote the urban and suburban sites in Hangzhou, respectively. ◆ and ★ denote the urban and suburban sites in Lanzhou, respectively.

beginning to phase-out CFCs, Guangzhou, one of the most populous and economically developed cities and the main manufacturing center in South China, was experiencing high temperatures (see GDP per capita in 2000 and temperature in Table 2). Therefore, the consumption of the refrigerant CFC-12 was relatively higher, which might account for the higher CFC-12 bank emissions.

3.2. HCFCs

The most abundant HCFCs in the atmosphere are HCFC-22, HCFC-141b, and HCFC-142b (Montzka et al., 2011) and their consumption accounts for more than 96% of the total HCFC consumption in China (SEPA, 2007). Therefore, they were the only

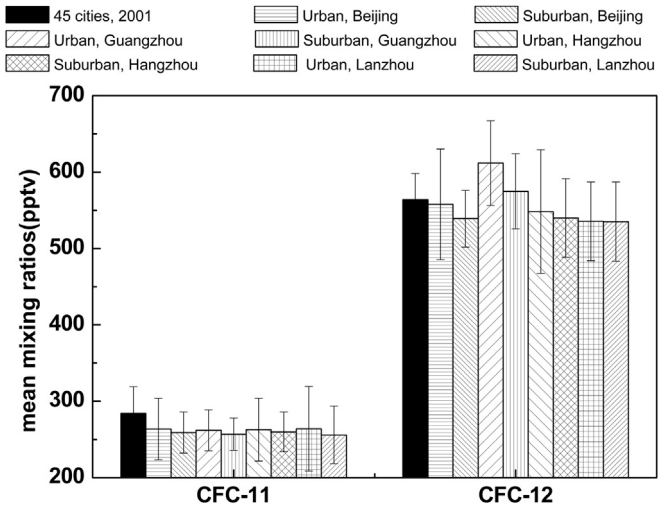

Fig. 3. Comparison between the CFC levels of four Chinese cities measured in this study and the average levels of 45 Chinese cities in 2001 (Barletta et al., 2006).

HCFCs examined. China is freezing HCFC production and consumption in 2013 and expects a phase-out by 2030 (UNEP, 2009). However, consumption and emissions of these HCFCs have been increasing yearly (UNEP, 2005, 2011; Wan et al., 2009).

The measurement results indicated that the HCFC-22 concentration was the highest of the HCFCs and comparable to that of CFC-11, whereas the HCFC-141b and HCFC-142b concentrations were relatively lower (Table 3). The concentrations of the HCFCs at each site, including suburban sites, were significantly higher than the Chinese background levels and the NH background levels (enhancements $>$ 20%) and had high concentration variability (GRSDs $>$ 20%, see Table 3), indicating the existence of significant regional emissions in China.

As shown in Fig. 2, the temporal variation of HCFCs during the sampling period was larger than that of CFCs, but no significant temporal variation trends were observed for HCFC-22 or HCFC-141b. However, there was very large temporal variation in HCFC-142b in urban Beijing, with two low mean mixing ratios in January. HCFC-142b is used mainly as a foaming agent of XPS board, which is used for thermal insulation in new construction. The HCFC-142b in the XPS board can be successively volatilized and released into the stratosphere. Therefore, lower temperatures could be the main reason for lower HCFC-142b emission in winter.

The eight sites were compared using ANOVA, and significant spatial differences were observed for all HCFCs ($P = 0.000 < 0.05$; see Table 4). To explore the spatial distribution differences among the four cities, the eight sites were divided into urban and suburban groups. Then, ANOVA was reapplied to determine whether the concentration differences were prominent in each group for each HCFC (see Table 4). No significant spatial variation was found in both the urban ($P = 0.651 > 0.05$) and suburban ($P = 0.086 > 0.05$) groups for HCFC-22. However, significant spatial differences were detected for HCFC-141b and HCFC-142b ($P < 0.05$). The comparisons among the four cities showed that (1) higher HCFC-141b concentrations were observed in Guangzhou and Hangzhou, indicating significant local HCFC-141b emissions, and (2) the highest HCFC-142b mean concentrations were detected in Beijing (131 and 52 pptv for urban and suburban sites, respectively). In comparison, the levels in the other cities were much lower and comparable to each other (38–44 pptv). HCFC-142b is used mainly as a foaming agent for XPS board, which was first used widely in new buildings in Beijing. Moreover, of the four cities, the floor space of buildings under construction is the largest in Beijing (Table 2), somewhat explaining the highest HCFC-142b level appearing in Beijing. (3) The concentrations of HCFC-141b and HCFC-142b in Lanzhou were both relatively lower.

