Halocarbons in the atmosphere of the industrial-related Pearl River Delta region of China

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[1] In a study conducted in 2000, 19 halocarbons from 78 canister air samples were measured in five industrial cities in the Pearl River Delta (PRD), one of the fastest growing industrial regions in China. Preliminary year 2000 halocarbon levels have been derived using available data and information. Comparisons have been made between the data obtained in this study and the corresponding estimated global/tropical surface mixing ratios obtained from the literature. With the exception of CFC-114 and halon-2402, the halocarbons had significant enhancements, presumably due to their recent increased production and extensive industrial uses. In contrast to the small enhancements (<7%) for two chlorofluorocarbons (CFC-11 and CFC-12), large enhancements (>30%) for three HCFC replacements (HCFC-22, -141b, -142b) were observed. In general, HCFCs have virtually replaced CFCs, except for some localized usage. The median of HFC-134a also had a 36% enhancement; however, 23% of the samples were near or at the global background level. These contradictory results could not give a clear situation of uses of this new chemical in the region. Our data also indicate that halocarbon-based cleaning solvents, including CFC-113, methyl chloroform, trichloroethene and tetrachloroethene, were still frequently used in PRD industries. High mixing ratios of these halogenated solvents were frequently measured in Dongguan, a city with light industry. Higher atmospheric levels of the three methyl halides ($-Cl$, $-Br$, and $-I$) were found in a coastal city, Jiangmen. These may be contributed to by industrial emissions and coastal terrestrial and coastal seawater sources.

1. Introduction

[2] Halocarbons are a subclass of volatile organic compounds (VOCs). Halocarbons with long atmospheric lifetimes (>0.5 year) are transported to the stratosphere, leading to the destruction of the ozone layer through photolysis. Because of their high ozone depletion potentials (ODPs), the production and consumption of some ozone depleting substances (ODSs) have been banned in developed countries. In China, the levels of some ODSs have been frozen since 1999 and are gradually being phased out [*United Nations Environment Programme* (*UNEP*), 2003]. Consequently, the global mixing ratios of some abundant ODSs have been decreasing during the past decade. A slowdown in the rate of accumulation of dichlorodifluoromethane (CFC-12) has been observed in recent years, but the concentration of bromochlorodifluoromethane (halon-1211) is still increasing. In contrast, substitutes of chlorofluorocarbons (CFCs), such as hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs), are significantly increasing [*Fraser et al.*, 1999; *Montzka et al.*, 1999; *Prinn et al.*, 2000; *Sturrock et al.*, 2001].

[3] The Scientific Assessment of Ozone Depletion [*World Meteorological Organization* (*WMO*), 2003] summarized major findings of recent studies on atmospheric mixing ratios of ODSs and changes in the ozone layer. The measured global surface mixing ratios reported were mainly based on three global ground-based measurement networks: Advance Global Atmospheric Gases Experiment (AGAGE) network; the National Oceanic and Atmospheric Administration/Global Monitoring Division (NOAA/GMD) network; and the University of California at Irvine (UCI) network. In these networks, the global surface mixing ratios were continuously monitored at multiple in situ and flask-sampling sites in very remote areas, such as Mace Head, Ireland and Cape Grim, Tasmania, over the past three decades. The air samples used to measure the global surface mixing ratios were selected because they are relatively unaffected by local emission sources. Estimated global surface mixing ratios in 2000 (Table 1) were used as a global reference baseline, which is not necessary for PRD background, but for comparison with the measured PRD halocarbon levels in later sections. In addition, estimated tropical surface mixing ratios summarized from TRACE-P data for five very short lived (VSL) halogen substances, with atmospheric lifetimes of a few months or less, were used. In

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Table 1. Estimated Global/Tropical Surface Mixing Ratios for Each Target Compound as a Reference Baseline in 2000, With Concentration Ranges and 10, 50, and 90 Percentiles of Each Halocarbon Mixing Ratio for 78 PRD Samples

Compounds (Chemical Formula)	Estimated Global/Tropical Surface Mixing Ratios, pptv	This PRD Study			
		10%	50%	90%	Range
Halon-1211 ($CBrClF_2$)	3.97[a]	7.11	18.1	51.9	$5-277$
Halon-2402 ($CBrF_2CBrF_2$)	0.41[a]	0.45	0.49	0.53	$0.41-0.69$
CFC-11 (CCl_3F)	263[a]	263	274	309	$259-1310$
CFC-12 (CCl_2F_2)	541[a]	548	578	645	$538-973$
CFC-113 (CCl_2FCClF_2)	81.7[a]	140	163	194	$117-291$
CFC-114 ($CClF_2CClF_2$)	16.4[a]	13.9	14.7	15.4	$13.3-16.5$
HCFC-22 ($CHClF_2$)	142[a]	177	214	347	$161-1970$
HCFC-141b (CH_3CCl_2F)	13.0[b]	14.7	17.5	38.6	$13-76$
HCFC-142b (CH_3CClF_2)	12.0[b]	14	17	42	$12-68$
HFC-134a (CH_2FCF_3)	14.0[b]	12	19	30.3	$8-76$
Chloroform ($CHCl_3$)	11.4[c]	18	30.5	46.3	$14-249$
Carbon tetrachloride (CCl_4)	97.9[a]	102	107	126	$100-16,000$
Methyl chloroform (CH_3CCl_3)	49.9[a]	54	68.5	152	$49-9330$
Methylene chloride (CH_2Cl_2)	34.0[c]	220	561	1750	$154-6010$
Trichloroethene (C_2HCl_3)	1.00[c]	4.27	38.1	143	$1.7-497$
Tetrachloroethene (C_2Cl_4)	6.50[c]	12.5	49.5	206	$9.8-3590$
Methyl chloride (CH_3Cl)	551[a]	600	701	838	$532-1090$
Methyl bromide (CH_3Br)	9.30[a]	11.1	13.4	16.4	$9.4-23.2$
Methyl iodide (CH_3I)	0.60[c]	1.28	2.13	3.22	$0.78-6.31$

[a]Calculated global surface mixing ratios (pptv) in the Ab baseline scenario [*Montzka and Fraser*, 2003].

