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ScienceDirect
Atmospheric Environment 40 (2006) 7706–7719
ATMOSPHERIC ENVIRONMENT
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Ambient halocarbon mixing ratios in 45 Chinese cities

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Received 17 February 2006; received in revised form 10 August 2006; accepted 13 August 2006

Abstract

During this study 158 whole air samples were collected in 45 Chinese cities in January and February 2001. The spatial distribution of different classes of halocarbons in the Chinese urban atmosphere, including chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), Halon-1211, and other chlorinated compounds is presented and discussed. Most of these compounds were enhanced compared to background levels. However, the mean enhancement of CFCs was relatively small, with CFC-12 and CFC-11 increases of 6% (range 1–31%) and 10% (range 2–89%), respectively, with respect to the global background. On the contrary, strongly enhanced levels of CFC replacement compounds and halogenated compounds used as solvents were measured. The average Halon-1211 concentration exceeded the background of 4.3 pptv by 75% and was higher than 10 pptv in several cities. Methyl chloride mixing ratios were also strongly elevated (78% higher than background levels), which is likely related to the widespread use of coal and biofuel in China.

Keywords: Urban air quality; Halocarbons; Montreal Protocol; Gas chromatography; China

1. Introduction

Halocarbons are an important sub-class of VOCs, and the emissions of many halocarbon species are regulated by the Montreal Protocol and its subsequent amendments because of their potential to deplete stratospheric ozone (WMO, 2002; UNEP, 2003). Once released in the atmosphere they can be transported into the stratosphere where they are photolyzed. The chlorine and bromine atoms released through photolysis can initiate catalytic cycles leading to stratospheric ozone depletion (WMO, 2002). Although the total tropospheric burden of bromine is much less than the chlorine burden, stratospheric ozone depletion by bromine is an important process because a bromine atom is about 50 times more effective at destroying stratospheric ozone than a chlorine atom (Montzka et al., 2003).

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doi:10.1016/j.atmosenv.2006.08.039

By 2001, when this study took place, many of the halocarbons discussed here had been phased out in developed countries under the Montreal protocol and subsequent amendments (by 1 January 1996 a 100% reduction of the base levels of production and consumption was established for many halogenated compounds), but were allowed to be produced and consumed in developing countries (UNEP, 2003). Although some halogenated compounds have strong natural sources, i.e. methyl halides (methyl chloride, CH_3Cl; methyl iodide, CH_3I; and methyl bromide, CH_3Br), most originate exclusively from anthropogenic emissions. Chlorofluorocarbons (CFCs) were first introduced as nontoxic and nonflammable refrigerants in cooling appliances in the 1930s, but they also found application as foam blowing agents, in air conditioning, and as aerosol propellants (McCulloch et al., 2003; Sturrock et al., 2002). Trichlorofluoromethane (CFC-11) together with 1,1,2-trichlorotrifluoroethane (CFC-113) have also been used as degreasing agents in the cleaning process for the production of refrigerator compressors and electronics. In many applications CFCs have been replaced by hydrochlorofluorocarbons (HCFCs) such as chlorodifluoromethane (HCFC-22), 1,1-dichloro-1-fluoroethane (HCFC-141b), and 1-chloro-1,1-difluoroethane (HCFC-142b), and more recently by the hydrofluorocarbon 1,1,1,2-tetrafluoroethane (HFC-134a). The HCFCs are mainly emitted from refrigeration units, air conditioning units or foam plastic applications (McCulloch et al., 2003). Halons, mainly bromochlorodifluoromethane (Halon-1211), 1,2-dibromotetrafluoroethane (Halon-2402) and bromotrifluoromethane (Halon-1301) have been used as fire-fighting chemicals (Butler et al., 1998), and are one of the most important anthropogenic source of bromine atoms in the stratosphere (Montzka et al., 2003). Several other halogenated compounds have applications in the industrial sector mainly as solvents and degreasers, for example tetrachloroethene (C_2Cl_4), trichloroethene (C_2HCl_3), 1,1,1-trichloroethane (CH_3CCl_3, methyl chloroform), and dichloromethane (CH_2Cl_2, methylene chloride), or in some cases as feedstock for CFC production, for example tetrachloromethane (CCl_4, carbon tetrachloride). Before being almost exclusively used as a chemical intermediate for CFC production, CCl_4 was also used as an industrial solvent and in other industrial applications (Altshuller, 1976; Sturrock et al., 2002).

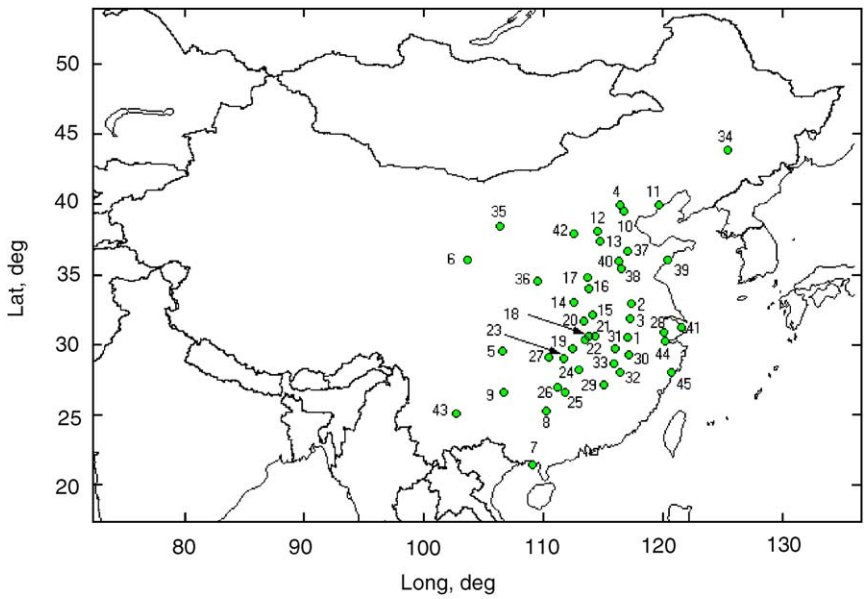
While halocarbon speciation and quantification in air from remote regions is well documented both temporally and spatially, often via global monitoring studies (e.g. Butler et al., 1998, 1999; Simmonds et al., 1998; Fraser et al., 1999; Khalil and Rasmussen, 1999; Montzka et al., 1999; Dimmer et al., 2001; Sturrock et al., 2002; Cox et al., 2003; Simpson et al., 2004), urban atmospheres are only beginning to be studied more comprehensively (Wang et al., 1998, 2000; Grosjean et al., 1999; Yamamoto et al., 2000; Mohamed et al., 2002; Rivett et al., 2003; Lasa and Sliwka, 2003; Lai et al., 2004).