To identify any significant spatial differences between urban and suburban sites within the same city, the independent-sample *t*-test was used for each HCFC in each city (see Table 5). The results revealed the following: (1) significant spatial differences in HCFC-22 were detected in every city ($P < 0.05$), with 30% higher mean concentration levels at the urban than the suburban sites. Higher population density at the urban sites (Table 2) could create greater demand for room air conditioning, leading to the larger HCFC-22 emission; (2) no statistically significant spatial differences in HCFC-141b were found in any city ($P > 0.05$); and (3) only Beijing had a significant spatial difference for HCFC-142b ($P < 0.05$), with a concentration level of 131 pptv, more than twice the amount observed at the suburban site (52 pptv). This could be explained by the highest HCFC-142b concentrations being observed in Beijing, and the large difference in the population density between the urban site (22,000 persons km^{-2}) and the suburban site (1300 persons km^{-2}, see Table 2).

Table 6 summarizes the Pearson correlation coefficients of the different HCFCs for each city. Although the samples were collected in different seasons at different sites, significant positive correlations were found between each pair of HCFC species in each city ($P < 0.05$), suggesting that HCFCs were emitted from similar or co-located sources or share similar emission patterns.

3.3. HFCs

HFC-134a is the most abundant and fastest-increasing HFC in the atmosphere (Montzka et al., 2011) and the most emitted HFC in China (Kim et al., 2010; Li et al., 2011). Therefore, this study focused on HFC-134a. The production and consumption of HFC-134a is controlled in many developed countries. However, it is still rapidly increasing in developing countries, especially China (Hu et al., 2009).

HFC-134a concentrations were significantly greater than the NH background levels at all sites (enhancement $>$ 20%; Table 3). Although China is just starting to produce and consume HFC-134a, regional concentrations are very high. Moreover, the GRSD was high at $>$20% at all sites (see Table 3), indicating significant HFC-134a emissions.

HFC-134a showed an increasing trend at four urban sites (Fig. 2), over the sampling period. Compared to previously reported values for Guangzhou in the similar sampling seasons, HFC-134a levels have increased significantly in recent years (see Table 1). It was determined that the HFC-134a increase has been caused by the increase in HFC-134a usage and emissions (Hu et al., 2009).

The ANOVA revealed significant spatial differences among the eight sampling sites, and within the urban and suburban groups ($P < 0.05$, Table 4). HFC-134a is used mainly as a refrigerant for vehicle air conditioners in China (Hu et al., 2009). The comparisons among the four urban sites showed that the HFC-134a concentrations were consistent with vehicle numbers, which were highest in Beijing, moderate in Guangzhou and Hangzhou, and lowest in Lanzhou (see Table 2). Therefore, HFC-134a levels might be greatly affected by automobile air conditioner usage and emissions.

In addition, *t*-tests were performed to compare the concentrations between the two sites in each city (see Table 5). For Beijing and Hangzhou, higher levels were detected at the urban site, owing to its higher population density (See Table 2). However, for Guangzhou and Lanzhou, no statistically significant HFC-134a spatial differences were found. The vehicle population in Lanzhou was the smallest of the cities, explaining the lowest HFC-134a levels at the two sites in Lanzhou, with enhancements of 10 and 9%, respectively. For

Guangzhou, the more balanced economic development between urban and suburban districts has led to a relatively large population density in suburban districts (19,400 persons km^{-2}, see Table 2). Therefore, significantly enhanced HFC-134a levels were observed at both sites.

4. Conclusions

To study the spatiotemporal variations and emissions of CFCs, HCFCs, and HFCs, 304 whole-air samples were collected at urban and suburban sites in four Chinese cities in each season from July 2009 to April 2011. The results showed that recent CFC concentrations at all sampling sites have declined to near the NH background levels, suggesting that the phase-out of CFCs in China is well underway. But bank emissions still exist in China, especially for CFC-12 in Guangzhou, which will continue to affect local CFC concentrations. As CFCs are phased out, their main substitutes HCFCs and HFC-134a, have risen to significantly higher concentrations than the NH background levels, with higher concentration variability, indicating that significant regional emissions exist in China. Moreover, local spatial variations were analyzed for HCFCs and HFC-134a. Significantly higher HCFC-22 levels were observed in the urban atmosphere, which might reflect the larger population density in urban areas. The mean concentrations of HCFC-141b were highest in Beijing, which could be somewhat explained by this city having the highest use of XPS board. The HFC-134a concentrations in different urban sites were consistent with vehicle numbers, which may be caused by automobile air conditioner usage. In addition, significant positive correlations were found between each pair of HCFC species in each city, suggesting the existence of similar sources or emission patterns for different HCFCs.

Controlled by the Montreal protocol, the production and consumption of HCFCs will be phased out by developing countries, including China, by 2030. To more promptly and accurately understand local concentration levels and emissions, urban halocarbon atmosphere observations should be more closely monitored, especially in some high-emission regions. These results will help to validate the effects of ODS phase-out and build sound phase-out strategies for ODSs and GHGs. These data can also provide inputs for receptor models to further identify and quantify the apportionment of halocarbon sources.

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