[b]Estimated global surface mixing ratios from measurements [*Montzka et al.*, 1994, 1999; *Simmonds et al.*, 1998b; *Prinn et al.*, 2000; *Sturrock et al.*, 2001; *Montzka and Fraser*, 2003].

[c]Median tropical surface (<1 km) mixing ratios summarized from the data of TRACE-P [*Ko and Poulet*, 2003].

general, PRD halocarbon background levels would be higher than the global air surface mixing ratios because of the higher anthropogenic activities in the Northern Hemisphere.

[4] Utilizing the year 2000 halocarbon data, the atmospheric mixing ratios of 14 ODSs are shown in Table 1. They include: CFC-11, -12, -113, -114, HCFC-22, -141b, -142b, HFC-134a, halon-1211, -2402, methyl chloroform (CH_3CCl_3), carbon tetrachloride (CCl_4), methyl chloride (CH_3Cl) and methyl bromide (CH_3Br). In addition, 5 VSL halogen substances were also studied. These included methylene chloride (CH_2Cl_2), trichloroethene (C_2HCl_3), tetrachloroethene (C_2Cl_4), chloroform ($CHCl_3$) and methyl iodide (CH_3I). The three methyl halides ($-Cl$, $-Br$, and $-I$) and $CHCl_3$ have important natural sources, whereas the other halocarbons, which are extensively used as foam-blowing agents, refrigerant gases, aerosol propellants, dry cleaning solvents, degreasing agents, feedstocks for chemical production, and fire extinguishing agents, are anthropogenic in origin [*Aucott et al.*, 1999; *Fraser et al.*, 1999; *McCulloch et al.*, 1999b; 2003].

[5] Extensive measurement studies on global trends and atmospheric abundances of halocarbons have been conducted in remote for the past three decades [*WMO* 2003 *and references therein*; *Simpson et al.*, 2004], but only limited studies have been conducted in urban [*Wang et al.*, 1998; *Yamamoto et al.*, 2000; *Rivett et al.*, 2003] and industrial areas [*Chang et al.*, 2001]. China is one of the "Article 5 Parties", that are allowed to produce and consume ODSs. The PRD region is a leading manufacturing center in China. Heavy air pollutant emission from this industrial region has aroused international concern. Yet recent studies were only restricted to characterizing chemical compositions of Asian continental outflow and polluted air masses transported from the industrial developing Asian countries [*Blake et al.*, 2003; *Palmer et al.*, 2003]. Although statistical data for halocarbon

production and consumption by industrial activities in the PRD region are still lacking, we have generated a preliminary year 2000 halocarbon picture using limited field data collected in five industrially developed cities. Information and field data on this region, especially on source inventory, source distribution and source strength emission, are spotty and scarce. Hence experiences and findings from other countries are used to supplement our knowledge in this region in the discussion of the implication of emissions. Some of the discussions are presumptions but it is to the best of our understanding of this region, and relevant references are used whenever applicable. Hopefully, this study can help us to gain a better understanding of industrial and domestic uses and emissions in China under the Montreal Protocol.

2. Experiment

[6] The PRD region (42,000 km^2) is situated within Guangdong province in southern China, on the Tropic of Cancer (23.5°N), and is composed of nine cities (Figure 1). Each city consists of a densely populated and developed central city surrounded by its perimeter county level cities, districts and towns. Seventy-eight ambient air samples were collected throughout five industrially active cities (Dongguan, Foshan, Guangzhou, Jiangmen and Zhongshan). Of theses five cities, Dongguan is characterized as having light industries, in particular electronic computers, peripherals, and soldering machinery; Foshan has heavy industries, in particular industrial ceramics and ceramics artwork; and Guangzhou has mixed industries including chemicals, transport equipment and electrical products. Both Zhongshan and Jiangmen have mixed industries (PRD Economic Profile, Hong Kong Trade Development Council (HKTDC), available at http://www.tdctrade.com/mktprof/china/prd.htm, assessed in April 2006, hereinafter referred to as HKTDC, 2006).

Figure 1. Air sampling sites in the Pearl River Delta (PRD), Guangdong, southern China.

[7] Sampling is focused on three categories of the sampling environment: industrial, industrial urban and industrial suburban, henceforth referred to as T1, T2 and T3, respectively (Table 2). The T1 samples were collected next to either an industrial point source or a cluster of industries. The T2 samples were intended to measure the ambient air in town/city sectors with active industrial activities. The T3 samples were collected in suburban and rural areas that had some industrial activities. This sampling scheme resulted in wide concentration ranges for most measured halocarbons (Table 1).

[8] Between 11 August and 19 September, 2000, a total of 78 ambient air samples were collected using evacuated 2L electropolished stainless steel canisters (with a bellows valve) throughout the five target cities. All samples were collected between 09:00 and 17:00 local time, when factories were under normal operation. A comprehensive description of the sample collection, chemical analysis and VOC speciation is given in *Chan et al.* [2006]. Among the compounds analyzed, CO, CH_4 and 28 NMHCs were previously reported [*Chan et al.*, 2006], while the remaining 19 halocarbons are discussed here. All halocarbons in all samples were present at mixing ratios above their detection limit. The precision of the halocarbon measurements varies compound by compound, and is 1–2% for CFCs, 2–4% for HCFCs, and 1–4% for the other halocarbons (except 5% for HFC-134a and CH_2Cl_2). The measurement accuracy also varies compound by compound, and is 2% for CFCs (except 5% for CFC-114), 5% for halons, HFC-134a, CH_3CCl_3, CCl_4, CH_3Cl and CH_3Br, and 10% for the other halocarbons. Details of the analytical system, data analysis and QA/QC are described in *Colman et al.* [2001].