The People's Republic of China is the world's most populated country with 1.3 billion people (21% of the world total in 2001; EIA, 2005a). The country is divided into 23 provinces, five autonomous regions, four municipalities, and two special administrative regions. The transition to a market economy, which started in the 1980s, makes China one of the world's fastest growing economies. China's most developed regions are urban coastal areas, particularly the Pearl River Delta (PRD) situated in the southeastern province of Guangdong, and the Yangtse River Delta (YRD) in the eastern provinces of Zhejiang, Jiangsu, Fujian and Shanghai. Emissions of halocarbons from the industrial sector are particularly interesting because China is one of the most populated, industrialized and fastest developing countries classified in the Montreal Protocol's "Article 5 parties" (developing countries still allowed to produce CFCs, halons and other halocarbons). Most of the halogenated compounds already phased out in the developed world are believed to be produced and used in China. Under the Montreal Protocol, China is required to phase out 50% of the 1995–1997 average baseline of CFC and Halon production and consumption by 2005, and 100% (based on the same baseline) by 2010. Despite the increasing international attention devoted recently to characterize emissions from China (e.g. Blake et al., 2003; Palmer et al., 2003; Streets et al., 2003), a comprehensive characterization of the halocarbon distribution in China is still lacking. In this study mixing ratios of 19 halocarbons measured in the urban atmosphere of 45 Chinese cities are presented and discussed.

2. Experimental

A comprehensive description of the sample collection is given in Barletta et al. (2005), where the NMHC fraction measured during this sampling

campaign was discussed. The analytical system is described in detail in Colman et al. (2001) and Barletta et al. (2002). Briefly, in collaboration with the Hong Kong Polytechnic University (HKPU) and Zhongshan University, a total of 158 whole air samples were collected in 45 cities in China in January and February 2001 (Fig. 1) using evacuated 2-L stainless steel canisters each equipped with a bellows valve. The samples were collected over a 1-min period at a height of about 2 m. The majority of the samples were collected in commercial, residential and industrial urban locations, while 25 samples were collected next to streets. The canisters were then shipped to our laboratory at the University of California, Irvine (UCI) and analyzed using a gas chromatographic (GC) system with electron capture detection (ECD), flame ionization detection (FID), and mass spectrometer detection (MSD). All halocarbons in all the samples were present at mixing ratios well above their detection limit. The precision of the halocarbon measurements varies by compound and is 1% for the CFCs and CCl_4; 2–4% for the HCFCs; 5% for HFC-134a and CH_2Cl_2; and 2% for Halon-1211, methyl halides, CH_3CCl_3, C_2Cl_4, and $CHBr_3$. The measurement accuracy also varies by compound and is 2% for CFCs (except



Province	City (**)	Province	City (**)	Province	City (**)
Anhui	1- Anqing (3)	Hubei	18- Hanchuan (2)	Jilin	34- Changchun* (5)
	2- Bengbu (3)		19- Shishou (3)	Ninxia	35- Yinchuan* (3)
	3- Hefei* (5)		20- Suizhou (3)	Shaanxi	36- Weinan (3)
Beijing(a)	4- Beijing (3)		21- Wuhan* (5)	Shandong	37- Jinan* (5)
Chongqing(a)	5- Chongqing (3)		22- Xiantao (3)		38- Jining (3)
Gansu	6- Lanzhou* (5)	Hunan	23- Changde (2)		39- Qingdao (3)
Guangxi	7- Beihai (2)		24- Changsha* (5)		40- Zoucheng (3)
	8- Guilin (4)		25- Qiyang (3)	Shanghai(a)	41- Shanghai (5)
Guizhou	9- Guiyang* (5)		26- Shaoyang (3)	Shanxi	42- Taiyuan* (6)
Hebei	10- Langfang (2)		27- Zhangjiajie (3)	Yunnan	43- Kunming* (5)
	11- Qinghuangdao (3)	Jiangsu	28- Wuxi (3)	Zhejiang	44- Hangzhou* (5)
	12- Shijiazhuang* (5)	Jiangxi	29- Ji'an (3)		45- Wenzhou (2)
	13- Tangshan (3)		30- Jingdezhen (3)		
Henan	14- Nanyang (3)		31- Jiujiang (2)		
	15- Xinyang (3)		32- Linchuan (3)		
	16- Xuchang (3)		33- Nanchang* (4)		
	17- Zhengzhou* (5)				

* Capital of Province or Autonomous Region.
(a) Municipality
(**) The number in parenthesis next to each city refers to the number of samples collected in that particular city

Fig. 1. Sampling sites for ground-level whole air samples collected in China in January/February 2001.

Table 1
Minimum city average, maximum city average and mean city average (pptv) of the quantified halocarbons; background levels are also provided. One sigma standard deviation (SD) is reported

Formula	Common Name	Min (SD)	Max (SD)	Average (SD)	Background (SD)[a]
CCl_2F_2	CFC-12	539 (10)	703 (156)	564 (34)	535 (1)
CCl_3F	CFC-11	265 (8)	489 (134)	284 (35)	259 (1)
CCl_2FCClF_2	CFC-113	83 (3)	133 (57)	90 (10)	79 (1)
$CClF_2CClF_2$	CFC-114	14 (1)	16 (3)	15 (0.5)	14 (0.1)
$CBrClF_2$	Halon-1211	4.8 (0.3)	26.3 (10.5)	7.5 (4.1)	4.3 (0.04)
CH_2FCF_3	HFC-134a	17 (1)	57 (59)	23 (8)	15 (1)
$CHClF_2$	HCFC-22	163 (3)	568 (312)	220 (71)	151 (2)
CH_3CClF_2	HCFC-142b	15 (0.1)	39 (26)	19 (5)	14 (0.3)
CH_3CCl_2F	HCFC-141b	16 (0.3)	71 (49)	20 (9)	15 (0.4)
$CHCl_3$	Chloroform	17 (2)	119 (75)	48 (27)	9 (1)
CH_3CCl_3	Methyl chloroform	44 (0.2)	69 (5)	49 (5)	40 (0.6)
CCl_4	Carbon tetrachloride	102 (6)	142 (33)	114 (11)	99 (0.6)
CH_2Cl_2	Methylene chloride	49 (1)	959 (743)	226 (232)	28 (4)
C_2HCl_3	Trichloroethene	3.3 (1.8)	262 (141)	21 (39)	0.4 (0.2)
C_2Cl_4	Tetrachloroethene	17 (2)	1008 (880)	129 (198)	5.0 (1)
CH_3Cl	Methyl chloride	651 (11)	2008 (1068)	952 (273)	535 (8)
CH_3Br	Methyl bromide	10 (0.04)	25 (17)	13 (3)	8.4 (0.2)
CH_3I	Methyl iodide	0.6 (0.1)	3.5 (2.7)	1.6 (0.7)	0.3 (0.1)
$CHBr_3$	Bromoform	1.2 (0.4)	5.0 (6.4)	1.9 (0.6)	0.9 (0.1)

[a]Lowest 25th percentile of airborne TRACE-P data collected below 1500 m (Blake et al., 2003 and unpublished data).

5% for CFC-114); 10% for the HCFCs, C_2Cl_4, CH_2Cl_2, CH_3I and $CHBr_3$; and 5% for Halons, HFC-134a, CH_3CCl_3, CCl_4, CH_3Cl and CH_3Br.

3. Discussion and results

3.1. General features

Nineteen halogenated compounds were identified and quantified in this study (Table 1). For each halocarbon, the ratio of the median mixing ratio of the ambient urban samples to the median mixing ratio of the roadside samples was calculated. The ratio was between 0.9 and 1.1 for 16 of the 19 compounds, 0.8 for C_2Cl_4 and HFC-134a, and 1.3 for C_2HCl_3. By comparison, the calculated ratios for ethyne and ethene, which are tracers of incomplete combustion such as fossil fuel use, were much lower (0.30 and 0.32, respectively). Overall the overlap between the two sets of halocarbon data (ambient and roadside samples) was excellent, indicating that vehicular emissions are not a major source of any of the halocarbons discussed in this paper. This is consistent with our understanding of the primary sources of these halocarbons (Sections 3.2–3.6). Therefore, the roadside samples and the ambient samples can both be considered representative of the urban area, and both were used in the following analyses.

An average mixing ratio was calculated for each compound for each city. The lowest, highest and mean city averages are reported in Table 1 for each species, together with background levels. Many of the measured compounds exhibit seasonal cycles, latitudinal gradients and long-term trends in the background atmosphere, and therefore we compared our measurements to the lower quartile of halocarbon mixing ratios measured at altitudes below 1500 m during the airborne NASA GTE Transport and Chemical Evolution over the Pacific (TRACE-P) field campaign (February–April 2001; Blake et al., 2003 and unpublished data). By using the lowest 25th percentile at low altitude we selected air masses most likely to approximate background values in the boundary layer. When TRACE-P samples collected at all altitudes are considered, the contribution from the much cleaner free tropospheric air (and possibly from intrusion of stratospheric air) results in lower background values, which are less likely to represent the remote boundary layer. For example, the lowest quartile for C_2Cl_4, CFC-12 and HCFC-134a for samples collected below 1500 m is 5.0, 535, and 15 pptv ($\sigma = 1$, 1, and 0.7), respectively, while the lowest quartile for the entire TRACE-P data set is 2.2, 531,

and 13.7 pptv ($\sigma = 0.6$, 6, and 0.7), respectively. The use of the lowest 25th percentile, rather than the whole data set, excludes samples affected by direct outflow from the Asian continent and highly concentrated samples collected during landing.

For most of the halocarbons, the lowest city average is slightly higher than background observations (within 10%), and in few cases background levels were measured (Table 1). These "near background" concentrations indicate that some regions of China were not greatly affected by local halocarbons sources. By contrast, the minimum mixing ratios of $CHCl_3$, CH_2Cl_2, C_2HCl_3, C_2Cl_4 and CH_3Cl are notably larger than background levels (20% for CH_3Cl and a factor of 2–8 for the rest), indicating local and perhaps regional emissions.

The lowest average CFC concentrations were measured in Shanghai (265, 83, and 14 pptv for CFC-11, CFC-113, and CFC-114, respectively). CFC-12 mixing ratios in Shanghai (547 pptv) were comparable to the minimum value measured in Xiantao (539 pptv). The lowest concentrations of HCFCs and HFC were measured in the southernmost city of Beihai, except for HCFC-22 (167 pptv compared to a minimum of 163 pptv measured in Qinghuangdao). Beihai and the northern cities of Yinchuan, Tangshan, and Zoucheng are among the cleanest cities for all of the remaining halocarbons.

Selected pollution plumes from TRACE-P have been well documented (Blake et al., 2003; Jacob et al., 2003). Five-day backward trajectories suggest that a fresh, well-defined plume downwind of Shanghai was sampled in the boundary layer on March 2001 ("Shanghai plume"). Elevated halocarbon levels were detected in this plume. In general, the halocarbon mixing ratios were not significantly different in the Shanghai plume than those measured in Shanghai during this study (Table 2).

3.2. CFCs and CFC replacements

The mean average CFC enhancement with respect to the background was 6% (1–31% range), 10% (2–89% range), 13 (4–68% range) and 10% (3–17% range) for CFC-12, CFC-11, CFC-113, and CFC-114, respectively. However, in certain cities enhancements higher than 20% were observed. For example, in Chongqing, Beijing and Changsha the average CFC-12 mixing ratios were 649 pptv ($\sigma = 49$), 681 pptv ($\sigma = 89$), and 703 pptv ($\sigma = 156$), respectively, compared to a background of 535 pptv (Fig. 2). CFC-11 levels were 489 pptv ($\sigma = 134$) and 354 pptv ($\sigma = 176$) in Hangzhou and Jinan, respectively, compared to a background of 259 pptv (Fig. 2). In Lanzhou, Wenzhou, Hangzhou, and Changchun, the average CFC-113 mixing ratios were 104, 133, 124 and 119 pptv, respectively ($\sigma = 18$, 57, 70, and 53), compared to background levels of 79 pptv. In each case, the high mixing ratios were not driven by a single high outlier, but by elevated mixing ratios in most or all of the samples. For example, in Hangzhou, all five samples had high CFC-11 mixing ratios (384, 715, 429, 505 and 412 pptv).

Table 2
Halocarbon levels measured in other cities worldwide (mixing ratios in pptv); one-sigma standard deviation given in parenthesis

	CFC-12	CFC-11	CFC-113	CFC-114	$CHCl_3$	CH_3CCl_3	CCl_4	CH_2Cl_2	C_2HCl_3	C_2Cl_4
China[a]	564 (34)	284 (35)	90 (10)	15 (0.5)	48 (27)	49 (5)	114 (11)	226 (232)	21 (39)	129 (198)
Shanghai[b]	547 (18)	265 (8)	83 (3)	14 (0.5)	38 (4)	54 (9)	107 (7)	648 (1052)	16 (9)	54 (17)
Shanghai[c]	566 (25)	280 (10)	90 (12)	15 (0.2)	76 (39)	51 (10)	127 (20)	210 (144)	32 (35)	56 (38)
Bristol (UK)[d]	566 (98)	301 (185)			45 (25)	54 (6)	98 (4)		73 (173)	37 (96)
Philadelphia (USA)[e]	567 (69)	273 (37)	81 (3)	15 (1)	27 (13)	50 (7)	98 (7)	97 (53)		116 (117)
Las Vegas (USA)[f]	545 (48)	259 (11)	79 (2)	15 (1)	28 (31)	46 (5)	99 (3)	133 (158)		159 (182)
Marseille (France)[g]	564 (40)	288 (26)	84 (3)	16 (4)	25 (17)	54 (49)	107 (6)	251 (324)	36 (56)	276 (449)
Background[h]	535 (1)	259 (1)	79 (1)	14 (0.1)	9 (1)	40 (0.6)	99 (0.6)	28 (4)	0.4 (0.2)	5.0 (1)

[a]Samples collected in January–February 2001 (this study; 45 city average).
[b]Samples collected in January–February 2001 (this study; Shanghai city average).
[c]Shanghai plume encountered during TRACE-P on March 2001, see text for explanation (Blake, personal communication; 7 samples).
[d]Samples collected in August–September 2000 (Rivett et al., 2003).
[e]Samples collected in February 2001 (Blake, personal communication; 27 total samples collected within the urban area).
[f]Samples collected in February 2001 (Blake, personal communication; 24 total samples collected within the urban area).
[g]Samples collected in June–July 2001 (Blake, personal communication; 148 total samples collected within the urban area).
[h]See Table 1.