3. Results and Discussion

3.1. Overview of the Regional Atmospheric Halocarbon Situation in the PRD

[9] Nineteen halocarbons were quantified from the 78 PRD canister samples. All ambient samples were affected by local industrial emission sources, to varying degrees. Table 1 lists the 10, 50, and 90 percentiles of mixing ratios, together with the concentration ranges, for each halocarbon in the 78 samples. Almost all of the halocarbons showed substantially large variations in their concentration ranges, especially for CFC-11, HCFC-22, CCl_4, CH_3CCl_3, CH_2Cl_2 and C_2Cl_4, due to some extremely high values measured in the proximity of industrial activities (T1). A significantly large difference between their maxima and 90 percentiles for these six compounds were also observed (Table 1). It was difficult sometimes to account for some very high mixing ratios found in some T2 and T3 samples. To a certain extent, this indicates that heavy uses of halocarbons were common in wide areas of the PRD with different land uses. Their impact was highly localized and not only limited to emissions from industrial areas nearby. The reasons for prompt emissions were likely related to poor emission controls and practices in industrial activities, and leakage from storage and distribution services.

[10] When we compared the estimated global/tropical surface mixing ratios in 2000 with the measured PRD halocarbon mixing ratios (Table 1), the characteristics of

Table 2. Sample Collection Throughout the Five Cities Based on the Three Categories of Sampling Environment

Districts	Sample Collection			
	T1[a]	T2[b]	T3[c]	Total
Dongguan (DG)	5	7	20	32
Foshan (FS)	3	7	5	15
Guangzhou (GZ)	7	5	5	17
Jiangmen (JM)	0	3	4	7
Zhongshan (ZS)	0	3	4	7
Total	15	25	38	78

[a]T1: Sampling outside the boundary of a significant industrial point source or an industrial complex (industrial).

[b]T2: Sampling in an area (away from any known point sources) mixed with industrial and urban areas (industrial urban).

[c]T3: Sampling in an area (away from any known point sources) mixed with industrial and suburban areas (industrial suburban).

atmospheric halocarbon levels in the region could be examined. From our knowledge, the surface mixing ratios of halocarbons are spatially and temporally dependent. Thus the global/tropical estimated values did not represent PRD regional background, and were just used as a global reference baseline for a general comparison with PRD air. Intensive halocarbon emissions from anthropogenic activities and usually less well-mixed air masses lead to slightly higher halocarbon background values measured in the Northern Hemisphere. Thus with the high industrial activities in the PRD, we would expect a higher PRD background than the estimated global values.

[11] Some properties of the global reference baseline are described below. First, the estimated global surface mixing ratios of most ODSs (Table 1) were given in the WMO scenario Ab [*Montzka and Fraser* [2003]]. The scenario Ab for the year 2000 was largely based on measured mixing ratios reported by AGAGE, NOAA/GMD, and UCI. Second, the values for HCFC-141b, HCFC-142b and HFC-134a were extracted from updated measurements in mid-2000, when the sustained uses of these new substitutes were prevalent. Third, the estimated tropical surface mixing ratios of the five VSL halogen substances were obtained from the data (<1km) of TRACE-P collected over the Western Pacific and the South China Sea (23.5°N to 8°N) in 2001 [*Ko and Poulet*, 2003], as there were no global estimated surface mixing ratios for these short-lifetime substances. The lifetime of CH_3I and C_2HCl_3 is about 3–5 days. We used the median tropical surface mixing ratios from the data (<1km) of TRACE-P as background levels near southern China. In general, the mixing ratios of VSL halocarbons have larger spatial and temporal differences than those of long-lifetime halocarbons.

[12] Most of the 10-percentile values for halocarbons in the PRD (Table 1) were higher than the corresponding global/tropical surface levels (reference baseline) (Table 1). Of the 19 target compounds, halon-1211, CFC-113, HCFC-22, HCFC-141b, HCFC-142b, $CHCl_3$, CH_2Cl_2, C_2HCl_3, C_2Cl_4, CH_3Br and CH_3I showed significantly large differences (>10%) with the reference baseline values, while the differences (<10%) were smaller in halon-2402, CFC-11, CFC-12, CCl_4, CH_3CCl_3 and CH_3Cl. Conversely, the 90 percentile of CFC-114 (15.4 pptv) and the 10 percentile of HFC-134a (12.0 pptv) were slightly lower than the reference baseline values (16.4 and 14.0 pptv), respectively. This rare observation may be affected by a difference in calibration between UCI and other institutions and the uncertainties of measurement accuracy at low concentrations. Overall, the data are consistent with the gradual phase out of CFCs and ODSs, and the increase in application of CFC replacements in China. The trend suggested from our measured data followed the change of China's ODS consumption in ODP tons between 1998 and 2000 (ODS Data Access, Ozone Secretariat 2004, United Nations Environment Programme (UNEP), Nairobi, Kenya, available at http://ozone.unep.org/Data_Access). Within these two years, consumption of CFCs, Halons and CCl_4 showed large reductions (−29.4%, −33.4% and −66.2%, respectively), while that of HCFCs showed a significantly large enhancement (417%). However, the situation of the application of one new CFC replacement, HFC-134a, was

uncertain in the PRD from our data. Details of each halocarbon are discussed below.

3.2. Phase-Out and Replacement of CFC-11 and CFC-12

[13] The Chinese government has committed to freeze the production and consumption of CFCs at the average level of the actual amount used during 1995–1997 together with the use of their replacements, starting from 1 July 1999 [*UNEP*, 2003]. Among the four target CFCs, the two most abundant ones (CFC-11 and CFC-12) were historically used in a variety of industrial activities, before CFC replacements were introduced. Both CFCs were used as foam-blowing agents, aerosol propellants and refrigerants [*McCulloch et al.*, 2001; 2003]. The minima of CFC-11 (259 pptv) and CFC-12 (538 pptv) were slightly lower than their estimated global surface mixing ratios (263 and 541 pptv), but their differences were smaller than 2% and were within the measurement accuracy of chemical analysis. The medians of CFC-11 (274 pptv) and CFC-12 (578 pptv) were only 4.2% and 6.8% higher than the corresponding global levels, respectively. Small enhancements of these two CFCs were found in the PRD. Along with CFC-11 and CFC-12, Figures 2 and 3 show the distribution of HCFC-22, HCFC-141b, HCFC-142b and HFC-134a within the five target cities (DG, FS, GZ, JM and ZS). The 78 discrete samples were arranged in ascending order of CH_3CCl_3 for each city. This ordering is designed to show the spatial deviation of halocarbon levels relative to solvent cleaning activities as discussed in Section 3.3, and is used throughout this paper.