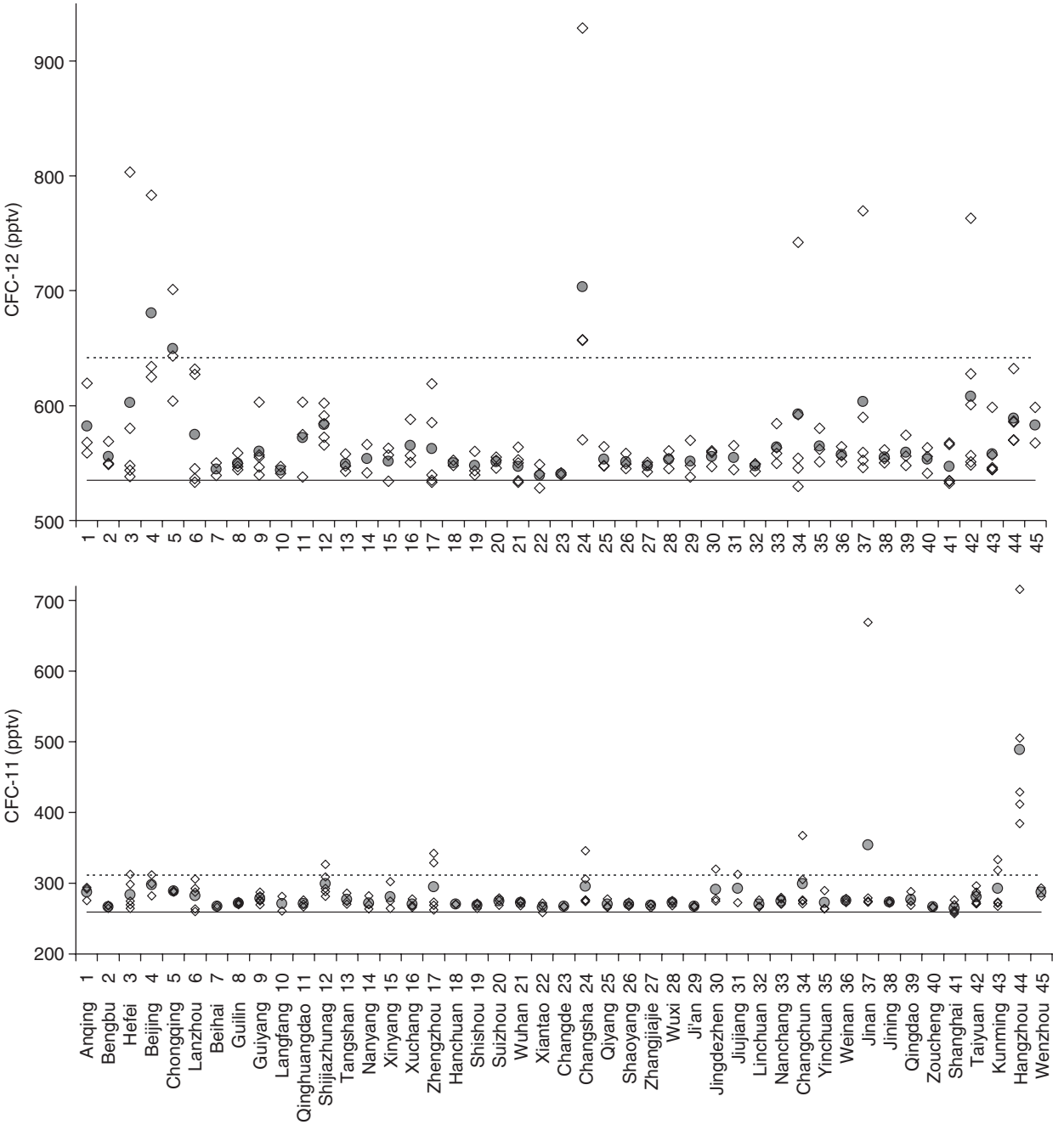


Fig. 2. Average mixing ratios measured in the 45 Chinese cities for CFC-12 and CFC-11 (solid circles). The solid line represents the background value as reported in Table 1; the dotted line indicates a 20% enhancement with respect to background; diamonds represent the mixing ratios of the single cans collected in a city.

The Multilateral Fund for the implementation of the Montreal Protocol was established to help developing countries comply with their obligations under the Montreal Protocol, and several ozone-depleting substance (ODS) phase-out projects have been approved during the past 10 years by different agencies to help China replace ODSs (UNEP, 2003). For example, in Hangzhou, where high levels of CFC-11 were measured, several projects have been implemented to help companies replace CFCs with HFCs or HCFCs (UNIDO, 2005). However, the strongly enhanced CFC-11 and CFC-113

concentrations measured during this study in selected cities indicates their continuing emissions from local activities/storage facilities where CFCs have not yet been replaced by ODS-free substances (i.e. HFC-134a) or other CFC-replacements.

Because levels of halocarbons regulated by the Montreal Protocol can be strongly dependent on the year when the samples were collected, a comparison with literature data must be carefully done. In general, CFC levels were comparable to levels measured in other cities worldwide within plus or minus six months of this study (Table 2). For example, the average CFC-12 level measured in urban China during this study was identical to that measured in Marseille, France at the same time in 2001. The generally low CFC enhancement with respect to the background, and the comparable levels measured with respect to other cities worldwide, is a remarkable and unexpected result. In particular, substantial CFC emissions from China have been estimated from the analysis of Asian outflow sampled during the TRACE-P study in spring 2001 (Palmer et al., 2003). Despite the allowance under the Montreal Protocol, CFC levels in China appear to be comparable to other cities worldwide for which urban CFC levels are available, which include developed cities that are more strongly regulated under the Montreal Protocol. This suggests that, to a large extent, CFCs have been effectively replaced in a majority of the Chinese cities sampled during this study. However, it is important to recognize that the low CFC emissions discussed here are restricted to the cities sampled during this study, and do not include important areas like the PRD (where Hong Kong and other major industrial cities are located), whose contribution to CFC emissions is not documented.

By contrast to the CFCs, the average enhancement of HFC-134a and HCFCs with respect to the background was 5 pptv (33%) for both HCFC-141b and HCFC-142b, 69 pptv (46%) for HCFC-22, and 8 pptv (57%) for HFC-134a (Table 1; Fig. 3). These results show a widespread usage of CFC replacements throughout most of urban China. In particular, high HCFC and HFC enhancements were often measured in cities where low CFC enhancements were observed (i.e. Langfang and Shanghai).

3.3. Halocarbons in the industrial sector

Halogenated compounds that are most commonly used as solvents or degreasing agents, were not significantly different than levels measured in other urban areas worldwide (Table 2). The highest C_2HCl_3 was measured in Hangzhou, with an average mixing ratio of 262 pptv (ranging from 93 to 471 pptv for individual samples, compared to a background of 0.4 pptv; Table 1). However, over 75% of the sampled cities had an average C_2HCl_3 mixing ratio lower than 20 pptv, though we note that this is still at least a factor of 10 above background (Table 1).

Chloroform mixing ratios ranged from 17 to 119 pptv, with the highest levels measured in Anqing (119 pptv, $\sigma = 75$) and Guiyang (102 pptv, $\sigma = 132$), though in the latter case a single high sample (336 pptv) affected the city average. Overall the $CHCl_3$ variability among the cities was relatively low, while a higher variability was observed for CH_2Cl_2 and C_2Cl_4 (Fig. 4). The highest CH_2Cl_2 mixing ratios were measured in Jinan (959 pptv, $\sigma = 743$) and Guilin (822 pptv, $\sigma = 1460$) compared to a background of 28 pptv (Table 1). In Jinan all samples had very high levels of CH_2Cl_2 (between 131 and 1889 pptv), although in Guilin one very high sample (3012 pptv) greatly affected the city average, and the remaining 3 samples were a factor of 3 above background. The highest C_2Cl_4 levels were measured in Chongqing (1008 pptv, $\sigma = 880$) and Lanzhou (755 pptv, $\sigma = 966$) compared to a background of 5 pptv. In Lanzhou 2 out of the 5 samples had very high mixing ratios (1654 and 1958 pptv), and the remaining 3 samples were 6–17 times above background.

The halocarbons reported in Fig. 4 and C_2HCl_3 do not show similar distributions to each other and no correlation was found among these gases ($R^2 < 0.2$). Instead, the cities where the highest levels were measured are different for each compound and are located in different areas of China (Fig. 5). That is, the sources of the solvents discussed here are spread throughout the 45 cities, suggesting that it is not possible to identify a localized industrial source area from this study.

3.4. Methyl chloroform and carbon tetrachloride

Methyl chloroform levels have rapidly decreased in the troposphere because of the global decline in its emissions coupled to rapid losses associated with its relatively short tropospheric lifetime of about 5 years (Montzka et al., 2000). A 24% average CH_3CCl_3 enhancement was measured relative to background, with one-fifth of the sampled cities

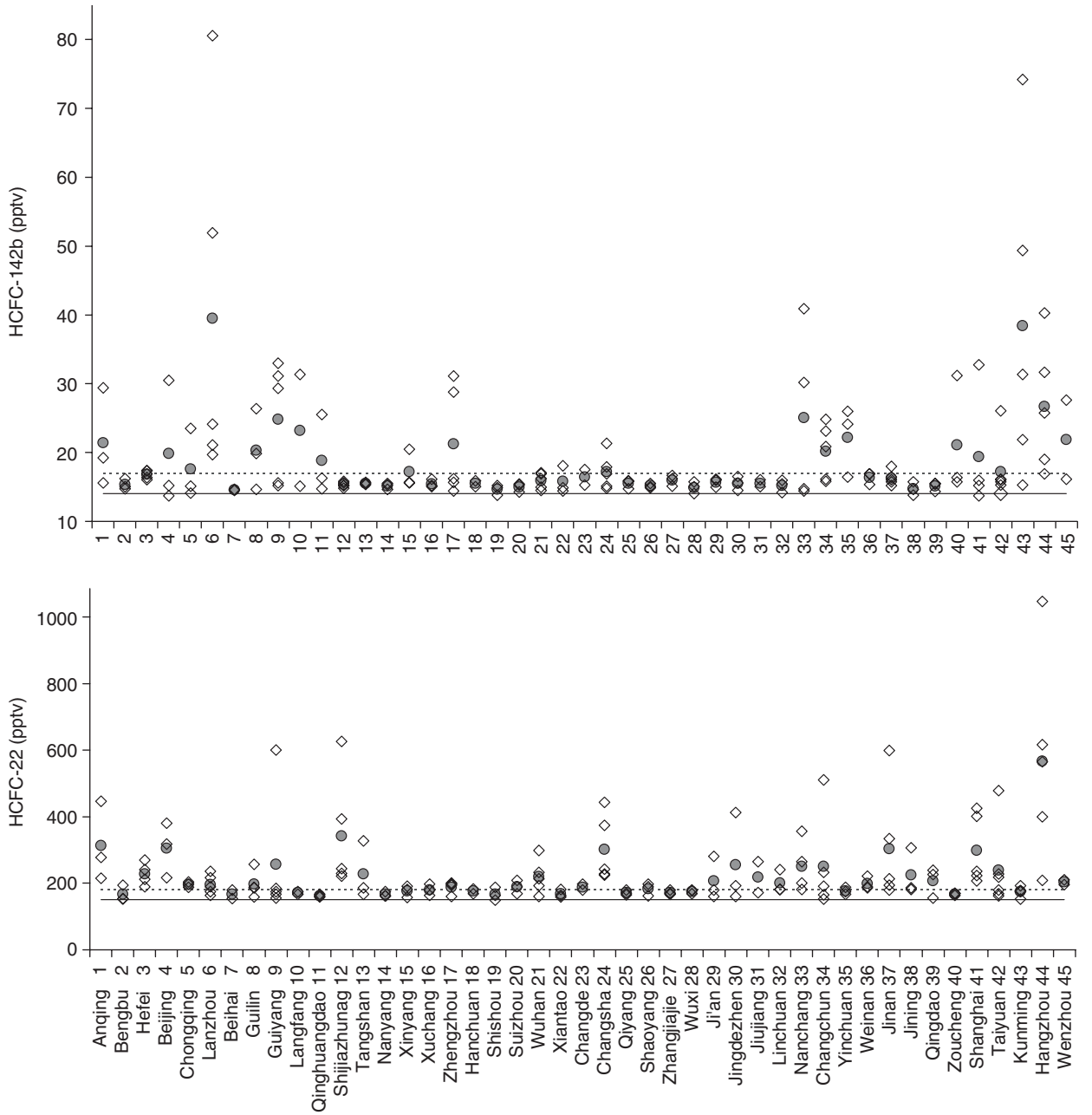


Fig. 3. Average mixing ratios measured in the 45 Chinese cities for HCFC-142b and HCFC-22 (solid circles). The solid line represents the background value as reported in Table 1; the dotted line indicates a 20% enhancement with respect to background; diamonds represent the mixing ratios of the single cans collected in a city.

showing an average CH_3CCl_3 level more than 30% higher than background (Fig. 6). The cities with the highest mixing ratios were Hangzhou (69 pptv, $\sigma = 5$), Chongqing, and Changsha (61 pptv, $\sigma = 13$ and 10, respectively), Weinan (60 pptv, $\sigma = 23$), and Anqing (58 pptv, $\sigma = 10$), compared to a CH_3CCl_3 background of 40 pptv at comparable latitudes in early 2001. No emission estimates have been inferred from this data set and it is still not clear to what extent CH_3CCl_3 is emitted by Asian countries (Blake et al., 2003). However, the enhanced CH_3CCl_3 levels in each sampled city indicate continuing use of CH_3CCl_3 throughout urban China.