[14] CFC-11 is mainly used in closed cell foam blowing in China [*Yu et al.*, 2000]. This CFC remains inside the products and minor leaking loss in the service life of the foam products leads to its steady emission into the atmosphere. Tremendous increases in some local atmospheres, like one 400% enhancement of CFC-11, were observed (Figure 2). High concentrations like this one are believed to be occasionally caused by other uses, such as open cell foam blowing agents and aerosol propellants. In contrast, larger enhancements of HCFC-141b (35%) and HCFC-142b (42%) were observed by comparing the medians to the global reference baseline (Figure 2). HCFC-142b, which is a new chemical and also primarily used in foam blowing [*Montzka et al.*, 1994; *Simmonds et al.*, 1998b], was enhanced in significantly more samples, suggesting that this HCFC is gradually replacing CFC-11 in industrial usage in the PRD. Another CFC replacement, HCFC-141b, was found to be as common as HCFC-142b. However, the spatial concentration spread of HCFC-141b was different from that of HCFC-142b, probably due to the variations in industrial use and in spatial distribution of industry among the five PRD cities.

[15] HCFC-22 and HFC-134a are major substitutes for the historical refrigerant gas (CFC-12). HCFC-22 is commonly used in commercial refrigeration (e.g., supermarkets) and refrigeration transport, while HFC-134a is principally used in mobile air conditioning (A/C) systems [*McCulloch et al.*, 2003; *Stemmler et al.*, 2004]. The median of HCFC-22 showed a higher percentage enhancement (51%) than that of CFC-12 (7%) when compared with the corresponding global reference baseline values. This result suggests that CFC-12 was gradually being phased out and
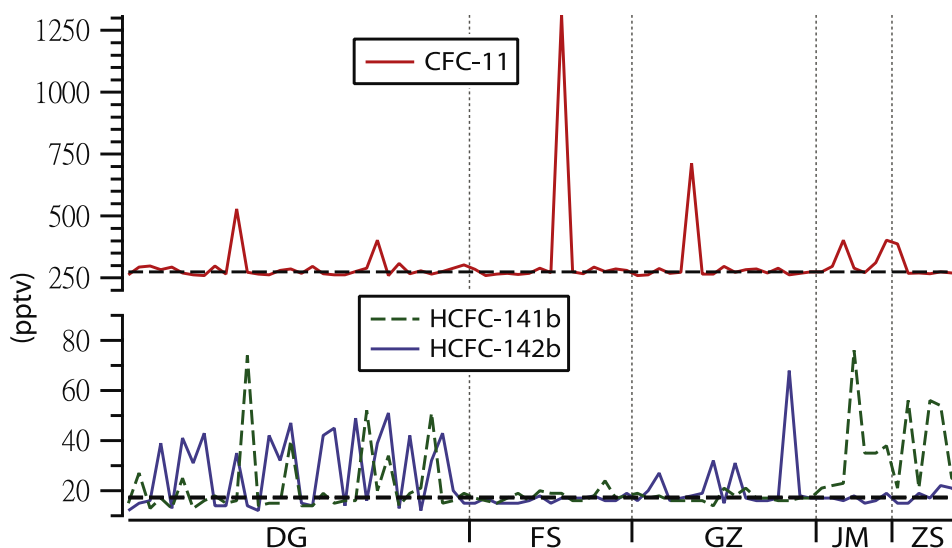
Figure 2. Distribution of CFC-11, HCFC-141b. and HCFC-142b concentrations among the five cities. The dashed straight lines indicate the medians of CFC-11 (274 pptv), HCFC-141b (18 pptv), and HCFC-142b (17 pptv) from the 78 samples. Note: The 78 discrete samples are arranged in ascending order of CH_3CCl_3 mixing ratio for each city.

substituted by HCFC-22 in the PRD. Similar to observations from other studies, HCFC-22 prevalence is the result of minor leaks from refrigeration systems, occasional emissions from uses such as aerosol propellant, solvent and foam-blowing agent, fugitive emissions from container filling for transport, leakage of refrigerants from malfunctioning A/C systems, and losses from venting and recharging of refrigerants from car repair shops [*Wang et al.*, 1998; *Aucott et al.*, 1999; *Baker*, 1999; *Stemmler et al.*, 2004]. Enhanced mixing ratios of CFC-12 and HCFC-22 were often observed in Guangzhou samples, and were more related to local halocarbon production and application. For example, a chemical enterprise in Guangzhou contributed

9.26% to the gross industrial output value from industry of raw chemical materials and chemical products in Guangdong Province in 1999 [*Statistical Bureau of Guangdong* (*SBG*), 2000]. Two Guangzhou samples were selected for discussion later (Section 3.4).