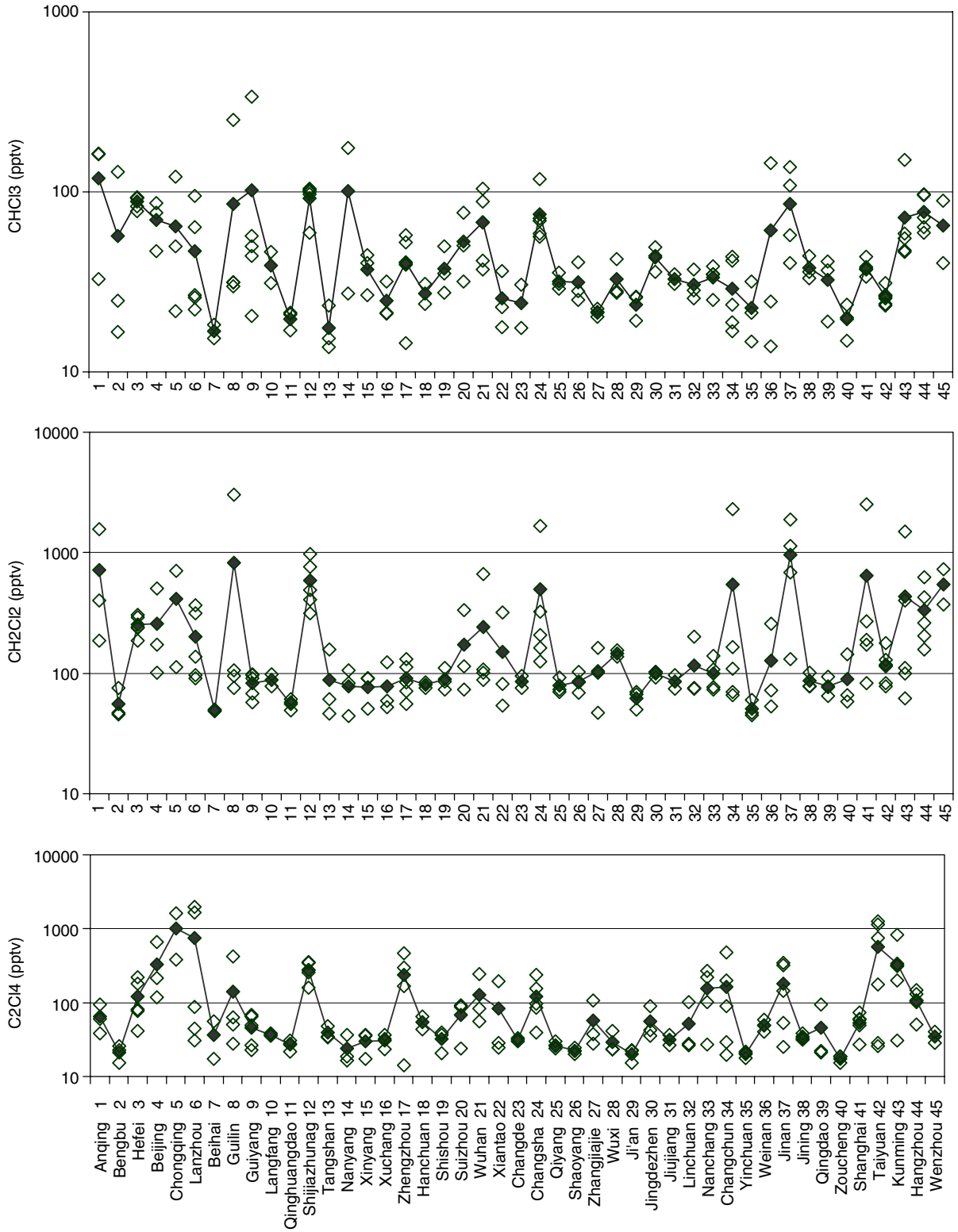


Fig. 4. City average (solid diamonds) and individual samples (diamonds) measured for $CHCl_3$, CH_2Cl_2, and C_2Cl_4 in the 45 Chinese cities sampled (logarithmic scale).

The lifetime of CCl_4 is about 35 years and its global mixing ratio, which was 99 pptv in 2001, has been declining since the early 1990s (Simmonds et al., 1998; Blake, 2004). Carbon tetrachloride was originally used as a cleaning solvent, but since the 1930s it has been primarily used for CFC production. Therefore developing countries, which are still allowed to produce CFCs, are potentially the leading contributors to CCl_4 emissions derived from CFC production, though the contribution from feedstock emissions are poorly quantified in China and all other countries. The average CCl_4 mixing ratio for the 45 Chinese cities (114 pptv, $\sigma = 11$) was 15% higher than the global background (Table 1). This is also higher than CCl_4 mixing ratios measured in other global cities (Table 2). Nanyang (142 pptv, $\sigma = 33$), Guyang (142 pptv, $\sigma = 24$), and Anqing (140 pptv, $\sigma = 29$) had the highest CCl_4 mixing ratios. Interestingly, those three cities were ranked only 26th (29th), 18th (18th) and 11th (12th) for CFC-12 (CFC-11) emissions, and no correlation was found between CCl_4 and CFC-12 or CFC-11, suggesting that the main CCl_4 emissions may not be primarily related to CFC production.

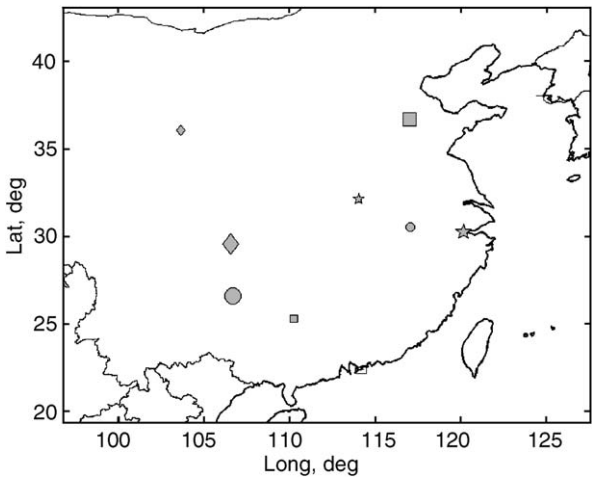


Fig. 5. Location of the cities where the two highest city average mixing ratios were measured for selected halocarbons used in the industrial sector. Diamond: C_2Cl_4; circle: $CHCl_3$; square: CH_2Cl_2; star: C_2HCl_3. The larger symbol identifies the city with the highest level.