[16] HFC-134a is a new alternative that has just been introduced in China. The Chinese automobile industry is still monitoring the trends in international development of technology related to HFC-134a mobile A/C systems [*Yu et al.*, 2000], because of concerns about its high global warming potential. New mobile A/C systems were imported from other developed countries and most of this HFC is presumably contained in the new mobile A/C systems
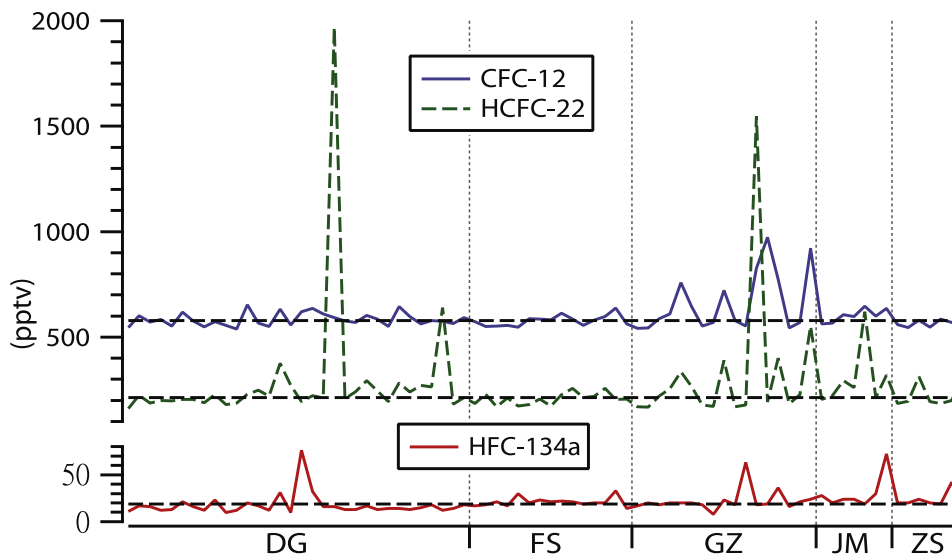

Figure 3. Distribution of CFC-12, HCFC-22, and HFC-134a concentrations among the five cities. The dashed straight lines indicate the medians of CFC-12 (578 pptv), HCFC-22 (214 pptv), and HFC-134a (19 pptv).
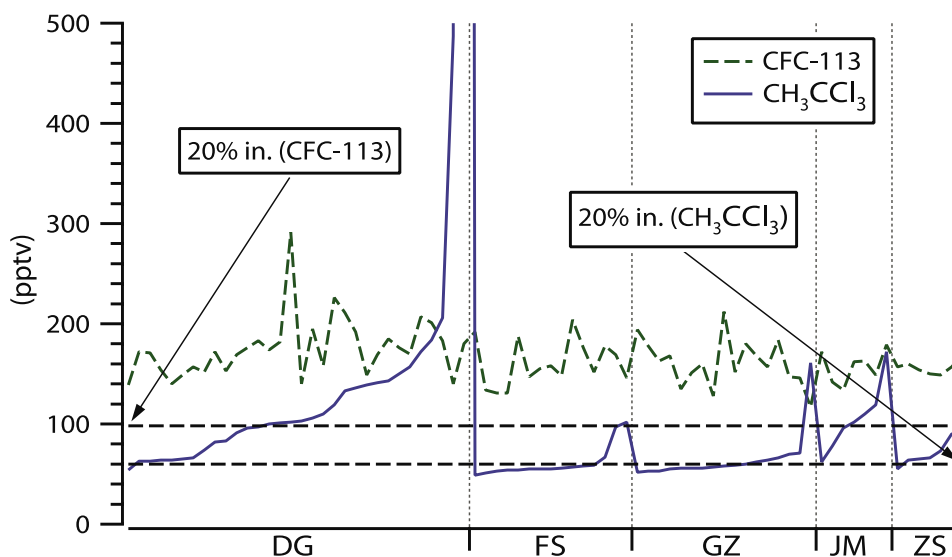
Figure 4. Distribution of CFC-113 and CHCl$_3$ concentrations among the five cities. The dashed straight lines indicate the 20% enhancement of CFC-113 (98 pptv) and CH$_3$CCl$_3$ (60 pptv) with respect to the global reference baseline (Table 1). One extremely high value of CH$_3$CCl$_3$ (9 ppbv) is not shown in the figure.

[*Baker*, 1999]. Consequently, there were smaller numbers of samples with largely enhanced mixing ratios of HFC-134a (Figure 3) than those of either HCFC-141b or HCFC-142b (Figure 2).

3.3. Rapid Emission of ODSs and VSL Halogen Substances From Solvent Cleaning

[17] CFC-113, methyl chloroform (CH$_3$CCl$_3$), methylene chloride (CH$_2$Cl$_2$), trichloroethene (C$_2$HCl$_3$) and tetrachloroethene (C$_2$Cl$_4$) were found to have different emission behaviors from CFC-11, CFC-12 and their substitutes, which were used in refrigeration and closed cell foam blowing. They are primarily used as cleaning solvents, are not contained in products, and are rapidly emitted into the atmosphere. In general, the majority of these halocarbons, like CFC-113, are released within a year of production (Production, Sales and Atmospheric Release of Fluorocarbons through 2003, Alternative Fluorocarbons Environmental Acceptability Study (AFEAS), Arlington, Virginia, 2005, available at http://www.afeas.org), and had an immediate effect on elevated regional atmospheric mixing ratios.

[18] CFC-113 and CH$_3$CCl$_3$ are primarily used as deflux or degreasing agents in the electronics industry [*Fraser et al.*, 1996; *Chang et al.*, 2001], and about 4700 tons of CFC-113 and 6700 tons of CH$_3$CCl$_3$ were consumed in solvent cleaning in China in 1997, respectively [*Yu et al.*, 2000]. Their industrial uses were also reflected in their measured atmospheric levels. We observed significant percentage increases in the medians of CFC-113 (100%) and CH$_3$CCl$_3$ (37%) (Table 1). The highly localized impact of their uses was demonstrated by the variation in mixing ratios in individual samples collected from different cities (Figure 4). Among the 15 samples collected in Foshan, which is located in the western part of the PRD and is characterized as a city with heavy industry (HKTDC, 2006), 13 samples showed lower mixing ratios of CH$_3$CCl$_3$ than its median of the 78 samples (68.5 pptv), and 12 samples were

lower than a 20% enhancement (60 pptv) of the global reference baseline. In contrast, among the 32 Dongguan samples, 7 samples were lower than the median, and only one sample did not exceed the 20% enhancement. In addition, one extremely high value of CH$_3$CCl$_3$ (9.33 ppbv) was observed in Dongguan. The higher CH$_3$CCl$_3$ level in Dongguan may stem from the fact that high technology and light industries have been intensively developed in Dongguan (HKTDC, 2006). The same figure also showed more common uses of CFC-113 as a cleaning solvent in the five cities, as all samples were higher than a 20% enhancement (98 pptv) of the global reference baseline. This indicates that uses of halocarbon-based cleaning solvents in the PRD were still prevalent at the beginning of the Beijing Amendments, 1999 [*UNEP*, 2003].