3.5. Halon-1211

Since the Montreal Protocol was implemented, the global atmospheric mixing ratios of CFC-11, CFC-113, CH_3CCl_3 and CCl_4 have declined, the mixing ratio of CFC-12 has leveled off, and the mixing ratio of Halon-2402 has been increasing more slowly (WMO, 2002). Halon-1211 concentrations are still increasing in the atmosphere because of remaining existing stocks throughout the world and continued production in developing countries (Montzka et al., 2003). The average Halon-1211 enhancement in the 45 sampled Chinese cities was 75% above the background of 4.3 pptv (Fig. 7). The

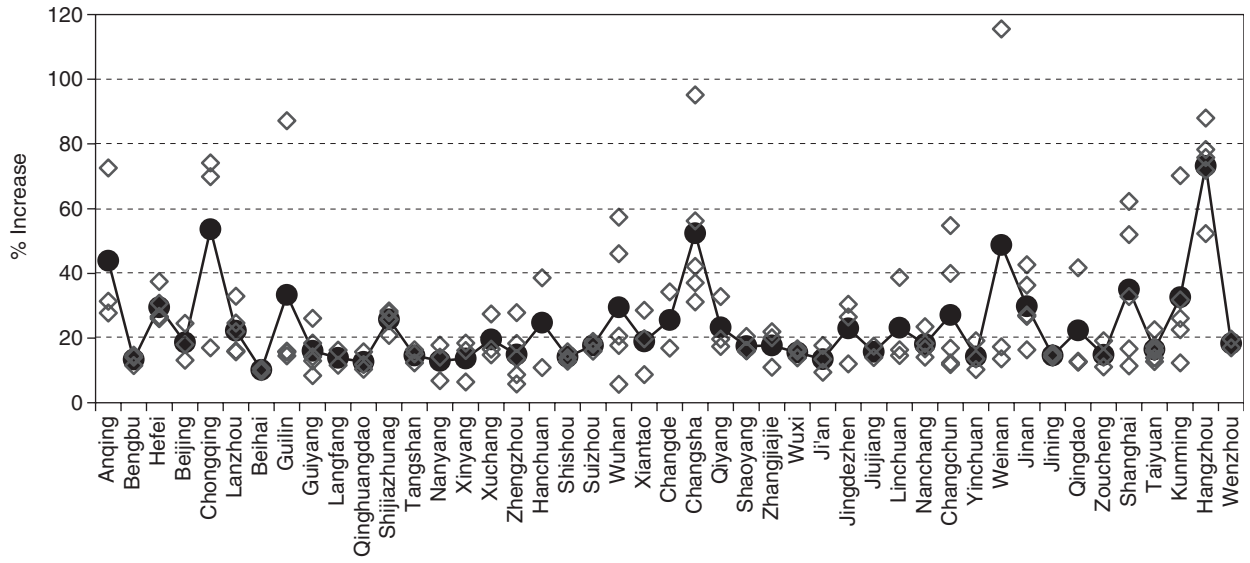


Fig. 6. Percentage enhancement of CH_3CCl_3 relative to the background mixing ratio. The solid circles represent the average city enhancement; the diamonds represent the enhancement of the single samples collected in a city.

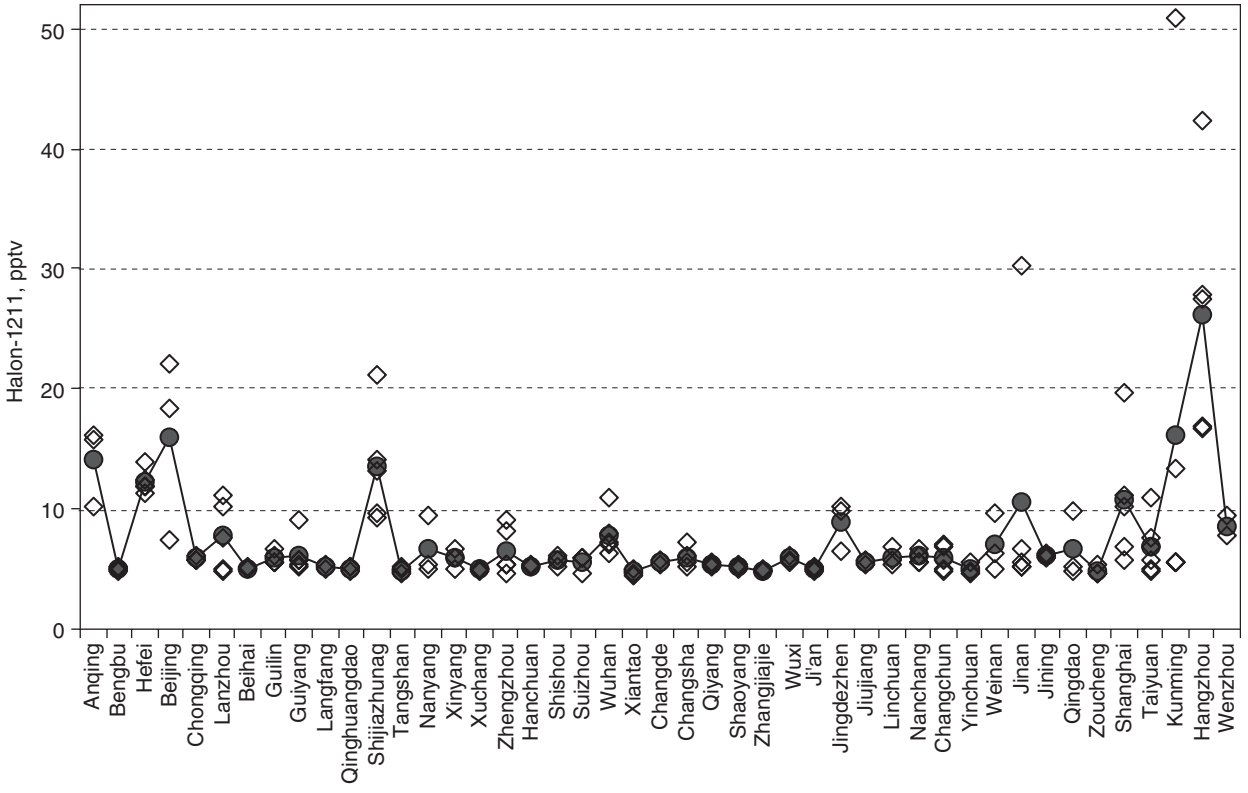


Fig. 7. Halon-1211 mixing ratios measured in 45 Chinese cities. The solid circles represent the city average; the diamonds represent the single cans collected in a city.

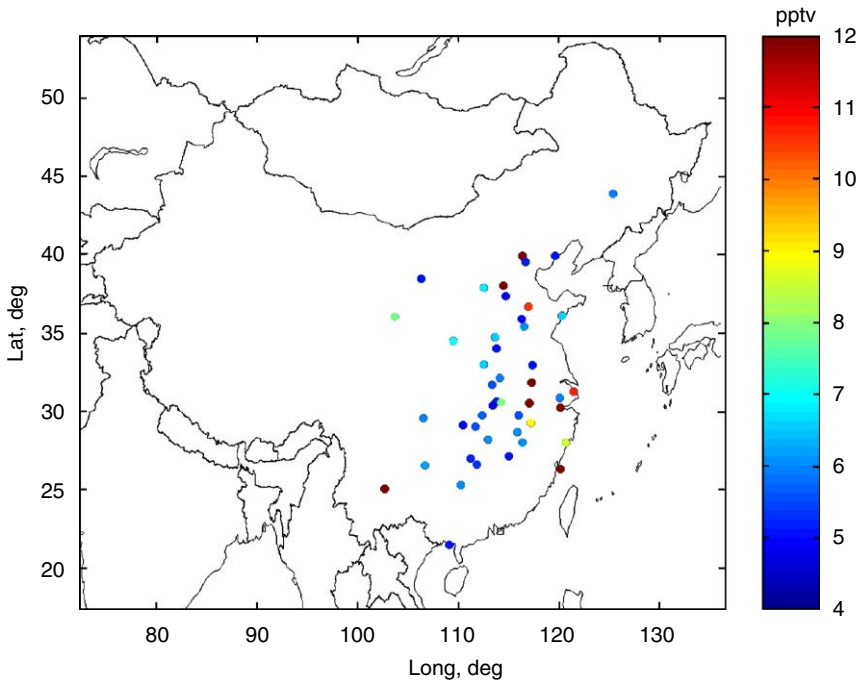


Fig. 8. Halon-1211 distribution in China based on samples collected in January–February 2001.

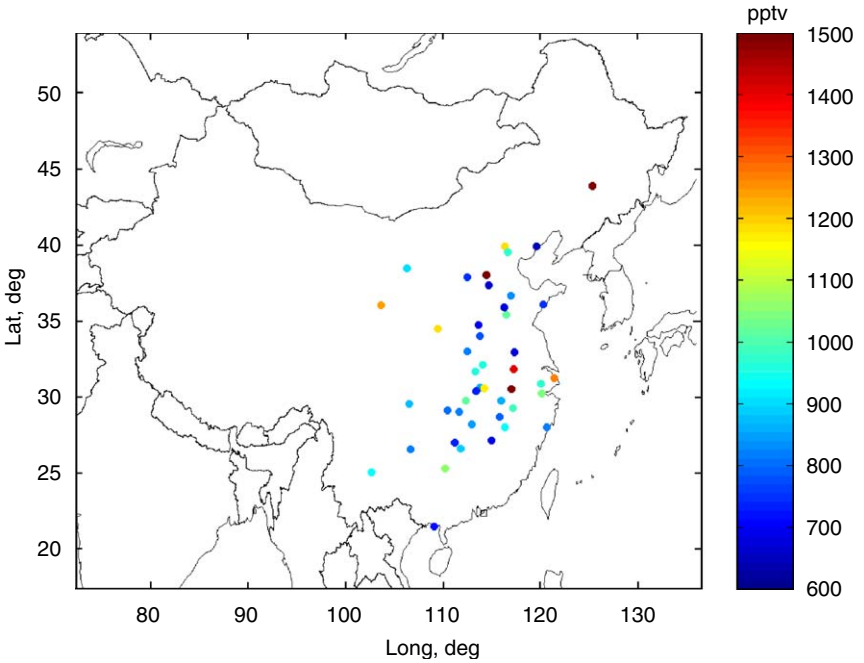


Fig. 9. Methyl chloride distribution in China based on samples collected in January–February 2001.

highest H-1211 levels were measured in Hangzhou, the city capital of Zhejiang Province in southeast China (26 pptv, $\sigma = 10$), where all 5 samples had very high mixing ratios (17, 17, 28, 28, and 42 pptv). In general, the cities with the highest levels of Halon-1211 were located in the northeastern and central-eastern areas of China (plus Kunming in the south), suggesting that production and/or storage of Halon-1211 is occurring in those areas (Fig. 8). Although the central provinces of China have fewer local sources and storage facilities than cities in the northeast and central-east, mixing ratios in these provinces were still 34% larger than background, indicating widespread use of Halon-1211 throughout China.

3.6. Methyl chloride

Methyl chloride is emitted by both biogenic sources (i.e. tropical plants and the oceans) and anthropogenic sources such as biomass burning and biofuel use, including coal burning (e.g. Blake et al., 1996; McCulloch et al., 1999). China is the world's largest consumer of coal (1422 million short tons in 2003, corresponding to 28% of the total global consumption; EIA, 2005b) and also the world's largest producer (1635 million short tons in 2003, or 30% of the global total; EIA, 2005b). Because of the widespread use of coal and biofuel in China, CH_3Cl emissions were expected to be high. The total average mixing ratio observed during this study was 952 pptv ($\sigma = 273$), almost double the global background (535 pptv; Table 1). Coal is used throughout China for industrial applications (mainly for industrial boilers and furnaces), in household cooking stoves, and for heating purposes. Therefore, the spatial distribution of CH_3Cl is affected by many different factors. The highest concentrations of CH_3Cl were measured in the central and northern areas of China (Fig. 9). The use of coal in the industrial sector can explain why the cities with high CH_3Cl levels (Anqing, Shijiazhunag Hangzhou, and Hefei) also have high levels of other industrially emitted halocarbons previously discussed. Wang et al. (2004) also observed comparable CH_3Cl mixing ratios in samples collected at rural and urban sites in China (1900–2300 pptv), suggesting that CH_3Cl is significantly emitted from biomass/biofuel in rural areas. These data and ours suggest the importance of CH_3Cl emissions in both urban and rural locations of China. The predominance of anthropogenic CH_3Cl sources is also suggested by the high CH_3Cl mixing ratios measured in all the samples collected in very populated and industrialized Chinese cities where strong biogenic sources (i.e. plants) are unlikely (Shanghai: 1218, 920, 1754, 826, 1615 pptv; Beijing: 879, 1347, 1306 pptv; Wuhan 1110, 1048, 1200, 1242, 1263 pptv). Moreover,

a moderate correlation between CH_3Cl and both Halon-1211 ($R^2 = 0.56$) and HCFC-22 ($R^2 = 0.52$) was found. Although different anthropogenic sources are responsible for their emissions, the correlation reflects the co-location of their urban sources.

4. Conclusions

This is the first reported study in which surface-level whole air samples were collected in a large number of Chinese cities and analyzed for halocarbons. Although this sampling campaign represents a brief "snapshot" of the Chinese urban environment during the winter of 2001, several new observations were made. Surprisingly, CFC levels were not significantly higher with respect to the global background and with respect to other cities worldwide, many in developed countries. Hydrofluorocarbons, HCFCs, and halocarbons used for industrial applications were enhanced compared to their background values. However, most of the halogenated compounds discussed here were comparable to literature values in other urban areas, which was surprising considering that in 2001 China was still allowed to produce and consume many of the halocarbons otherwise phased out in developed countries. Average CCl_4 concentrations, which were enhanced by 15% compared to background levels, appear to be unrelated to CFC production. Average CH_3CCl_3 levels were 24% higher than the background, suggesting continued use of this compound in the Chinese cities that were investigated. Halon-1211 and CH_3Cl concentrations were significantly enhanced in the sampled Chinese cities compared to background values. In the latter case, the widespread use of coal and subsequent emissions from coal combustion in urban areas is a likely source of the high levels measured.

Acknowledgements

The authors would like to thank the Comer Foundation, the Research Grant Council of Hong Kong (projects number 5037/00E and 5131/04E) and Brent Love for technical support.

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