[19] In addition to these two ODSs, three VSL halogen substances are used in metal degreasing and dry cleaning, specifically methylene chloride (CH$_2$Cl$_2$), trichloroethene (C$_2$HCl$_3$) and tetrachloroethene (C$_2$Cl$_4$) [*Wadden et al.*, 1991; *McCulloch et al.*, 1999b]. C$_2$HCl$_3$ was used as a cleaning solvent in PRD electronics industry [*He et al.*, 2002]. In view of the hundred to thousand percentage increases in the medians of these three VSL halogen compounds with respect to the estimated tropical surface mixing ratios (Table 1), it is clear that they are substantially used in PRD manufacturing industries. These enormous enhancements outweigh the reducing effect due to seasonal variation in the atmospheric abundance of hydroxyl radical [*Wang et al.*, 1995; *Simpson et al.*, 2004]. For the spatial variations of C$_2$HCl$_3$ and C$_2$Cl$_4$ (Figure 5), like that of CH$_3$CCl$_3$, most of the Dongguan samples were higher than their medians in the 78 samples, while few Foshan samples exceeded their medians. The spatial variation of CH$_2$Cl$_2$ was different from those of C$_2$HCl$_3$ and C$_2$Cl$_4$. It was occasionally in parts per billion levels in the atmosphere of the five PRD cities. As reported, both C$_2$HCl$_3$ and C$_2$Cl$_4$ are industrial cleaning solvents that were not commonly
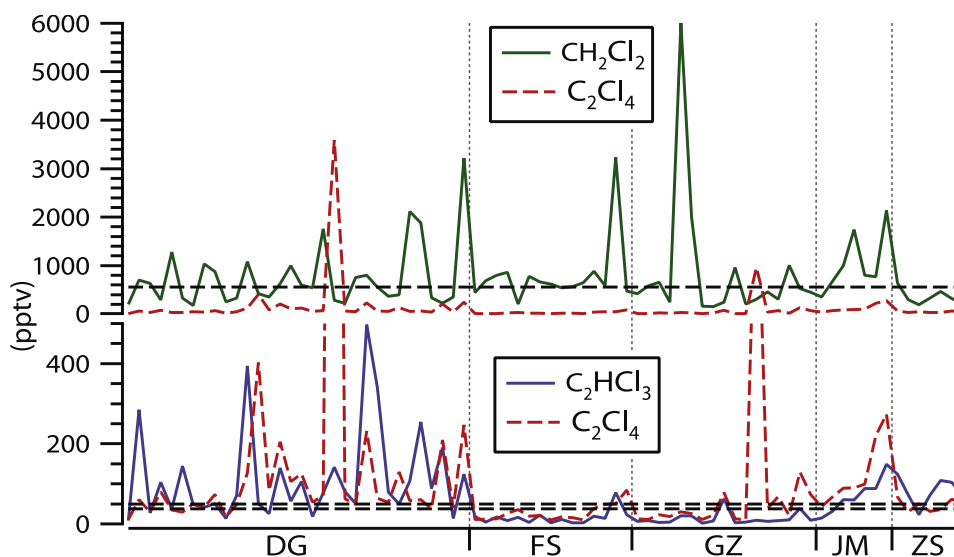
Figure 5. Distribution of CH_2Cl_2, C_2Cl_4, and C_2HCl_3 concentrations among the five cities. The dashed straight lines indicate the medians of CH_2Cl_2 (561 pptv), C_2Cl_4 (50 pptv), and C_2HCl_3 (38 pptv) from the 78 samples.

used for retail and commercial purposes, whereas CH_2Cl_2 was used in more industrial and domestic activities. In China, CH_2Cl_2 was mainly consumed in plastic film production (50%), the pharmaceutical industry (20%), and in cleaning solvent and chemical production (20%) [*Jiang*, 2004]. In Japan, the Pollutant Release and Transfer Resister survey in 2005 [*Japan Pharmaceutical Manufacturers Association* (*JPMA*), 2005] showed that CH_2Cl_2 was heavily emitted from the pharmaceutical industry.

3.4. Carbon Tetrachloride, Chloroform, and Halon-1211

[20] Carbon tetrachloride (CCl_4) and chloroform ($CHCl_3$) are mainly used as feedstocks for CFC-11, CFC-12 and HCFC-22 production [*Simmonds et al.*, 1998a; *Aucott et al.*, 1999]. HCFC-22 production consumed about 75% of $CHCl_3$ in China, followed by the pharmaceutical industry [*Jiang*, 2004]. In Japan, $CHCl_3$ (52 tons) was the fifth in aerial emission from the pharmaceutical industry [*JPMA*, 2005]. A small quantity of CCl_4 (100 tons) was reported to be used as cleaner in China in 1997 [*Yu et al.*, 2000]. There were two Guangzhou samples (A and B) with significantly high mixing ratios of both compounds (Figure 6). The maxima of $CHCl_3$ (249 pptv) and CCl_4 (16 ppbv) observed in sample B were 8- and 150-fold higher than their medians (30.5 and 107 pptv), respectively. This sample was collected near a government building in Guangzhou (Figure 7). The next most abundant sample (A) was collected outside a gas
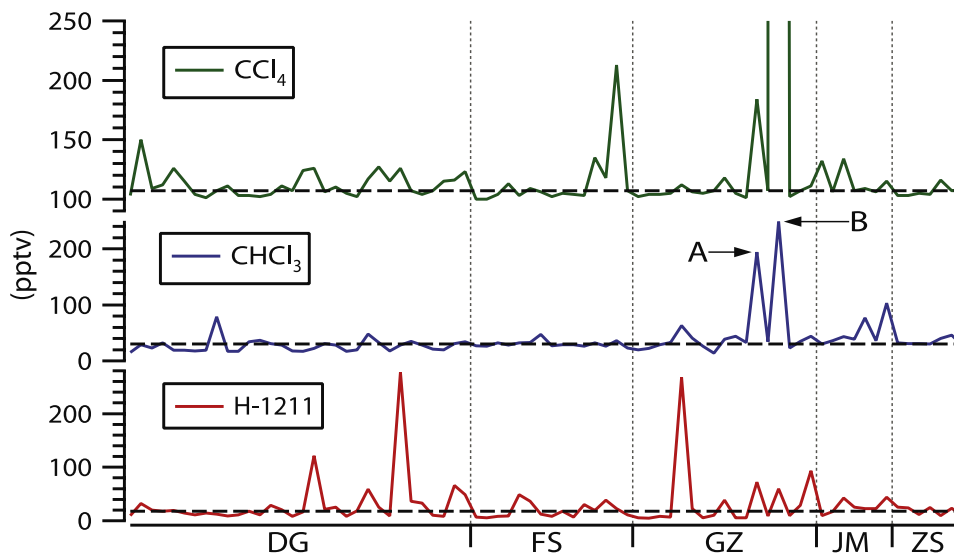

Figure 6. Distribution of CCl_4, $CHCl_3$ and halon-1211 concentrations among the five cities. The dashed straight lines indicate the medians of CCl_4 (107 pptv), $CHCl_3$ (31 pptv), and H-1211 (18 pptv) from the 78 samples.
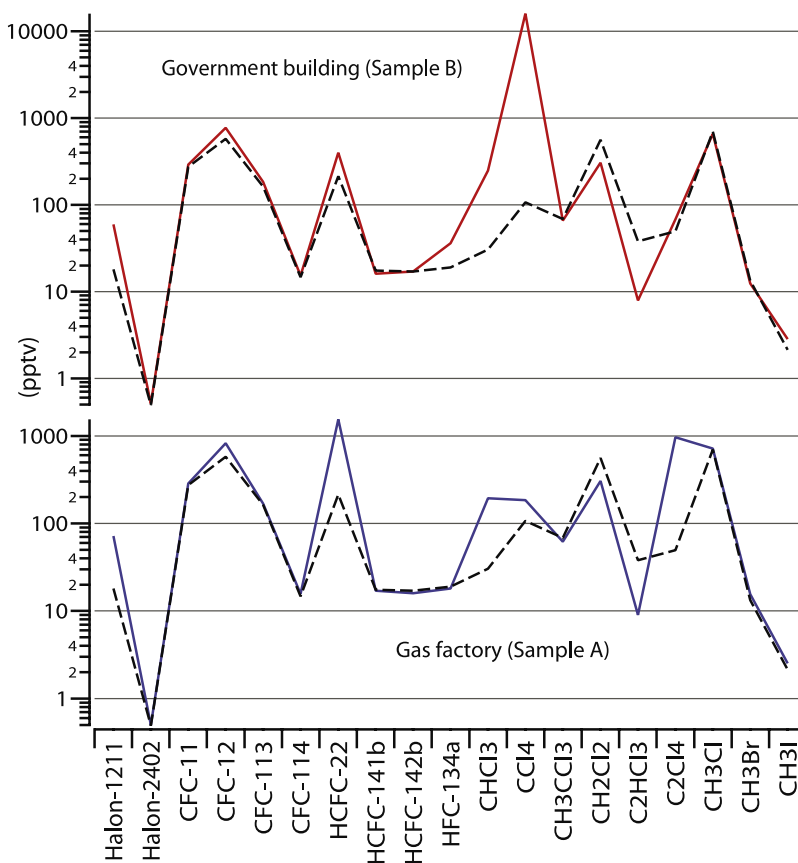
Figure 7. Two samples with high levels of CCl_4 and $CHCl_3$ collected in Guangzhou. The dashed lines indicate the median of each halocarbon from the 78 samples.

factory in the central part of the city, which mainly manufactures oxygen, nitrogen and noble gases for industrial and medical uses. When we further investigated these two samples, the increases in CFC-12 and HCFC-22 with respect to their medians were simultaneously found (Figure 7). These high levels of CCl_4 and $CHCl_3$ were probably associated with leakage or fugitive emissions from their feedstocks in neighboring storage tanks or chemical plants. Guangzhou is more advanced in petroleum and chemical industries than other PRD cities (HKTDC, 2006). Also, these results explain why the mixing ratios of CFC-12 and HCFC-22 were much enhanced in the Guangzhou samples (Figure 3). This further illustrates the bias that can be induced by a few high mixing ratios if the averages were used instead of the medians for our limited number samples analysis. This effect would be much reduced if there were more samples available for analysis.

[21] Bromofluorocarbons (halons) are commonly used as fire extinguishing agents. Their sources are mainly related to fire fighting or leaks from fire fighting systems [*Fraser et al.*, 1999; *Montzka et al.*, 1999]. We do not have information on fire counts in the PRD for general comparison. As halon production is still allowed in China, high halon-1211 levels (>6.1 pptv) were observed in air masses transported from one of the high-GDP Chinese cities, Shanghai, during TRACE-P [*Palmer et al.*, 2003]. Comparing the reference baseline value of halon-1211 (4.0 pptv) with its median (18.1 pptv), an over 300% enhancement indicates possible emission from leaks in fire fighting systems or from halon production. Simultaneous

elevated levels of halon-1211 and HCFC-22 in the two Guangzhou samples (Figure 7) favor the presumption of fugitive emissions from halon production, as halon-1211 can be produced by the bromination of HCFC-22.

3.5. Uncommon Uses of CFC-114 and Halon-2402

[22] Among the 19 target halocarbons, there were two species, CFC-114 (14.6 ± 0.7) and halon-2402 (0.49 ± 0.04), with small consumption, close means and medians, as well as very small standard deviations and ranges (Table 1), indicating that they were rarely used in PRD industrial and domestic activities. This was consistent with a small consumption (250 tons) of it in China in 1997 [*Yu et al.*, 2000]. CFC-114 was restricted to special applications, such as low-temperature refrigeration. The mixing ratio of halon-2402 ranged from 0.41 pptv to 0.69 pptv, and its median (0.49 pptv) had a 19.5% enhancement when compared with the reference baseline. The enhancement of halon-2402 level in the PRD was likely associated with emissions from halon "banks" (e.g., existing equipment), as its production and consumption is not as common as halon-1211 because of its higher ODP.

3.6. Anthropogenic and Natural Sources of Methyl Halides

[23] The three methyl halides, including CH_3Cl, CH_3Br and CH_3I, had significant anthropogenic and natural sources. In this PRD study their distributions were more complicated than other halocarbons discussed, which are
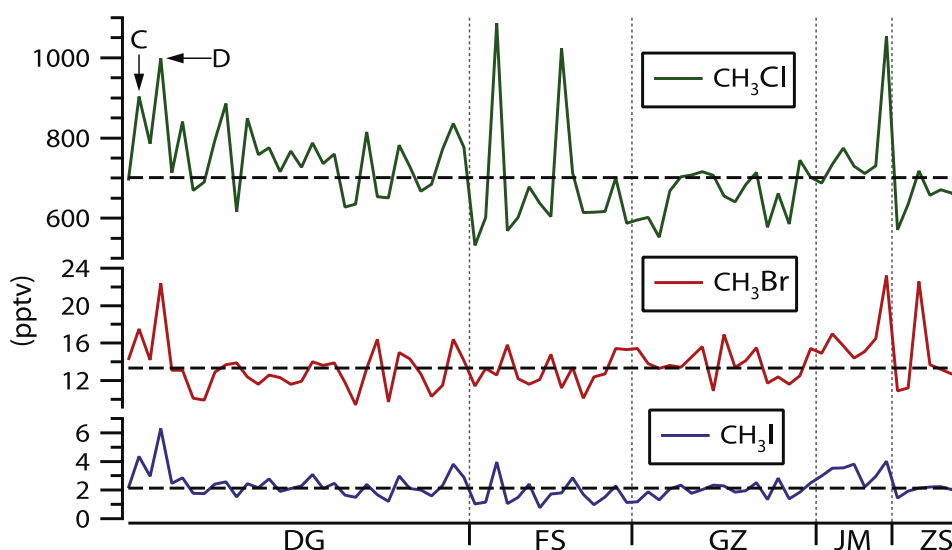
Figure 8. Distribution of CH_3Cl, CH_3Br and CH_3I among the five cities. The dashed straight lines indicate the medians of CH_3Cl (701 pptv), CH_3Br (13.4 pptv), and CH_3I (2.1 pptv) from the 78 samples.

purely anthropogenic in origin. Coal combustion, biomass burning and incineration were anthropogenic sources of these methyl halides, especially for CH_3Cl [*Lobert et al.*, 1999; *McCulloch et al.*, 1999a]. Two T1 samples (C and D) were selected for further investigation to examine their substantial enhancements (Figure 8). Both samples were collected in Dongguan, and were affected by emissions from neighboring paper factories. Experiences in other countries show that increases in mixing ratios could be related to combustion exhaust from coal-fueled boilers, which provide heat and steam for cooking pulp and drying paper [*U.S. Environmental Protection Agency (USEPA)*, 2002]. CH_3Cl is also commonly used as a solvent, process agent and feedstock for chemical production in China [*Jiang*, 2004]. It was more frequently enhanced, relative to CH_3Br and CH_3I (Figure 8). Occasional enhancements of CH_3Br may be also due to fumigation of soil, as considerable agricultural activities are widely distributed around the PRD.

[24] Among the five target cities Jiangmen, situated along the coast, is clearly different from the other four cities. Coastal terrestrial and coastal seawater regions are known to be natural sources of these three methyl halides, and the open ocean is a significant source of CH_3I [*Cox et al.*, 2003; 2005]. We observed that, among the seven Jiangmen samples, all samples had higher levels of CH_3Br and CH_3I than their medians (13.4 and 2.1 pptv), and six samples had higher levels of CH_3Cl than their median (701 pptv). All three medians were at least 27% higher than the corresponding reference baseline values. However, a limited number of samples keeps us from strongly relating the higher mixing ratios of methyl halides in Jiangmen to coastal terrestrial and coastal seawater sources. In addition, a transport of biogenic emissions from tropical to subtropical regions may be another source of CH_3Cl [*Khalil and Rasmussen*, 1999].

4. Conclusion

[25] A preliminary survey of year 2000 halocarbon levels was conducted and a total of 78 PRD samples were collected in five target cities. All samples were affected by industrial sources, to varying degrees. Except for CFC-114 and halon-2402, the other 17 analyzed halocarbons showed large variations for all samples. The percentage increases of the three HCFCs was significantly larger than CFC-11 and CFC-12. In general, HCFCs had practically replaced CFCs, except in some localized usage, but the situation of the use of a new substitute, HFC-134a, was uncertain in the PRD in 2000. In addition, halocarbon-based cleaning solvents (CFC-113, methyl chloroform, trichloroethene and tetrachloroethene) were commonly used in the PRD, especially in Dongguan. Significantly high levels of methylene chloride were commonly observed in wide areas of the PRD, because of its prevailing industrial and domestic uses. Elevated levels of chloroform, carbon tetrachloride, CFC-12, HCFC-22 and halon-1211 in some samples in Guangzhou suggest that CFC, HCFC and halon production made significant contribution to the local atmospheric halocarbon levels. Elevated mixing ratios of three methyl halides (−Cl, −Br, and −I) in a coastal city, Jiangmen, were also associated with coastal terrestrial and coastal seawater sources.

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